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Catalytic chemistry and technology of C_1 compounds

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ABSTRACT. New reactions of one-carbon compounds in the presence of heterogeneous and homogeneous catalysts as well as new approaches to the selection of catalysts and the carrying out of traditional catalytic processes involving C_1 compounds are examined. The bibliography includes 214 references.

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I. Introduction

Compounds with one carbon atom have found extensive applications in modern industrial chemistry. The catalytic conversion of methane by water vapour is the principal method for the manufacture of hydrogen and the synthesis gas. Hydrocyanic acid and chloromethanes are obtained from methane. Acetylene is produced by the high-temperature pyrolysis of methane. The synthesis gas obtained by the conversion of methane is the raw material for the manufacture of methanol, which can in its turn be converted into olefins, liquid hydrocarbons, formaldehyde, and other products.

Procedures for the utilisation of C_1 compounds in the preparation of certain petrochemical products (monomers, intermediates, and motor fuels) have been developed vigorously in recent years.

Studies in this field are prosecuted on a broad front: new types of reactions of C_1 compounds are being investigated, new catalysts for processes already known are being developed, and new technological processes are being devised.

The present review deals with a series of new aspects of the chemistry of C_1 compounds of current interest (reactions in the presence of metal complex catalysts, including carbon dioxide fixation processes under mild conditions, direct catalytic synthesis of ethylene from methane, and the conversion of methane into liquid hydrocarbons) and of the technology of certain traditional processes (a new approach to the preparation of catalysts for the conversion of carbon dioxide by water vapour in the synthesis of methanol, the conversion of methane in thermochemical solar energy converters, the use of the principle governing the non-stationary technology in the synthesis of methanol and the oxidation of methanol to formaldehyde under adiabatic conditions). All these aspects are being vigorously developed at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences.

II. Direct catalytic syntheses of hydrocarbons from methane

Reactions involving the direct conversion of methane into valuable chemical products occupy an important place in the problem of catalytic syntheses on the basis of one-carbon compounds. The direct synthesis of ethylene—the key compound in fundamental organic synthesis—from methane is of greatest interest. The development of an effective method of preparation of ethylene from methane would permit a change-over of many petrochemical manufacturing processes to a non-petroleum raw material without altering the structure of these processes.

The conversion of methane into liquid hydrocarbons is also an important and currently interesting problem whose solution will make it possible, apart from all its other aspects, to facilitate the transport of hydrocarbon raw materials from gas deposits to sites where it is utilised.

1. Oxidative dehydrodimerisation of methane

The possibility of converting methane into ethylene even at very high temperatures is limited by the thermodynamic equilibrium.[1] High conversions can be attained only when the reaction is carried out with the participation of oxidants.

The necessity for the use of oxidants greatly hinders the selection of catalysts for this reaction, because, while effectively activating methane, they should at the same time activate oxygen only slightly in order to prevent the extensive oxidation of methane and its conversion products. This factor precludes the use in the given reaction of effective catalysts for the activation of hydrocarbons such as, for example, platinum metals.

The above difficulty can be obviated by carrying out the process in two stages: in the first stage, pure methane is dimerised using the oxygen in the catalyst (oxygen-free dimerisation), while in the second the catalyst is reoxidised by an oxygen-containing gas. In this version, a fairly high selectivity is attained but it is technologically complex and requires the use of catalysts with a high oxygen capacity.

Both a two-stage periodic and a one-stage continuous method for the oxidative dehydrodimerisation of methane are being developed at the present time. The periodic version of the process (with reoxidation of the catalyst) is being developed predominantly by

American investigators, while the continuous method is being studied vigorously in the Federal Republic of Germany, Japan, and the Soviet Union as well as the USA.

Fairly numerous publications devoted to the investigation of the mechanism of the catalytic oxidative dehydrodimerisation have been published during the last two years: the determination of the pathways leading to the formation of the reaction products, the nature of the active centres of the catalyst, and the role of homogeneous stages in the overall process.

(a) Catalysts

The first studies on the dehydrodimerisation of methane to ethylene using solid catalysts were published as late as the 1980's.

The Exxon Company took out a patent for the oxidative condensation of methane with the preferential formation of ethylene.[2] Solid oxides with deposited noble metals were used as the reactant-catalysts. The reaction was carried out with pure methane at 700 °C, the conversion of the methane reaching 44.8% with formation of 8% of ethylene, 3.2% of ethane, and 14.4% of benzene (the residue was coke). The catalyst became rapidly saturated with coke and required prolonged regeneration with oxygen-containing gas.

The interaction of methane with a large number of metal oxides deposited on silica gel has been investigated at 800 °C and a pressure of 15 mmHg.[3,4] At low degrees of conversion, the main reaction products were ethane and ethylene. Thorium dioxide proved to be the most effective catalyst.

Systematic studies on the oxidative dehydrodimerisation of methane via a two-stage mechanism on a large number of metal oxides deposited on Al_2O_3 [5] made it possible to divide these oxides into three groups: inactive, weakly active, and active (Fig.1). The highest yield of the oxidative dehydrodimerisation products (5% for an overall selectivity of 45% with respect to C_2 hydrocarbons) was obtained in the presence of manganese oxide. Here and henceforth the yield of the oxidative dehydrodimerisation products is defined as the fraction of carbon atoms in CH_4 which have been converted into C_2 hydrocarbons (C_2H_4 and C_2H_6) on contact with the catalyst and the selectivity is the fraction of carbon atoms which have been converted into C_2 hydrocarbons relative to the total number of carbon atoms of the methane which has reacted.

A still higher yield is attained in two-stage processes patented by investigators at the Atlantic Richfield Company.[6-22] Deposited oxides of manganese, Group IIIA, IVA, and VA elements, and the lanthanides with added alkali and alkaline earth metals and phosphate ions served as the catalysts in the above studies. The carriers were aluminium, silicon, magnesium, and titanium oxides. Best results were obtained on the $NaMnO_4/MgO-SiO_2$ [18] and Mn_3O_4/SiO_2 [14] systems. The yield of C_2 hydrocarbons at 800 °C was 13.4 and 15.2% respectively in the presence of these systems. The catalysts operate in very short cycles (1–2 min), after which their regeneration is required.

Later analogous catalytic systems were tested under single-stage continuous conditions using a reaction mixture containing oxygen together with methane.[23,24] The maximum yield of hydrocarbons on the Mn_2SiO_4 system at 800 °C was 12.2%.[24]

A higher yield of C_2 hydrocarbons was achieved using nitrous oxide as the oxidant.[25] In the presence of a catalyst containing 12.5% $NaMnO_4$ on MgO at 800 °C and for a reaction mixture containing 50% each of CH_4 and N_2O, yields of 11.7% of ethylene and 5.4% of ethane were attained.

The continuous oxidative conversion of ethane in a mixture with oxygen into C_2 hydrocarbons was first achieved on lead, bismuth, tin, antimony and manganese oxides deposited on alumina and other carriers.[26-28] Best results were obtained on deposited lead oxide catalysts. While the selectivity of the conversion of methane into C_2 hydrocarbons was 50–60%, the yield of the latter was 5%.

Much higher yields were obtained subsequently by the same group of investigators on basic catalysts. In the presence of the 6% NaOH/CaO system at 740 °C and CH_4 and O_2 pressures of 0.35 and 0.14 atm respectively, the yield of C_n ($n \geqslant 2$) hydrocarbons reached 17%.[29,30]

A series of catalysts based on magnesium oxide with added transition metal oxides have also been tested under continuous conditions.[31] The experiments were performed at atmospheric

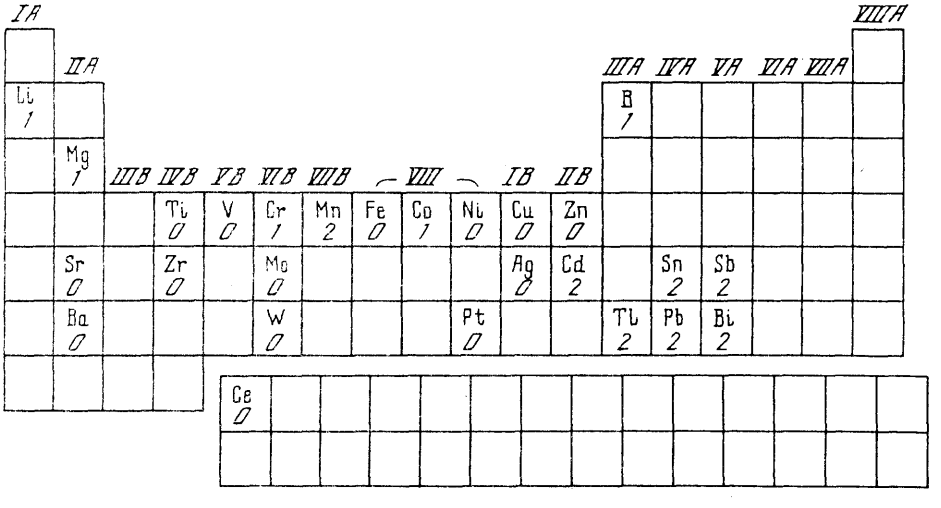


Figure 1. The activity of the oxides of elements in the formation of C_2 hydrocarbons from methane:[5] (*0*) inactive: (*1*) weakly active; (*2*) active.

pressure in a mixture containing 90% CH_4 and 10% O_2. The selectivity of the formation of C_2 hydrocarbons increased with increasing temperature and with decrease in contact time. Best results were obtained on unpromoted magnesium oxide: at 900 °C, the selectivity was 70% for a methane conversion of 9%. Deposited catalysts containing the oxides of Group IIIB elements were also tested under flow conditions.[32] The highest yield of C_2 hydrocarbons (2.3%) was reached in the presence of thallium oxide deposited on an aluminosilicate.

Catalysts not containing variable-valence elements have also been proposed for the oxidative dehydrodimerisation of methane.[33-35] On the 7% Li/MgO catalyst at 720 °C and CH_4 and O_2 pressures of 58 and 26 mmHg respectively, the yield of C_2 hydrocarbons was 19.4% for the ratio $C_2H_4:C_2H_6 = 1:5$. With increase in the pressures of the reactants, the yield falls. An appreciable decrease in the catalyst activity has also been observed during its use for several hours. The low stability of the system has also been noted in another study.[36]

The possibility of the oxidative dimerisation of methane has likewise been demonstrated on lanthanum oxides.[37] Under comparable conditions (725 °C, 40% CH_4, and 1% O_2), approximately the same results were obtained on this catalyst as on the lithium–magnesium system (the yield of C_2 hydrocarbons was approximately 2.5%). The best results were achieved at 725 °C and CH_4 and O_2 pressures in the reaction mixture of 57 and 17 mmHg (the remainder was helium). The yield of C_2 hydrocarbons amounted to 4.7%.

In a study of a series of MgO-based catalysts to which various elements (alkali metals and Group IIIA, IIIB, IVA, and IVB transition elements) had been added,[38] it was established that the yield of C_2-hydrocarbons increases with decrease in the oxidising activity of the catalyst. The latter was estimated from the temperature corresponding to 50% conversion of oxygen. The lowest yield of C_2 hydrocarbons was obtained on catalysts promoted by transition metals and the highest was on the Na/MgO system. At 800 °C and for a methane concentration in the mixture of 2.7%, the yield of C_2 hydrocarbons was 22.4%. An increase in the methane concentration in the mixture produced a sharp fall in the yield of C_2 hydrocarbons.

The influence of the nature of the support on the activity of the lead oxide catalysts in the formation of C_2 products has been investigated.[39] Basic supports proved to be best. The maximum yield of the dimerisation product was reached in the presence of the PbO/MgO system (6.6% of C_2 hydrocarbons at 750 °C and CH_4 and O_2 concentrations of 14 and 1% respectively).

Zeolitic catalysts have also been tested in the reaction involving the oxidative condensation of methane to C_2 hydrocarbons.[40] The Mn/HNa(HSZ)† catalyst, in the presence of which the selectivity in the formation of C_2 reached 50–65% for a methane conversion of 7–19%, was most effective.

Comparative tests under flow conditions on a large number of metal oxides in the oxidative methane dehydrodimerisation reaction have been carried out at 700 °C in the presence of a mixture containing 0.4% O_2 and 18.2% CH_4, the remaining being helium.[41,42] According to the results obtained,[41] which are presented in Fig.2, and in conformity with the results of previous studies, lead and bismuth oxides are some of the most active oxides in the given reaction. Furthermore, a new active catalyst of the oxidative dehydrodimerisation of methane has been discovered, namely samarium oxide. The selectivity of the formation of C_2 hydrocarbons in the presence of this catalyst reached 93%. Unfortunately the authors do not indicate the degree of conversion of methane to which this selectivity corresponds.

Subsequently an attempt was made to improve the catalytic properties of samarium oxide by adding alkali metal compounds.[43] A yield of C_2 hydrocarbons of 21% was attained on samarium oxide modified with lithium at 750 °C and methane and oxygen pressures of 50 and 20 mmHg respectively.

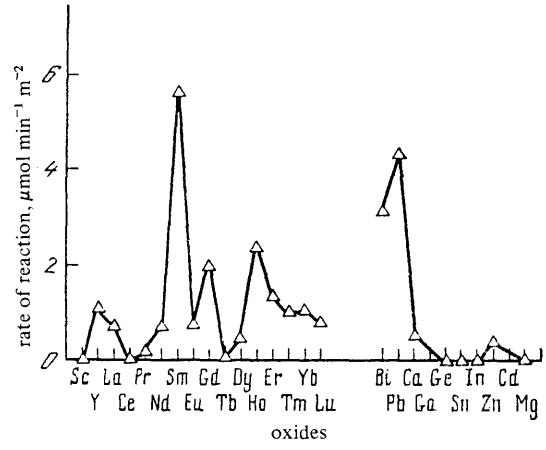


Figure 2. Comparative activities of various metal oxides in the oxidative dimerisation of methane.[42]

On lanthanum aluminate, the yield of C_2 hydrocarbons at 710 °C in a reaction mixture containing 50% of methane and as much air amounted to 12.5%.[44,45] An increase in temperature decreased the yield.

Attempts have been made in a number of studies to improve the properties of the catalysts of the oxidative dehydrodimerisation of methane by promoting them with halides and chalcogenides.[46-51]

Thus it has been suggested that compounds of the chalcogens (S, Se, and Te) be introduced into the catalyst beforehand and that the solid component be periodically made good as the chalcogen is consumed.[46,47] Halogens, especially chlorine, are introduced into the catalyst and a stage involving the treatment of the catalyst with a gaseous promoting agent (methyl chloride) is included in the cycle. Treatment of the catalyst with methyl chloride makes it possible to increase the selectivity with respect to C_n hydrocarbons ($n \geqslant 2$) by 15–20% for the periodic version of the process with reoxidation of the catalyst.

The addition of alkali metal halides to nickel, manganese, samarium, titanium, and zinc oxides[48-51] leads to an overall increase in the yield of C_2 hydrocarbons, mainly as a consequence of the appreciable increase in the yield of ethylene. Thus the yield of C_2 hydrocarbons on nickel(I) oxide promoted with Li_2CO_3 at 750 °C and at methane and oxygen concentrations of 5 and 2.5% respectively reaches 12.7% for a yield of ethylene of 6.9%. When lithium carbonate is replaced by the chloride, the above values are respectively 18.6 and 14.3%.[49] Catalysts promoted with halides are unstable and their activity falls sharply as the halides are decomposed.

†HSZ = high silica zeolite (Translator).

Thus a series of catalytic systems capable of operating under continuous conditions using a reaction mixture incorporating methane and oxygen have now been discovered. The most active catalysts are lead, bismuth, samarium, and manganese oxides. The addition of alkali metals increases the yield of the oxidative dehydrodimerisation products, but diminishes the stability of the catalyst. Promotion with halides also improves the yield of the C_2 hydrocarbons, but these catalysts are rapidly deactivated as a consequence of the loss of the halogen.

The majority of the catalysts ensure a high yield of oxidative dehydrodimerisation products only at a low methane concentration in the reaction mixture and the concentration of ethylene in the converted gas is therefore low even when its yield is high, which hinders its isolation and makes it more expensive.

Table 1 presents the yield of C_2 hydrocarbons in the oxidative methane dimerisation reaction obtained by different workers under continuous conditions.

Table 1. Oxidative dehydrodimerisation of methane in the continuous regime.

Contents in initial mixture		Yield of C_2, %	Refs.
CH_4	O_2		
5	2.5	22.3	[51]
7.6	3.8	19.0	[35]
2.7	1.35	22.4	[38]
20	0.5	6.7	[38]
35	14	17	[29]
50	10	12.2	[24]
30	20	24	Data from the
80	20	20	Institute of Catalysis

(b) The reaction mechanism

The first mechanism of the formation of ethylene from methane and oxide catalysts when the reaction is carried out in accordance with a two-stage scheme using the oxygen of the catalyst was proposed by Keller and Bhasin.[5] The authors suggest that the reaction proceeds via the formation of adsorbed CH_3 groups, which dimerise in the adsorbed state, and that the ethane obtained under these conditions undergoes subsequent catalytic oxidative dehydrogenation to ethylene:

$$2CH_4 + 2M^{2n+}O_n^{2-} \rightarrow 2OH_{ads} + 2CH_{3\,ads} + 2M^{(2n-2)+}O_{n-1}^{2-}, \quad (1)$$

$$2CH_{3\,ads} \rightarrow CH_3-CH_{3\,ads}, \quad (2)$$

$$2OH_{ads} \rightarrow H_2O + O_{ads}, \quad (3)$$

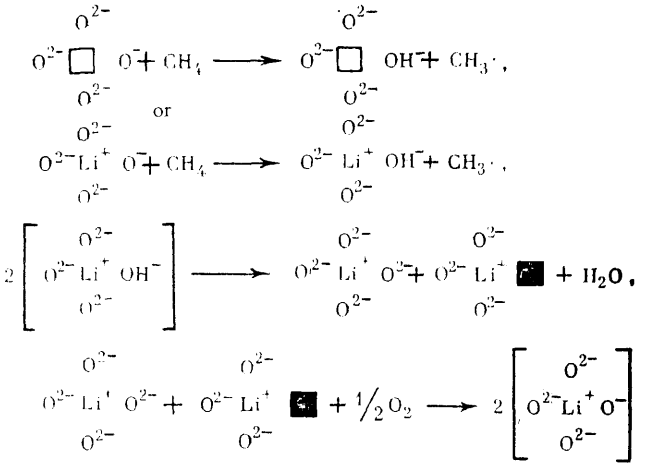
$$2M^{(2n-2)+}O_{n-1}^{2-} + O_2 \rightarrow 2M^{2n+}O_n^{2-}, \quad (4)$$

$$CH_3-CH_{3\,ads} + M^{2n+}O_n^{2-} \rightarrow CH_2=CH_2 + M^{(2n-2)+}O_{n-1}^{2-} + H_2O. \quad (5)$$

Estimation of the free energy of stage (1) yielded the conclusion that, for the majority of active oxides, this stage is thermodynamically allowed.[5] The involvement of adsorbed methyl groups in the oxidative methane dehydrodimerisation reaction has also been suggested in another study.[52] The source of the extensive oxidation products, which are also formed in this process, may be the methyl groups in the carbonium ion form arising when methane interacts with the acid surface centres.[52]

There exists also another view, according to which methyl radicals pass to the gas phase where the dimerisation products are actually formed.[33-35,53-60] In studies of the interaction of methane with the oxide catalysts of its oxidative dimerisation, methyl radicals were detected in the gas phase.[53] The same result was obtained by the lead mirror method in a study of the interaction of methane with deposited manganese oxide catalysts.[56] In their investigation of the generation of $CH_3^{\cdot}$ radicals on the Li/MgO catalysts, Driscoll et al.[53] concluded that the methyl radicals are formed with participation of the O^- ions on the catalyst surface. Reactions leading to the generation of active centres in the formation of methyl radicals according to these workers[55] are presented in Scheme 1:

Scheme 1



where ■ and □ are the anionic and cationic vacancies respectively.

According to the concept developed by Lunsford and co-workers,[35] the appearance of a radical centre in a binary oxide system is associated with the replacement of the divalent magnesium ion by the univalent lithium ion, which has a suitable radius. The introduction of larger ions (for example, Na^+) should not promote the appearance of such centres, which has in fact been confirmed in experiments where sodium carbonate had been added to MgO.[35] On the other hand, the addition of sodium ions to calcium oxide makes it possible, according to the authors' views, to increase the yield of dehydrodimerisation products.

However, it was shown later that, when magnesium oxide is promoted by sodium ions, it is possible to obtain a more effective catalyst of the dimerisation of methane than the lithium–magnesium system.[38] These results throw doubt on the concept of the methane activation mechanism described above.

It has been suggested[61,62] that the peroxide ions O_2^{2-} can function as the active centres of catalysts based on alkaline earth metal oxides modified by alkali metal ions.

In a study of the mechanism of the dehydrodimerisation of methane on lanthanum oxide,[37] it was not possible to observed O^- ions on the catalyst surface. A methane activation mechanism with participation of O_2^- ions was proposed for this oxide. According to the authors,[37] the extensive oxidation products are formed preferentially via two pathways: with participation of the oxygen of

the catalyst surface:

$$CH_3^{\cdot} + O^{2-} \rightarrow CO,\ CO_2$$

and via methylperoxy-radicals:

$$CH_3^{\cdot} + O_2 \rightarrow CH_3O_2^{\cdot} \rightarrow CO,\ CO_2.$$

Another concept of the activation of methane in its oxidative dimerisation reaction has also been put forward.[63-65] It has been established[63] that the overall rate of conversion of methane and the rate of formation of the dehydrodimerisation products increase with increase in the concentration of the basic centres on the catalyst surface. Furthermore, an increase in the formation of C_2 products is promoted by the presence of electron acceptors in the catalyst.[64] In view of these facts and bearing in mind the overall characteristics of the selective reactions of hydrocarbons involving the C–H bond,[65] by analogy with the scheme proposed previously for the activation of propene with formation of the allyl radical,[66] the following scheme may be proposed for the activation of methane in which the involvement of the basic centres of the catalyst and of electron acceptors is postulated:

$$CH_4 \xrightarrow[-H^+]{Nu^-} CH_3^- \xrightarrow[-e^-]{A} CH_3^{\cdot},$$

where Nu^- is the basic centre of the catalyst and A is an electron acceptor. The methyl radical formed should be relatively weakly bound to the catalyst surface. It may be desorbed to the gas phase and dimerise or it may be converted into the methylperoxy-radical $CH_3O_2^{\cdot}$ after interaction with an oxygen molecule.

The mechanism of the gas-phase reactions in the oxidative dimerisation of methane, which has been analysed in detail,[58-62] includes the following main pathways in the reactions of the methyl radical formed as a result of the heterogeneous activation of methane:

$$CH_3^{\cdot} + CH_3^{\cdot} \rightarrow C_2H_6,$$
$$CH_3^{\cdot} + O_2 \rightleftarrows CH_3O_2^{\cdot},$$
$$CH_3O_2^{\cdot} \rightarrow CO,\ CO_2.$$

Analysis of this scheme taking into account the known rate constants for the individual stages yielded an expression for the limiting selectivity in the formation of C_2 hydrocarbons, which agrees well with experimental data.[66]

Thus fairly selective catalysts of the oxidative dimerisation of methane have now been found and the principal features of the process mechanism have been established. However, a high selectivity is attained as a rule at low reactant concentrations or at low conversions, so that the yield of the target products, in the first place ethylene, is low after a single pass. The stability of the catalyst remains an unsolved problem. The question of the nature of the centres for the activation of methane, without the elucidation of which a purposeful selection and improvement of catalytic systems are impossible, also remains controversial.

Nevertheless, on the basis of the results already obtained, one may hope that an effective industrial process for the synthesis of ethylene from methane will be created in the next few years.

2. Conversion of methane into liquid hydrocarbons on zeolitic catalysts

Zeolitic catalysts are widely used in various hydrocarbon reactions. The appearance of new generation zeolites (pentasils) also made it possible to achieve the syntheses of hydrocarbons from compounds containing one carbon atom in the molecule. In particular, the processes leading to the conversion of methanol into hydrocarbons, the preparation of hydrocarbons from the synthesis gas, and the oxidative synthesis of higher hydrocarbons from methane have been achieved. The first two processes have been studied in detail and the results have been surveyed in a number of reviews.[67-70] The synthesis of higher hydrocarbons from methane on zeolites is a comparatively new and little investigated field.

As a consequence of the chemical inertness and thermodynamic stability of methane, the use of high temperatures is suggested in the known single-stage methods for its conversion into other organic compounds. The reactions of methane at 600 °C in the presence of decationated platinum-containing zeolites of the type of pentasil have been investigated at 600 °C.[71] The only hydrocarbon reaction product was benzene, whose yield reached 6%, while the rest consisted of the products of the extensive oxidation of methane. The absence of higher hydrocarbons is apparently associated with thermodynamic limitations.

The "cracking" of methane on nickel-containing pentasil-type zeolites above 400 °C is of interest.[72] The catalyst specimens subjected to a reducing treatment proved to be inactive. Zeolites of the faujasite type also did not exhibit an appreciable activity in this process. Unfortunately, the authors do not quote the composition of the methane reaction products.

The synthesis of higher hydrocarbons from methane in a single technological stage is thermodynamically possible under milder conditions when oxidants are used. Such a process can be achieved via a stage involving the formation of intermediates of type CH_3X, which are obtained in the oxidation of methane:

$$CH_4 + X{-}R \rightarrow CH_3X + HR$$
$$(X - R = \text{oxidant}),$$

and a stage in which CH_3X is converted into hydrocarbons:

$$nCH_3X \rightarrow nHX + C_nH_m.$$

The catalyst of such a process must be bifunctional, i.e. it must contain a component active in the oxidation stage and a zeolite which propagates the conversion of CH_3X into hydrocarbons.

The reactions of methane on zeolitic catalysts in the presence of oxidants (Cl_2, Br_2, O_2, NO, N_2O, NO_2, and SO_3) have been investigated at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences.[73-75] Catalysts of the chlorination or bromination of methane ($ZnCl_2$ and $CuCl_2$) and catalysts of the oxidation of methane (iron, copper, molybdenum, and cobalt oxides) were added, via impregnation, ion exchange, or mechanical blending to the high-silica zeolite in order to accelerate the oxidation stage. In the presence of molecular oxygen, chlorine, or bromine, the extensive oxidation or halogenation products were formed preferentially. In the presence of nitrous oxide as well as halogens at low concentrations, the formation of higher hydrocarbons was observed. On pentasil-type zeolites without acid transition elements, the selectivity of the formation of aromatic hydrocarbons exceeded 90%

under optimum conditions when N_2O was used as the oxidant and the yield relative to the methane passed through the system reached 40%.

The possibility of carrying out the oxidative synthesis of aromatic hydrocarbons from methane on pentasils using N_2O as the oxidant has also been confirmed in another study.[76]

Thus, in the presence of nitrous oxide, it is possible to attain an appreciable yield of liquid hydrocarbons from methane. Further studies should be directed to the replacement of N_2O by a cheaper and more readily available oxidant.

III. New approaches to the synthesis of catalysts and the carrying out of traditional catalytic processes with participation of C_1 compounds

As already mentioned, large-scale catalytic processes based on C_1 compounds, such as the conversion of methane and carbon monoxide, the conversion of methanol into formaldehyde, etc., have now been achieved in practice in the chemical industry. Despite this, the search for effective catalysts of these processes and of new applications of the reactions underlying them is being vigorously continued together with the development of new technological principles governing their occurrence.

In particular, at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences, methods of synthesis of low-temperature catalysts for these processes via the anionic modification of oxides are being developed, studies are being made of the possibility of using the conversion of methane in the thermochemical solar energy converter, and the technology of the synthesis of methanol under artificially created non-stationary conditions and a new technology of the oxidation of methanol to formaldehyde in reactors with adiabatic beds of an oxide catalyst are being developed.

1. Catalysts of low-temperature processes involving the synthesis of methanol and the conversion of carbon monoxide

The application of refined methods for the purification of the synthesis gas by eliminating sulphur-containing compounds promoted a wide-scale introduction of processes involving the synthesis of methanol and the vapour-phase conversion of CO (the ammonia synthesis stage) at low temperatures. The need to purify the gas is associated with the fact that the low-temperature copper-containing catalysts, which are highly effective in these processes, are deactivated in the presence of even small amounts of sulphur compounds as impurities. Both processes take place mainly on copper–zinc–aluminium, copper–zinc–chromium, or copper–zinc–chromium–aluminium catalysts. The importance of these processes for the chemical industry promoted extensive investigation of the mechanism of the reaction of copper-containing catalysts, their phase composition, and the active state of copper.

(a) The active state of copper

In the very first studies on the catalytic properties of copper-containing catalysts of the synthesis of methanol[77–79] and the conversion of CO,[80,81] it was established that copper oxide is rapidly deactivated at temperatures from 200 °C upwards. The introduction of zinc oxide appreciably improves the properties of the catalyst,[78,79,82] while the addition of a third oxide increases its efficiency still more. Aluminium,[83–85] chromium,[82,86,87] cerium,[88] and manganese[89,90] oxides as well as the oxides of other elements are used as the third component of this kind. Aluminium and chromium oxides are the most effective. Catalysts containing these additives have found industrial applications.

It has been suggested[77–79,82] that the rapid loss of activity by copper oxide is caused by its reduction to the metallic state. The introduction of promoting oxides increases the stability of copper oxide. The above hypothesis lacked experimental confirmation for a long time. On the other hand, the view that the activity of the catalyst in the reactions considered is determined by the metallic copper phase, formed on the surfaces of stable aluminium and chromium oxides or zinc–aluminium and zinc–chromium spinels on activation of the catalyst or under the influence of the reaction medium, gained currency.[91–98] In many cases, the metallic copper phase appears in highly active catalysts after the synthesis of methanol or the conversion of CO. According to numerous data,[92,93,97–100] the activity of the catalysts diminishes with increase in the size of the copper crystals. Catalysts containing 50–70 Å copper crystals are the most active in the conversion of CO.[97] However, numerous attempts[101–104] to find a quantitative relation between the area of the metallic copper, determined by the "chemisorption" method, and the activity of the catalysts in both reactions considered proved unsuccessful. The absence of such a dependence makes the idea that the mechanism of the action of copper-containing catalysts is associated with the formation of the metallic copper phase under the reaction conditions less convincing. In principle, one can postulate that the catalytic reaction between the reactants can occur both on the metallic copper and on surface copper ions in oxide compounds stable under the reaction conditions. The overall activity is in this case determined by the surface area of the active components (phases) and the atomic (ionic) activity of copper in these components. In order to solve the problem of the nature of the active phase, it would be necessary to compare the catalytic properties of metallic copper in a specimen where the possibility of the presence of the ionic form of copper has been ruled out with the catalytic properties of various copper-containing compounds stable under the reaction conditions to such an extent that this completely excludes the formation of metallic copper. However, it proved difficult to characterise the catalytic capacity of purely metallic copper, because the massive specimens have a low surface area and the application of deposited catalysts makes it impossible to guarantee the absence of copper in the ionic form.

Thus it has not yet been possible to characterise quantitatively the catalytic properties of metallic copper in reactions involving the synthesis of methanol in the water vapour conversion of CO. On the other hand, the catalytic properties of compounds in which copper is known to be in the ionic form have been investigated for both reactions.

(b) Catalytic properties of copper-containing oxide compounds

The catalytic properties of copper chromites, ferrites, aluminates, and chromite ferrites, in which part of the copper has been substituted by zinc, magnesium iron(II), and other metal ions, have been investigated in CO conversion reactions.[105–107] Partial substitution

of copper ions ensures the stability of the above compounds in the reaction medium up to high temperatures which prevents the formation of metallic copper under the reaction conditions at 200–270 °C. These compounds have the spinel structure, but contain copper ions in different crystallographic positions, surrounded by oxygen ions in tetrahedral and octahedral configurations. In addition, studies have been made of the properties of solid solutions of copper ions in magnesium oxide which are stable under the reaction conditions.[107] It was found that the specific activities of the spinel are comparable to those of the best industrial catalysts, while the solid solution of copper ions in magnesium oxide is much more active than the latter at 270–300 °C. The activation energy depends on the positions of the copper ions: if they are in tetrahedral positions, the activation energy is 9–10 kcal mol^{-1}, while for the octahedral positions it amounts to 19–20 kcal mol^{-1}. In the presence of the copper–zinc–aluminium–chromium industrial catalyst, the activation energy is 8–13 kcal mol^{-1}.[91]

Depending on the component ratios and the conditions of the synthesis in the copper–zinc–aluminium system, the following copper-containing compounds are formed after heat treatment at 350–400 °C (the temperature at which the industrial catalyst is prepared): copper oxide, solid solutions of zinc and aluminium ions in copper oxide,[108–110] a solid solution of copper ions[109–113] or copper and aluminium[109,110,112,114] in zinc oxide, the copper–zinc–aluminium spinel,[99,109,110,115,116] and a solid solution of copper ions in the spinel.[115] As already mentioned, copper oxide and solid solutions based on it are unstable under the conversion reaction conditions and are rapidly deactivated. The copper–zinc–aluminium spinel and the solid solution of copper and aluminium ions are stable in the reaction medium at least up to 500 °C and their activity is not inferior to that of the most active industrial catalysts.

Among the compounds formed in the copper–zinc–aluminium system, only the solid solution of copper and aluminium ions in zinc oxide is not inferior as regards its activity in the synthesis of methanol and the stability under the conditions of this reaction to the most effective of the known industrial catalysts. The copper–zinc–aluminium spinel is stable under the conditions of the synthesis of methanol, but is much less active than in the conversion reaction.[110,117] These results suggest that the rate of synthesis of methanol depends very greatly on the state of the copper ions and that the state of the copper ions which ensures the necessary activation of the reactants obtains only in the solid solution based on zinc oxide. This explains the marked dependence of the activity of the copper–zinc–aluminium catalyst in the synthesis of methanol on the conditions governing its formation, noted by Bondar' et al.[83] and Shishkov et al.[84] The catalytic properties of the system in the CO conversion reaction also depend on the state of the copper ions, but not so markedly.

The first indication of the high activity of copper ions dissolved in zinc oxide was obtained in a study[112] where it was shown that about 10 at.% of copper is dissolved in zinc oxide in the active copper–zinc catalyst. On the other hand, it is known[118] that the method involving substitution in zinc oxide can lead to the dissolution of not more than 1–2 at.% of copper(II). This is due to the low tendency of copper(II) ions to be involved in tetrahedral coordination with oxygen. It has been suggested that the increased solubility is attained as a result of the dissolution of copper(I) ions. Indeed, an increase in the dissolution of copper in a reducing medium has been observed[112,119] and it has been concluded that the aluminium oxide in the copper–zinc–aluminium catalyst plays the role of a support increasing the surface area of the zinc oxide-based solid solution. However, it has been shown[113,115,117,120] that aluminium fulfils more complex functions in this catalyst.

Copper zinc hydroxoaluminate with a high M(II) : M(III) ratio, having a structure of the hydrotalcite (pyroaurite) type,[115,121,122] and copper-aluminium-zinc hydrocarbonate having a structure of the hydrozincite[84,112,113] or aurichalcite[123] type, are precursors of the active zinc oxide-based solid solution in the preparation of the catalyst by the method involving the precipitation of hydroxo-compounds or the mixing of the components. A study by EPR or electronic spectroscopy of the state of copper in the hydroxo-aluminate with a structure of the hydrotalcite (pyroaurite) type and in the copper-zinc and copper-zinc-aluminium hydroxocarbonates with a structure of the hydrozincite type showed[124] that the copper(II) ions are distributed preferentially at distorted octahedral sites. The concentration of copper(II) ions in the hydroxo-compounds exceeds the maximum possible concentration in zinc oxide.[113] As a result of heating at 350 °C,[125] the above hydroxo-compounds decompose with formation of a solid solution of copper and aluminium ions in zinc oxide and, when the content of copper and aluminium is in excess of a certain level, copper oxide and an aluminium spinel are also formed. The content of copper(II) in zinc oxide is (with retention of the homophase structure) approximately 10 at.% in the copper–zinc system and up to 20 at.% in the copper–zinc–aluminium system. If the copper content in zinc oxide in the copper–zinc–aluminium system reaches 35 at.%, then a certain amount of copper oxide is formed simultaneously.

Heat treatment at higher temperatures is accompanied by the evolution of water vapour and CO_2 and leads to a decrease in the copper content in zinc oxide to 1–2 at.%. According to the data of Hadzhieva et al.,[124] 1–2 at.% of copper(II) substitutes the zinc ions in tetrahedral positions in the zinc oxide, while the remainder is distributed in the form of clusters consisting of several ions. The copper ions in the clusters are apparently in a strongly distorted octahedral environment comprising oxygen ions. In the solid solution of copper and aluminium ions in the low-temperature zinc oxide, virtually all the copper(II) ions exist as associated species. The possibility of such distribution of copper ions is apparently determined by the appearance of defects in the zinc oxide structure as a result of the complete removal of OH^- and CO_3^{2-} groups from the oxide. The impurity anions are removed at a fully defined temperature and the low-temperature zinc oxide is therefore anionically modified.

The formation of anionically modified oxides at low temperatures is characteristic of many metals. For example, anionically modified nickel, magnesium, and copper oxides as well as aluminium and chromium spinels have been obtained.[125]

The degree of oxidation of copper ions on the surfaces of copper-containing compounds, stable under the conditions of the reactions considered, has been investigated by various workers.[111,114,126–132] The results obtained suggest that, under the influence of the reaction medium, the copper ions are reduced to copper(I). According to some data,[133,134] the conversion reaction proceeds via intermediate complexes of the formate type formed from the copper(I) ions. There exist contradictory views concerning the mechanism of the synthesis of methanol. Various mechanisms have been examined in reviews.[135,136]

It follows from the data obtained in the studies examined above that the catalytic activity of the ionic forms of copper is sufficiently high to attribute to these forms the high activity of the industrial copper-containing catalysts of the synthesis of methanol and of the water vapour conversion of CO. Among these forms, a high

activity in both processes is shown by associated copper ions forming part of the composition of the low-temperature anionically modified zinc oxide.

(c) Catalytic properties of the skeletal catalysts

As a result of the leaching of copper-zinc and copper-zinc-aluminium alloys, metal oxide systems are formed[137,138] which can be regarded as metallic copper on the surface of which copper and zinc oxides are present.

According to some data,[139,140] leaching results in the formation of porous copper which is responsible for the activity of the catalyst in the synthesis of methanol. Studies by the XPES and XRES‡ methods[132] have shown that, after leaching, structures resembling those formed on the surface of the copper-zinc–aluminium oxide catalyst predominate on the surface of the skeletal [Raney] copper-zinc-aluminium catalyst, namely associated copper ions incorporating also zinc and oxide ions. Under the reaction conditions, copper ions in the +1 oxidation state catalyse the interaction of the adsorbed CO and H_2O. Consequently the activity of skeletal catalysts in the CO conversion reaction is determined by the copper ions in the oxide compounds.

(d) Resumé

The data examined show that the high activity of all the catalysts investigated, apparently including the skeletal catalyst, can be accounted for by the formation of compounds stable under the reaction conditions and containing copper in the ionic form. In the copper–zinc–aluminium and copper–zinc–chromium catalysts, such compounds in the CO conversion reaction may be the copper-zinc-aluminium and copper-zinc-chromium spinels and a solid solution of copper and aluminium (or chromium) ions in zinc oxide, while in the synthesis of methanol a solid solution of copper and aluminium (or chromium) ions in zinc oxide is a formation of this type. In the case of skeletal catalysts, these compounds are apparently formed as films.

A high concentration of copper in zinc oxide is attained by virtue of the formation at low temperatures (below 500- °C) of zinc oxide with a defective structure—anionically modified by CO_3^{2-} and OH^- groups. This structure ensures the stabilisation of copper ions in the form of associated species in which the copper ions are most probably surrounded by oxygen ions in a square planar configuration. The number of defects (and hence the concentration of copper) and, what is most important, the thermal stability of the anionically modified states in air and under the reaction conditions increase after the incorporation of chromium(III) or aluminium(III) ions in the structure.

One should note that the change in the miscibility of copper and zinc oxides as a result of the anionic modification of the oxide matrix, observed in two investigations,[120,125] has been confirmed in a number of other oxides, including oxides with a complex composition. Presumably this phenomenon may be used to regulate the properties of the oxide catalysts not only in the synthesis of methanol and the water vapour conversion of CO but also in other oxidation-reduction reactions.

2. The synthesis of methanol under artificially created non-stationary conditions

A new highly effective method for the synthesis of methanol, based on catalytic processes under artificially created non-stationary conditions, is examined in the present Section.[141–143] The advantages of such processes are manifested when reversible exothermic reactions are carried out. In this case the optimum regime from the standpoint of the yield of the useful product can be obtained under non-stationary conditions in only one catalyst bed and not in several beds as happens in current large-scale industrial plant. This significantly simplifies the apparatus and makes the process less expensive.

(a) The principle of the method

Suppose that the stationary bed of a copper-containing catalyst was heated beforehand to approximately 260 °C, whereupon synthesis occurs at an appreciable rate. The introduction into the catalyst bed of the reaction mixture with an overall concentration of carbon oxides $c_{CO} + c_{CO_2} \simeq 6$–8 vol. % and a hydrogen concentration $c_{H_2} \simeq 80$ vol. % begins at time $t = 0$. The mixture is at a low temperature (~50 °C), at which the rate of synthesis of methanol is negligible. Under these conditions, the sections of the catalyst bed adjoining the point of entry of the reaction mixture begins to cool down and the reaction mixture is gradually heated to the temperature corresponding to the onset of reaction. The central part of the bed then retains a high temperature for a long time for two reasons: owing to the high ratio C_c/C_r of the heat capacities of the catalyst (C_c) and the reaction mixture (C_r) as a consequence of the evolution of the heat of reaction. According to Kiselev and Matros,[144] the thermal front of the exothermic chemical reaction is formed under these conditions and migrates along the bed at a rate which is lower by a factor approximately equal to C_c/C_r than the rate of penetration of the reaction mixture. At a time approximately equal to $(C_c/2C_r)t_c$, where t_c is the time of contact between the reaction mixture and the catalyst bed, the direction of the supply of the reaction mixture is reversed and the thermal front also begins to migrate in the opposite direction. After several such switch-overs, a cyclic reaction regime is established in the catalyst bed.

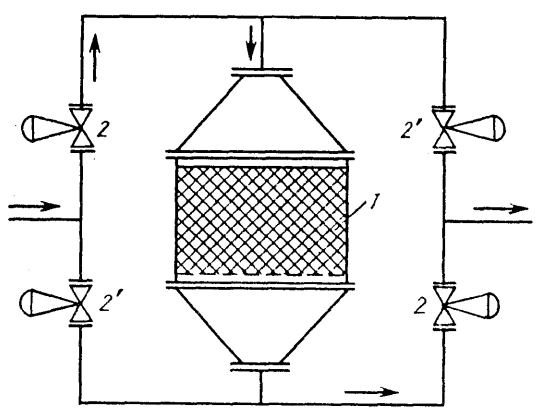


Figure 3. Schematic technological diagram of a reactor with a stationary catalyst bed working in the regime involving the periodic alteration of the direction of supply of the reaction mixture: (*1*) catalyst bed; (*2*) and (*2'*) valves.

The technological scheme for the non-stationary synthesis of methanol described above is fairly simple (it is illustrated in Fig.3). The valves *2* and *2'* shown in the figure open (*2*) and close (*2'*) periodically and simultaneously during the first half-period and

‡X-Ray photoelectron spectroscopy and possibly X-ray fluorescence spectroscopy (Ed. of Translation).

conversely close (*2*) and open (*2'*) during the second half-period, which ensures the establishment of a non-stationary technological regime.

We shall consider briefly the principal disadvantages of the method proposed[145] for the synthesis of methanol under the conditions of the periodic alteration of the direction of supply of the reaction mixture into the stationary catalyst bed.

1. Apart from its principal function of accelerating the chemical reaction, the catalyst plays the role of a regenerative heat exchanger. This makes it possible to make do almost completely without heat exchange equipment, which greatly reduces the requirement for metal in the catalytic unit. For example, the apparatus comprising an expensive and cumbersome external heat exchanger is eliminated in the proposed procedure.

2. Without the introduction of additional energy in the corresponding heat exchange equipment, it is possible to process industrial gases with a low content of carbon oxides, down to $c_{CO} + c_{CO_2} \simeq 0.4$ vol. %. This is of fundamental importance, for example, in the processing of straight-run gases.

3. Conditions which are theoretically nearly optimal from the standpoint of the yield of the useful product are created in the catalyst bed. This makes it possible to employ simple and cheap catalytic apparatus, which is not inferior as regards its characteristics to more expensive and cumbersome industrial apparatus working under traditional stationary conditions. The reason for this is as follows. The synthesis of methanol is a reversible exothermic process and, in the ranges of the temperatures and pressures indicated above, it proceeds close to equilibrium conditions. In the theoretically optimum regime, a decrease in the reaction temperature with increase in the degree of conversion of carbon oxides into methanol is required. When the process takes place in adiabatic catalyst beds under stationary conditions, the opposite picture naturally obtains. Therefore in practice part of the cold gas is conducted through a bypass between the catalyst beds or intermediate heat exchangers are set up in which the reaction mixture is cooled. In the non-stationary regime, there is a section at the exit of the reaction mixture from the catalyst bed where the temperature is reduced and the amount of methanol formed increases. Thus, in a single catalyst bed it is possible to achieve yields of methanol which in the stationary regime are attained when several adiabatic beds are used. Consequently, as a result of a closer approach to the theoretically optimum conditions than in the stationary regime, the design of the reactor and the entire process are greatly simplified.

4. In a catalyst bed working in a non-stationary regime, it is possible to reduce the average temperature by approximately 100 °C. Other conditions being equal (identical initial composition and linear flow rate of the reaction mixture, grain size, and amount of the catalyst), this lowers the hydraulic resistance of the bed by approximately 30%. Furthermore, the overall hydraulic resistance of the system is reduced as a result of the significant simplification of the design of the catalytic apparatus and decrease in the overall length of the tubing.

5. As a result of the simplification of the design of the catalytic unit, which incorporates one catalyst bed, the heat losses to the surrounding medium are reduced severalfold, which is particularly important for the utilisation of straight-run gases for the processing of which it is difficult to create an autothermal regime under traditional stationary conditions.

6. In the existing stationary methods of synthesis, it is necessary to achieve the stabilisation of the initial composition, temperature, and charge of the initial reaction mixture. This requires the creation of a cumbersome and complex automatic control system, especially if account is taken of the time variation of the activity of the catalyst. The non-stationary method permits the processing of the reaction gases with both constant and variable parameters and does not require the development of a special automatic control system.

(b) Mathematical modelling

As already mentioned above, there is no unanimous view concerning the mechanism of the synthesis of methanol on copper-containing catalysts. Thus Pomerantsev et al.[146] and Rozenfel'd and Rusov[147] believe that the process proceeds in accordance with the scheme $CO_2 \rightleftarrows CO \rightleftarrows CH_3OH$. However, in other studies[148,149] it has been suggested that the scheme $CO \rightleftarrows CO_2 \rightleftarrows CH_3OH$ is more probable. The following expressions have been obtained[150] for the rates of synthesis of methanol from CO_2 (w_1) and of conversion of CO (w_2):

$$w_1 = \frac{k_1 c_{H_2}}{1 + b_{H_2O} c_{H_2O}} \left(1 - \frac{c_{CH_3OH} c_{H_2O}}{K_1 c_{H_2}^3 c_{CO_2}}\right),$$

$$w_2 = \frac{k_2 c_{H_2}}{1 + b_{H_2O} c_{H_2O}} \left(1 - \frac{c_{CO} c_{H_2O}}{K_2 c_{H_2} c_{CO_2}}\right),$$

where k_1 and k_2 are the rate constants for the formation of methanol and the conversion of CO respectively, K_1 and K_2 are the corresponding equilibrium constants for the same reactions, b_{H_2O} is the adsorption coefficient for water, and c_i (i = H_2, H_2O, CH_3OH, CO, and CO_2) are the corresponding concentrations.

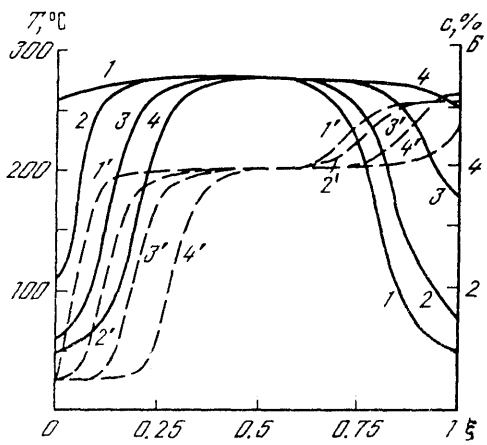


Figure 4. The temperature distribution (continuous lines) and methanol concentration (dashed lines) along the length of the catalyst bed ξ ($0 \leqslant \xi \leqslant 1$) in an established cyclic regime according to mathematical modelling data.[151] The gas moves from left to right. Composition of the initial mixture (vol. %); CO, 3.74; H_2, 81.9; CH_3OH, 0.474; CO_2, 2.033; H_2O, 0.078; N_2, 1.558; CH_4, 10.189. The conventional contact time is 0.5 s, which corresponds to a space velocity of 7200 h^{-1}. Pressure 7.2 MPa; mixture temperature at entry 50 °C; duration of cycle 10 min. The different curves correspond to different times t after the switch-over: (*1*) 0 min (start of half-cycle); (*2*) 1 min; (*3*) 3 min; (*4*) 5 min (end of half-cycle).

Fig. 4 presents examples of the calculation of the temperature and concentration fields in the catalyst bed on the basis of the so called two-phase model taking into account the external heat and mass exchange between the outer surface of the catalyst grain and the stream of the reaction mixture, the longitudinal heat transfer along the catalyst bed, and the internal diffusion inhibition of the reaction within the porous catalyst grain.[151] As can be seen from this figure, a decrease in temperature in the reactor with increase in the degree of conversion of carbon oxide is characteristic of the proposed method. For example, if the initial mixture contains ~5.75 vol. % of carbon oxides and ~0.47 vol. % of methanol, this makes it possible to obtain more than 5 vol. % of methanol at the exit from the bed. We may note that the equilibrium methanol content at 275 °C in the central part of the bed is ~3.9 vol. %, i.e. is appreciably lower.

Calculations have shown that the removal of the heat of the chemical reaction from the central part of the catalyst bed via a heat exchanger permits an increase in the yield of methanol by approximately 15% and an additional gain of heat, which is potentially highly utilisable. In practice both these possibilities are extremely useful. We may note that the yield of methanol in the system considered is much higher than in the traditional four-bed reactor with bypasses for the introduction of the cold gas between the catalyst beds, operating under optimum conditions. An experimental test in the reactor charged with three litres of the catalyst confirmed the possibility of synthesising methanol in a non-stationary cyclic regime and the validity of the principal conclusions reached from the results of mathematical modelling.

3. Oxidation of methanol to formaldehyde in a reactor with adiabatic oxide catalyst beds

The formation of formaldehyde from methanol on oxide catalysts is more economical than on silver-containing catalysts. In connection with the growth of the requirement for formaldehyde, it has become necessary to create plants with a unit capacity in excess of 50 000 to 60 000 tonnes per year. The application of tubular and combined reactors[152] with such capacity is difficult owing to the complexity of their construction and operation. Reactors with adiabatic catalyst beds appear to be most promising.[153]

The principal results of the development of a reactor of this type found by mathematical modelling studies of the kinetics and the temperature and concentration fields in the catalyst bed are briefly summarised in the present Section. The processes within a porous catalyst grain were described in terms of a quasi-homogeneous model. Stationary regimes in the adiabatic bed were determined by analysing the ideal displacement model with respect to matter and heat. The transient regimes in the stationary catalyst bed were calculated with the aid of a model taking into account the mass and heat exchange between the external surface of the grain and the gas stream and also the longitudinal transfer of heat along the skeleton of the catalyst bed.

Since the iron-molybdenum oxide catalyst works at temperatures in the range 220–350 °C[154] and the oxidation of methanol to formaldehyde is accompanied by an appreciable evolution of heat, the process must be carried out in several adiabatic beds arranged in series with removal of heat between them. However, when the process is carried out in this way, the output parameters of the reaction mixture, especially in the first beds, are very sensitive to changes in its input parameters. This hinders the use of catalytic apparatus of this type in carrying out processes involving the partial oxidation of hydrocarbons. Using mathematical modelling methods, it has been possible to put forward a process regime whereby the above difficulties can be overcome.

This required the solution of the following problems: (1) to ensure conditions under which the parametric sensitivity of the output parameters to changes in the input parameters does not exceed that required for technological reasons; (2) to develop an automatic control system which ensures the stabilisation of the technological parameters within specified limits.

The solution of the first problem reduced to the selection of the optimum grain size along the catalyst beds. In the oxidation of methanol to formaldehyde in the presence of the iron–molybdenum catalyst, two consecutive reactions take place: the oxidation of methanol proper and the oxidation of formaldehyde. Kinetic studies have shown[155] that the first reaction is of first order with respect to methanol and is inhibited by water. Formaldehyde hardly influences the rate of oxidation of methanol. The oxidation of formaldehyde is of first order with respect to formaldehyde and is inhibited by methanol and water.

Numerical analysis of the processes occurring on the catalyst grain led to the construction of a model of the observed reaction rates on grains of different size and shape in the temperature range 200 to 350 °C.[154] The characteristics obtained served as the basis for the mathematical modelling of the industrial reactor.

The catalyst grain size was chosen to ensure the permissible parametric sensitivities with retention of a sufficiently high process selectivity. The parametric sensitivity can be reduced by lowering the observed activation energy. When the process passes from the kinetic to the internal diffusion region, the observed activation energy E diminishes by a factor $\exp(\Delta T_{ad}x/RT_0^2)(E/2)$, where ΔT_{ad} is the adiabatic temperature rise in the mixture, x the degree of conversion, and T_0 the input temperature. For the iron-molybdenum catalyst in the specified temperature range, the increase in grain size is virtually the only parameter with the aid of which it is possible to reduce appreciably the activation energy.[156] An increase in grain size improved also the dynamic properties of the adiabatic bed. Furthermore, as a result of the decrease in the observed activation energy with increasing grain size, the possibility of the so called dynamic stoppages is diminished and the transient regimes develop more slowly. Ultimately favourable conditions are created for the automatic control of the process in the bed. However, an increase in grain size, which leads to an increase in the internal diffusion resistance, tends to increase the contribution of the side reaction involving the oxidation of formaldehyde to carbon monoxide and water and requires an increase in the catalyst charge. Thus it is essential to select an optimum catalyst grain size.

For this purpose, calculations have been made of the temperature and concentration fields in the reactor with adiabatic catalyst beds for an initial methanol concentration of 6–6.5 vol. %. The results obtained show that an increase in the grain size R_0 to 3 mm has a significant effect on selectivity in beds III and especially IV but has virtually no influence on the selectivity in beds I and II. The parametric sensitivity greatly diminishes with increase in R_0, reaching the minimum values for $R_0 \geqslant 3$ mm. The analysis led to the selection of the following catalyst grain sizes, R_0 (in mm) in the beds: 3 in beds I and II, 1.5 in bed III, and 1 in bed IV.

It follows from the mathematical modelling data that the adiabatic catalyst beds have the same parametric sensitivity to different input perturbations. Therefore, in order to ensure the stable and reliable operation of the reactor, a special system was developed for the automatic control of the process with removal of

part of the reaction gases via lines bypassing the intermediate heat exchangers.[157]

The results of the mathematical modelling of the reactor with adiabatic catalyst beds were tested and confirmed on the experimental plant of the Novosibirsk Chemical factory with an output of 18–25 kg of 37% formalin per hour. Prolonged use of the experimental plant confirmed that the system for the automatic stabilisation of the temperature regime in the reactor makes it possible to maintain the input parameters to within 1–1.5 °C and the output parameters to within 10–15 °C.

The principal technological and design characteristics of the reactor with adiabatic oxide catalyst beds with an output of 120 000 tonnes of 37% formalin per year are presented below:

Diameter of apparatus, m	4.2
Initial methanol concentration, vol.%	6.5
Blowing rate, $nm^3 h^{-1}$	70000
Linear flow rate, nm s^{-1}	1.4
Overall degree of conversion, %	99.3–99.8
Yield of formaldehyde, %	93.5–94.5
Consumption coefficient with respect to methanol, kg $tonne^{-1}$	423–428
Overall hydraulic resistance, atm	0.4
Conventional contact time	0.38

Thus the possibility, in principle, of oxidising methanol to formaldehyde in a reactor with adiabatic oxide catalyst beds arranged in series has been demonstrated. The application of reactors of this type makes it possible to create plants with a high unit output, such reactors being simple as regards apparatus and easily regulated.

4. The use of the catalytic conversion of methane for the thermochemical transformation of solar energy

The promising nature of yet another somewhat unexpected application of the catalytic reactions of C_1 compounds has been demonstrated most recently. It was established, initially theoretically[158] and then experimentally,[159–161] that the highly endothermic catalytic water vapour or carbonic acid conversion of methane into the synthesis gas can be used for the direct highly effective transformation of solar energy into the energy of chemical fuels. Such transformation is achieved by heating the catalytic reactor with concentrated sunlight up to temperatures of the order of 600–700 °C at which the thermodynamic equilibrium in the mixture of methane with water or CO_2 is displaced towards the high-energy mixture of CO and H_2. The energy stored in the course of the conversion of methane can then be released in another reactor in the form of heat, which is potentially highly utilisable, by carrying out the reverse reaction, also catalytic, involving the conversion of the synthesis gas into methane. With the aid of the above sequence of reactions, it is possible to create fairly effective energy devices with a closed cycle involving the utilisation of C_1 compounds as a chemically active "working heat".

Naturally, in opaque solar catalytic reactors, chemical processes take place in exactly the same way in the presence of the same catalysts as under traditional conditions. However, the efficiency of the solar energy devices definitely depends on the way in which high-density heat fluxes are transferred to the catalyst bed. The design of the catalytic reactors differs greatly in the given case from the usual reactors. A number of such designs with a useful output of several kilowatts have been developed at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences and have been tested under natural conditions.[159–161] In the course of these tests, efficiencies up to 45% in the storage of solar energy and above 20% in the generation of potentially highly utilisable heat (gas temperature up to 700 °C) were recorded during the operation of the closed thermochemical cycle as a whole. Such efficiencies are at present the maximum attained in chemical methods for the transformation of solar energy and the solar catalytic power generating devices developed can be regarded as prototypes of industrial designs.

The prospect for the practical utilisation of chemical methods for the transformation of solar energy depend nowadays on two factors. Firstly, we have the economic factor. All the methods of utilising solar energy known at the present time are more expensive than the traditional methods of generating energy, such as, for example, the combustion of organic fuels, nuclear reactions, etc. In this situation it is to be expected that solar energy will win through gradually as it becomes cheaper, as a result of the scientific and technical progress in this field, while the traditional sources of energy become gradually dearer due to their exhaustion.

The second factor is ecological. Much depends on how dangerous the thermal and chemical pollution of our planet by modern power engineering really is. If it proves intolerable, the development of the ecologically clean solar power engineering may become essential.

IV. Metal complex catalysis in reactions of C_1 compounds

Since its establishment, metal complex catalysis has been and remains a promising field of catalytic chemistry which is associated, firstly, with the possibility, as in this instance, of applying a broad spectrum of highly informative physicochemical research methods and, secondly, with the existence of a solid theoretical basis comprising extensive practical data concerning the reactivity of various coordination and organometallic compounds and the mechanisms of their reactions, which are used in the purposeful search for catalytic systems.[162–169] In order to predict the composition of metal complex catalytic systems, one may use thermodynamic and kinetic analyses of different combinations of stoichiometric reactions of metal complexes, which can be formally incorporated in a closed catalytic cycle.[170] Using this approach, a series of new catalytic systems, suitable for carrying out a wide variety of reactions involving carbon monoxide and formaldehyde, have been discovered at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences.

The problem of the involvement in chemical syntheses of one of the C_1 compounds produced on a large scale, namely carbon dioxide, is of great interest. Here too the application of metal complex catalysts may prove to be extremely promising.

1. Catalytic reactions with participation of carbon monoxide

The liquid-phase conversion of carbon monoxide has been achieved[173] under conditions (temperature, solvent composition, and the nature of the ligands L) such that two stoichiometric reactions with participation of metal complexes can take place simultaneously and at a high rate:

$$L_2MX_2 + CO + H_2O \xrightarrow{2L} L_4M + CO_2 + 2HX, \quad (1)$$

$$L_4M + 2HX \xrightarrow[-2L]{} L_2MX_2 + H_2. \quad (2)$$

The incorporation of these reactions in a closed cycle leads to the

catalytic reaction

$$CO + H_2O \xrightarrow{L_2MX_2} CO_2 + H_2. \quad (3)$$

Special studies led to the discovery of the conditions in the case where M = Pd, L = PPh_3, and X = CF_3COO for reactions (1) [reduction of phosphine complexes of palladium(II)[171]] and (2) [the interaction of $Pd(PPh_3)_4$ with acids[172]] and hence to the determination of the optimal conditions for reaction (3)[173] (Table 3, system *3*).

We may note that the above study[173] was preceded by only two communications[174,175] demonstrating the possibility of achieving the liquid-phase conversion of carbon monoxide (Table 2, systems *1* and *2*).

After the publication of the above investigation,[173] more than twenty metal complex catalytic systems for the liquid-phase conversion of carbon monoxide [the best known of these are presented in Table 2 (systems *4*, *5*, and *6*)], but the catalytic composition proposed by Zudin et al.[173] still remains one of the most active and makes it possible to carry out the reaction under mild conditions (temperature up to 100 °C, atmospheric CO pressure).

Table 2. Catalytic systems for the liquid-phase conversion of carbon monoxide.

No. of system	Composition of complex	Reaction conditions	Activity, mol H_2(mol M)$^{-1}$ h^{-1}	Refs.
1	$Fe(CO)_5$	15% aqueous NH_4OH solution with added $Ba(OH)_2$; 80 °C	0.03	[174]
2	$Rh_6(CO)_6$	aqueous pyridine solution; 450 atm; 210 °C	2.1	[175]
3	$(PPh_3)_2Pd(OAc)_2$	80% aqueous CF_3COOH; 70 °C; CO pressure 0.3 atm	3.0	[173]
4	$K_2PtCl_4 + SnCl_4 \cdot 5H_2O$	20% HCl solution in acetic acid containing 20% of water; 90 °C; CO pressure 0.5 atm	1.0	[176]
5	$Pd(ClO_4)_2 + Ph_2P$– 	aqueous solution; 85–100 °C; CO pressure 0.5 atm	0.25	[177]
6	$HRh(PEt_3)_3$	pyridine; 100 °C; CO pressure 20 atm	10.0	[178]

Catalytic synthesis of hydrogen peroxide via the coupled oxidation of carbon monoxide and water has been achieved under conditions ensuring the incorporation in a closed cycle of three stoichiometric reactions of phosphine complexes of palladium:

$$L_2PdX_2 + CO + H_2O \rightleftarrows L_2Pd + CO_2 + 2HX, \quad (4)$$

$$L_2Pd + O_2 \xrightarrow{-2L} L_2PdO_2, \quad (5)$$

$$L_2PdO_2 + 2HX \xrightarrow{L = PPh_3} L_2PdX_2 + H_2O_2. \quad (6)$$

As can be seen, the combination of reaction (4)–(6) in a catalytic cycle makes it possible to achieve the catalytic synthesis of hydrogen peroxide from oxygen and water in accordance with the equation

$$H_2O + O_2 + CO \xrightarrow{L_2PdX_2} H_2O_2 + CO_2. \quad (7)$$

It is noteworthy that in this process the highly endoergic stage involving the oxidation of H_2O by molecular oxygen to H_2O_2 is coupled energetically with the highly exoergic stage involving the oxidation of CO to CO_2. Previously such coupling of endoergic and exoergic stages was achieved in the catalytic synthesis of acetic anhydride from acetic acid, CO, and O_2.[179]

Reaction (7) was initially predicted on the basis of the considerations formulated above and was then achieved in practice.[180] The catalytic solution consisted of the two-phase water–dichloromethane system. The CH_2Cl_2 phase contained $Pd(OAc)_2$ and PPh_3, while the aqueous phase was a 3% solution of titanium(IV) sulphate, which served as a "trap" for the hydrogen peroxide formed. At 20 °C and atmospheric pressure of the gas phase ($CO:O_2$ = 1:1), the rate of formation of hydrogen peroxide was 0.5 mol (g-atom Pd)$^{-1}$ h^{-1}.

The possibility of the coupled oxidation of alkenes and carbon monoxide by molecular oxygen is determined by the same factor as for systems containing hydrogen peroxide, the oxo-complexes of molybdenum and tungsten being effective epoxidising agents. The idea of combining reaction (7) with the reactions

$$L'_nMO_r + H_2O_2 \xrightarrow{-H_2O} L'_mMO_{r-1}(O_2), \quad (8)$$

$$L'_mMO_{r-1}(O_2) + R{-}CH{=}CH_2 \xrightarrow{H_2O} L'_nMO_r + R{-}\underset{OH}{CH}{-}\underset{OH}{CH_2}, \quad (9)$$

arose. Here M = Ti(IV) or Mo(VI) and L' = Ph_3CO. It would thus be possible to achieve the catalytic process

$$CO + R{-}CH{=}CH_2 + O_2 + H_2O \xrightarrow[L'_nMO_r]{L_2PdX_2} CO_2 + R{-}\underset{OH}{CH}{-}\underset{OH}{CH_2}. \quad (10)$$

Experimental test showed that catalytic solutions containing phosphine complexes of palladium and oxo-complexes of molybdenum or tungsten permit the possibility of the coupled oxidation of carbon monoxide and propene to CO_2 and propylene glycol esters respectively. The most complete utilisation of hydrogen peroxide is attained when a mixture of acetic acid and acetic anhydride is used as the solvent. Thus the rate of formation of propylene glycol diacetate (the product of the interaction of epoxypropane or propylene glycol with acetic acid) was 3.6 mol (g-atom Pd)$^{-1}$ h^{-1} for a selectivity in the conversion of propene into this product of 56% in a system comprising (in mol litre^{-1}) $Pd(OAc)_2$ (5×10^{-3}), Na_3MoO_4 (5×10^{-2}), PPh_3 (5×10^{-2}) and $OPPh_3$ (0.1), using the $HOAc:AC_2O$ = 5:1 (by volume) solvent mixture, at 70 °C and a pressure of the $C_3H_6:CO:O_2$ = 1:1:1 gas phase of 1 atm.

In the absence of carbon monoxide, the rate of oxidation of propene is lower by two orders of magnitude than in its presence and the oxidation products are then exclusively carbonyl compounds. The oxidation of the alkene is in this case caused by the oxidation of PPh_3 by palladium(II) acetate, which leads to the formation of $Pd(PPh_3)_4$ and then $(PPh_3)_2PdO_2$. The latter oxidises the alkene in an acid medium to a carbonyl compound.[181]

Reaction (10) has also been achieved in the absence of a solvent, i.e. under the conditions of heterogeneous catalysis. The catalyst consisted of silica gel grains impregnated with PPh_3, $OPPh_3$, $Pd(OAc)_2$, and Na_2MoO_4, the composition of the gas mixture was $C_3H_6:CO:O_2$ = 1:1:1, the temperature was 90 °C, and the space velocity was 15 000 h^{-1}. Epoxypropane was formed with a

selectivity up to 20%. The increase in space velocity to 100 000 h^{-1} increased the selectivity to 45%. In the absence of carbon monoxide from the gas phase, epoxypropane was not formed.

Both homogeneous and heterogeneous catalysts very rapidly lost their activity as a result of the occurrence of the PPh_3 oxidation processes.

The synthesis of diethyl ketone from ethylene, carbon monoxide, and water. If the stoichiometric reaction (2) proceeds via the intermediate formation of palladium hydride complexes (experimental proof of this when M = Pd, L = PPh_3, and X = CF_3COO has been published[182,183]), then one may expect that, under conditions ensuring the conversion of carbon monoxide, hydrogen and CO will be inserted in the ethylene double bond. Experimental tests showed[184] that the catalytic reaction involving the hydrocarbonylation of olefins to dialkyl ketones does indeed take place in this case:

$$2C_2H_4 + 2CO + H_2 \xrightarrow{Pd^{2+},PPh_3} C_2H_5{-}\underset{\underset{O}{\|}}{C}{-}C_2H_5 + CO_2. \qquad (11)$$

It is known that diethyl ketone is formed together with other oxygen-containing compounds via reaction (11) in the presence of $PdCl_2$ and pyridine dissolved in 12 M HCl at 195–220 °C and 550–650 atm.[185] In the catalytic system,[184] diethyl ketone is formed at an appreciable rate and with a fairly high selectivity (~80%) already at 30–70 °C and atmospheric pressure.

The addition of hydrogen to the CO + C_2H_4 gas mixture in the system[184] increases the selectivity and especially the rate of formation of diethyl ketone (DEK), which reaches 70 moles of DEK per gramme-atom of palladium per hour at the catalytic solution temperature of 70 °C and atmospheric pressure of the $C_2H_4:CO:H_2$ = 2:1:1 gas mixture. This composition is one of the most active among all the known catalytic systems for the synthesis of DEK from C_2H_4, CO, and H_2.

The catalytic synthesis of the DEK from ethylene, carbon monoxide, and hydrogen can be achieved by the gas-phase method using as the catalyst a solution of the phosphine complexes of palladium and an aromatic sulphonic acid injected into the pores of a mineral carrier, the example, silica gel. The highest selectivity in the formation of DEK (96%) and the highest activity (3 moles of DEK per gramme-atom of Pd per hour) at 80 °C and the $C_2H_4:CO:H_2$ = 1:1:2 composition of the gas phase were achieved using sulphosalicylic acid as the "deposited solvent".

Immobilised metal complexes and catalysts of reactions with participation of CO. The search for new catalytic compositions can be greatly extended using the idea of immobilising metal complexes on the surfaces of carriers. In this case, the synthesis of the catalyst reduces to deliberate construction on the carrier surface of a heterogeneous active centre having the composition and structure which we would have required in solution to effect the specified reaction and which cannot be obtained in solution owing to fundamental difficulties (insolubility, mutual deactivation of the components, etc.).[170,187]

When this approach is used, it is possible to synthesise immobilised active centres containing several different transition metal ions selectively activating definite substrates.

Immobilised phosphine palladium-cobalt complexes as catalysts of the hydroformylation of propene. Cobalt carbonyl complexes are known to be catalysts of the hydroformylation of alkenes. This process takes place under fairly severe conditions—at elevated pressure and temperature. The stage involving the decomposition of acylcobalt carbonyl on treatment with hydrogen, leading to the formation of the target product—an aldehyde, is assumed to be the slowest.[188]

Palladium complexes are known to be effective catalysts of the hydrogenation of both different organic and saturated groups and of metal–carbon bonds.[189] In this connection, the idea arose of using a bimetallic palladium-cobalt phosphine complex to facilitate the hydrogenolysis of the Co–C(O)R bond.

The attempts to realise this idea in the "homogeneous version" were not however successful owing to the high lability of the carbonylphosphine-palladium–cobalt complexes, which are rapidly converted into insoluble compounds. A "heterogenised version" of the synthesis of the heterogeneous palladium-cobalt active centre was therefore effected.

Without dwelling on the details of the "assembly" of such a centre on the silica gel surface (they have already been described[190]), we may note that the activity of the immobilised palladium–cobalt complex in the hydroformylation reaction did indeed greatly exceed the activity of the individual palladium and cobalt complexes. The formation of C_4 aldehydes and alcohols on the $\mathbf{P_3}PdCo_2(CO)_6$ catalyst [where $\mathbf{P_3}$ is the $-O-Si(CH_2CH_2CH_2PPh_2)_3$ ligand group immobilised on SiO_2] was observed already at 40 °C ($H_2:C_3H_6:CO$ = 1:1:1 gas mixture, pressure—3 atm), whereas the $\mathbf{P_3}Pd^0$ and $\mathbf{P_3}Co_2(CO)_6$ catalysts were completely inactive under these conditions. The selectivity in the formation of products with a normal structure reached 88% for the heterometallic complex.[190,191]

The following concept concerning the mechanism of the catalytic action of the heterometallic complex was formulated on the basis of the results obtained by kinetic and physicochemical research methods:[192,193]

the active centre incorporates palladium and cobalt atoms separated by a distance permitting their linkage via the CO bridge bond;

the activation of hydrogen and the alkene takes place at the palladium atom, where the alkyl fragment is also stabilised;

CO is activated following its insertion in the Pd–R bond at the cobalt atom, where the acyl fragment is also stabilised;

the hydrogenolysis of the Co–C(O)R bond takes place with participation of hydrogen activated at the palladium atom.

Thus the action of the bimetallic Pd–Co centre resembles that of a conveyor belt at which each participant performs his operation in the most professional manner: palladium hydrogenates and cobalt carbonylates; their closeness ensures the rapid transfer of the "half-finished product" from one to the other.

2. The hydrocondensation of formaldehyde on metal complexes

The hydrocondensation of formaldehyde,

$$nCH_2O + H_2 \rightarrow C_nH_{2n+2}O_n \qquad (12)$$

has attracted the attention of investigators as a possible method of synthesis of polyols from an extremely readily available raw material—formaldehyde and hydrogen. Reaction (12) is usually carried out in two stages.

(a) Condensation of formaldehyde to a "formose"—a mixture of carbohydrates in which the number of carbon atoms in the molecule is between 5 and 7:

$$nCH_2O \rightarrow C_nH_{2n}O_n. \qquad (13)$$

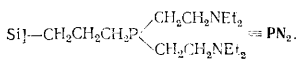
(b) Hydrogenation and hydrogenolysis of the "formose" to polyols, mainly to ethylene glycol, propylene glycol, and glycerol:

$$C_nH_{2n}O_n + H_2 \rightarrow C_2H_6O_2;\ C_3H_8O_2;\ C_3H_8O_3 + H_2O. \qquad (14)$$

The first stage—the condensation of formaldehyde to formose, discovered a long time ago by Butlerov, takes place readily in alkaline aqueous solutions and is catalysed by calcium hydroxide. Much more severe conditions are required to achieve the second stage (H_2 pressure 200 atm, temperature 230–280 °C, catalyst—copper-containing spinels).

The mechanism of the catalysis by calcium(II) ions of the condensation of formaldehyde has been fairly thoroughly investigated. It is believed that the growth of the carbon chain of the carbohydrate takes place when a formaldehyde molecule interacts with the enolic form of the carbohydrate molecule coordinated to a calcium(II) ion.[194] In this connection, the idea arose of introducing into the composition of the active centre for the condensation of formaldehyde a palladium ion, which is capable of catalysing the hydrogenation of the C=C bond of the enol and hence of effecting the synthesis of polyols via reaction (12) in a single stage under mild conditions.

The condensation of formaldehyde takes place in media at pH > 8. The application of the above idea in the "homogeneous" version is therefore difficult, since under these conditions the majority of transition metal ions, including palladium(II) ions, tend to form soluble hydroxides. Difficulties arise also when an attempt is made to apply this idea in the "heterogenised" version. Indeed, the heterogenisation of calcium(II) ions as active centres for the condensation of formaldehyde is problematical, since in alkaline media there is no suitable ligand for this ion with which it might be possible to immobilise it on the carrier surface. It therefore becomes necessary to replace the calcium(II) ion by the ion of another element, for example, chromium(III), which is very close to calcium(II) as regards some of its characteristics (octahedral coordination sphere, ionic radius about 1 Å). Taking into account the ability of chromium ions to form very stable complexes with amine ligands, which are stable in alkaline media, it was decided to use immobilised aminepalladiumchromium complexes to effect reaction (12). The phosphinoamine



was used as the ligand for the synthesis of a heteroatomic palladium–chromium complex. Here it was postulated that the phosphorus atom can serve as a site for the coordination of zerovalent palladium ions while, the ethylamine ligands coordinate chromium(III) ions.

An experimental test showed[194] that the immobilised palladium–chromium complex $PN_2PdCr(OH)_3$ does indeed exhibit an appreciable activity [2.1 mol H_2(g-atom Pd)$^{-1}$ h^{-1}] in reaction (12) under mild conditions (temperature 60 °C, H_2 pressure 1 atm, aqueous formaldehyde solution, HCHO concentration 0.1 M) in contrast to the immobilised monometallic palladium complex $P.Pd^0$ ($P = CH_2CH_2PPh_2$ ligand group immobilised on SiO_2) and the chromium complex $N_2Cr(OH)_3$ [$N_2 = CH(CH_2NEt_2)_2$ ligand group immobilised on SiO_2]. The yield of ethylene glycol amounted to 75% relative to the formaldehyde which had reacted.

The results of the study by physico-chemical methods of the state of palladium and chromium ions in the immobilised complexes and also the analysis of the observed kinetics permitted the conclusion that the synergistic effect is caused by the geometrical proximity in the heterometallic active centre of the fragments responsible for the condensation of formaldehyde and the stabilisation of the enolic form [amine complexes of chromium(III)], on the one hand, and for the activation of hydrogen and the hydrogenation of the C=C bond (phosphine complexes of palladium), on the other.

The preferential formation of ethylene glycol can apparently be explained by the higher rate of hydrogenation of the enolic form of glycolaldehyde compared with the rate of the interaction with the next formaldehyde molecule, leading to the synthesis of glyceraldehyde. The absence of catalytic activity for the hydrocondensation of formaldehyde of catalysts consisting of a mixture of immobilised phosphine complexes of zerovalent palladium and diamine complexes of chromium(III) can be explained by the fact that in this case the "palladium" and "chromium" fragments are not close to one another.

3. The reduction of CO_2 under mild conditions

The photosynthetic "fixation" of carbon dioxide by its reduction to carbohydrates, which occurs in all plants and photosynthesising micro-organisms, annually produces up to 10^{11} tonnes of complex organic substances.[196] An important feature of natural photosynthesis, which constitutes its advantage over the majority of industrial catalytic processes, is its occurrence under extremely mild conditions—close to room temperature and at normal pressures in aqueous solutions at a pH close to 7. The high selectivity of photosynthesis is also striking.

The photosynthetic fixation of CO is usually described by the overall reaction

$$CO_2 + 4H^+ + 4A^- \rightarrow {}^1/_6(C_6H_{12}O_6) + 4A, \qquad (15)$$

where A^- are strong one-electron reductants formed under the influence of light in the photocatalytic charge separation and capable of entering into reversible oxidation-reduction reactions.[196,197]

Naturally, at the present time there is as yet no acute need to reproduce reactions of type (15) on an industrial scale. Nevertheless, the interest in artificial systems capable of reducing CO_2 under mild conditions has increased significantly during the last decade. This is due primarily to the intense development of photocatalytic solar energy converters and the consequent natural endeavour to reproduce the principal chemical reactions underlying natural photosynthesis.[158,198] The solution, in principle, of the problem of the modelling of the photosynthesis in plants, where the reduction of CO_2 is coupled with the oxidation of water to O_2, is especially interesting. The reductants A^- in the photocatalytic systems being developed are as a rule photogenerated strong electron donors: either the reduced forms of several organic or metal complex compounds or the conductivity electrons of a series of semiconductors. Even more work has been carried out on systems in which the reductants A^- are generated by cathodes placed in the reaction volume.

It is noteworthy that studies on the reduction of CO_2 under mild conditions are still in the initial stage and are as a rule restricted to the consideration of the possibility of obtaining under such conditions only the simplest compounds—carbon monoxide, the formate ion, methanol, methane, and, rarely, oxalate and glycolate ions, etc.

The principal difficulties in achieving the reduction of CO_2 under mild conditions (in aqueous solutions of carbonate and/or bicarbonate ions or carbon dioxide at a low pressure of the latter)

can be observed even in a cursory analysis of the characteristic features of the process thermodynamics (Table 3). With the exception of the case of the eight-electron reduction of CO_2 to methane, the equilibrium electrochemical potentials of the reduction of CO_2 are significantly more negative than the equilibrium potential of the two-electron reduction of H^+ ions to molecular hydrogen. Thus the reduction of H^+ to H_2 is thermodynamically preferable to any CO_2 reduction process (with the exception of its reduction to methane). In view of the high energy content of the free products of the one-electron reduction of CO_2 as well as other reduced forms of CO_2 with an odd number of electrons,[202,203] the preparation of stable products necessitates the use of special catalysts ensuring the occurrence of multi-electron processes. As a consequence of the specificity of the characteristics of the CO_2 reduction processes mentioned above, these catalysts must be sufficiently selective to prevent the occurrence of the competing process involving the formation of molecular hydrogen.

Table 3. Standard electrode potentials $E°$ of certain H^+ and CO_2 reduction reactions in aqueous solutions at pH 0 (according to data in Refs. 199–202).

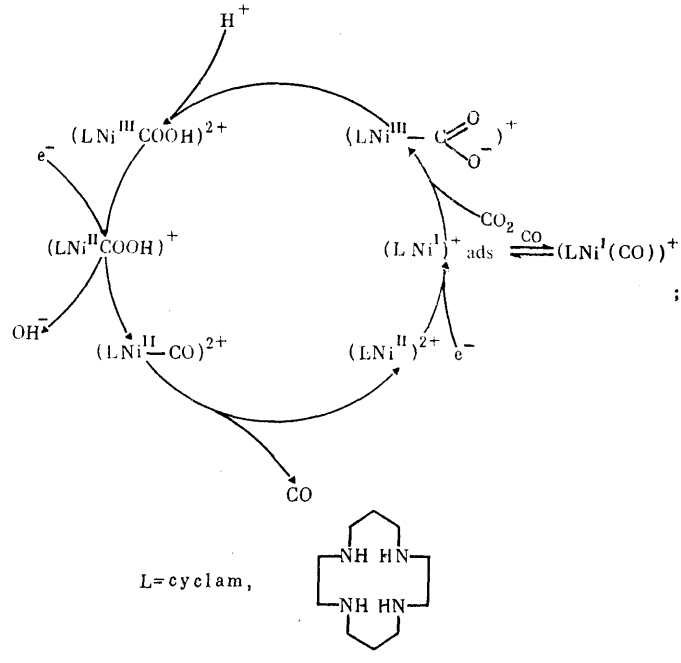
Electrode reaction	$E°$, V (w.r.t.n.h. e-de)
$2H^+ + 2e \rightarrow H_2$	0.00
$CO_2 + e \rightarrow CO_2^-$	−1.31
$CO_2 + 2H^+ + 2e \rightarrow CO + H_2O$	−0.12
$CO_2 + 2H^+ + 2e \rightarrow HCOOH$	−0.19
$2CO_2 + 2H^+ + 2e \rightarrow H_2C_2O_4$	−0.49
$CO_2 + 4H^+ + 4e \rightarrow HCHO + H_2O$	−0.11
$CO_2 + 6H^+ + 6e \rightarrow CH_3OH + H_2O$	−0.04
$CO_2 + 8H^+ + 8e \rightarrow CH_4 + 2H_2O$	0.17

The insufficient selectivity of metallic electrodes as catalysts has in fact precluded significant advances in the development of methods for the selective electrochemical reduction of CO_2 at these electrodes. As was to be expected, at noble metal and also iron and nickel cathodes, where the evolution of hydrogen takes place with a low overpotential, the current yield in the reduction of CO_2 does not usually exceed 10%. The selectivity in relation to the reduction of CO_2 is significantly higher when one uses electrodes made of non-noble metals such as Cd, Sn, Pb, In, and Zn, at which H_2 is evolved with a high overpotential.[204,205] Apparently molybdenum cathodes exhibit the greatest, almost 100%, selectivity in relation to the reduction of CO_2 (in particular to methanol), but this result is attained only at low current densities (up to 1 mA cm^{-2})[199] or when the process is carried out in aprotic solvents.[204,206]

The failures suffered when metallic cathodes were used necessitated the search for other catalysts of both homogeneous and electrode reduction of CO_2. At the present time definite progress has been achieved in this field, which has developed in the very recent years. A fairly wide range of compounds capable of acting as catalysts in the reduction of CO_2 in both electrochemical and photocatalytic systems have been discovered. As was to be expected, the coordinatively unsaturated complexes of certain variable valence metals, which readily incorporate a CO_2 molecule in their coordination sphere, are especially promising.[207,208] Homogeneous or heterogenised cobalt, nickel, and copper complexes with planar nitrogen-containing ligands such as porphins, phthalocyanines, and tetra-azamacrocycles exhibit the highest catalytic activity. For example, the water-insoluble phthalocyanine complex of cobalt(II) deposited on a graphite cathode, which has been investigated at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences, manifested a significant activity and selectivity in the electrocatalytic reduction of CO_2 to CO.

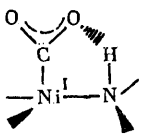
It has been suggested that, in the presence of catalysts of the above type, the reduction of CO_2 takes place in several stages and includes (1) the initial addition of a CO_2 molecule to the central atom of the metal complex subjected to preliminary reduction at the cathode and (2) the reduction of CO_2 and the subsequent release of the reaction products from the coordination sphere of the complex with regeneration of the initial form of the latter. Thus the following schematic catalytic cycle for the electrochemical reduction of CO_2 to CO (Scheme 2) has been proposed[209,210] in the case of a typical catalyst of this kind—the complex $Ni(cyclam)^{2+}$, where cyclam = 1,4,8,11-tetra-azacyclotetradecane.

Scheme 2



It has been established fairly reliably that the substrate for the formation of compounds with reduced forms of carbon does actually consist of CO_2 molecules and not of carbonate or bicarbonate ions from the solution. It has also been suggested that the reduction of CO_2 in the presence of the above catalyst is promoted by the two-centre coordination of the CO_2 molecule via an electrophilic centre (carbon atom) to the nickel(I) ion and via a basic centre (oxygen

atom) to the ligand hydrogen atom bound to nitrogen:



Nevertheless the selectivity in the reduction of CO_2 on the catalyst indicated cannot yet be regarded as entirely satisfactory: a considerable proportion of the reductant is consumed on the evolution of H_2 and not on the reduction of CO_2. Furthermore, CO and the simplest organic C_1 compounds predominate in the products of such reduction, as at metallic electrodes.

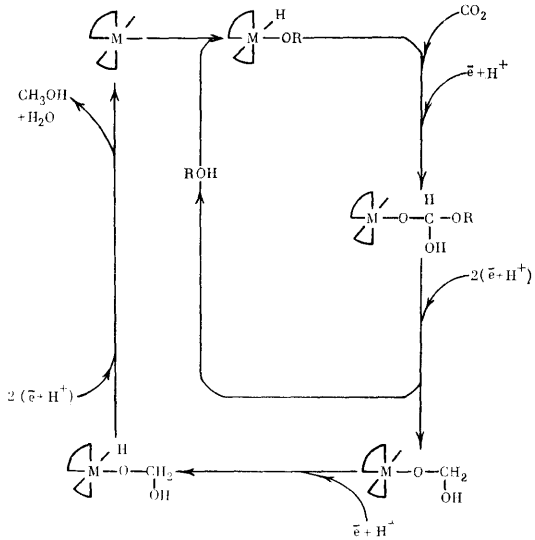
The impression has been created that the modest nature of the advances in devising artificial highly selective systems for the extensive reduction of CO_2 is associated with the fact that the direct reduction of the coordinated CO_2 molecule cannot be sufficiently effective by virtue of the specific thermodynamic features of the process noted above. Indeed, nature has followed another pathway, reducing carbon atoms not directly in the CO_2 molecule itself but in the products of the preliminary carboxylation of certain organic compounds, which can be regarded as cocatalysts of the CO_2 reduction process.

Thus in the classical "Calvin cycle"—a cyclic sequence of reactions leading to the fixation of CO_2 in many plants—the reduction of CO_2 is preceded by its binding to the phosphorylated sugar ribulose-1,5-diphosphate, which decomposes in the presence of the enzyme ribulose diphosphate carboxylase into two molecules of 3-phosphoglyceric acid; only this intermediate gives rise, when acted upon by a powerful reductant, to sugars as the final products with a high selectivity and liberates the initial substrate for carboxylation.

Thus one can assume that, in the development of artificial systems for the extensive reduction of CO_2, it is also useful to employ the reaction sequence "carboxylation of the organic substrate-cocatalyst—reduction of the intermediate carboxylic acid". The first experimental data indicating the reality of this approach have also appeared. Thus a study has been made[211-214] of the electrochemical reduction of CO_2 to methanol in the presence of homogeneous catalysts—the iron complexes of Tiron (1,2-dihydrobenzene-3,5-disulphonate) and oxalate and cyanide anions and chromium oxalate and chloride complexes. The electrochemical reduction took place at electrodes passivated with respect to the evolution of hydrogen by an insoluble but electrically conducting layer of Prussian Blue $KFe^{(III)}[Fe^{(II)}(CN)_6]$. It was observed that the process proceeds only in the presence of primary alcohols and under conditions such that the coordination sphere of the metal complex used as the homogeneous catalyst contains at least one labile ligand capable of being substituted by an alcohol molecule. For example, the aquated iron(III) pentacyanide with a labile water molecule in the first coordinated sphere is catalytically active, while iron(III) hexacyanide or nitroprusside does not show any catalytic activity. The primary alcohol molecule plays the role of a cocatalyst and the process itself is believed to proceed in accordance with Scheme 3. In this scheme, as in the photosynthetic fixation of CO_2, a carboxylated organic compound, coordinated to the homogeneous catalyst in the case considered, is reduced.

Presumably further development of this field will make it possible to create in the future fairly selective and therefore practically important systems for the extensive oxidation of CO_2 under mild conditions.

Scheme 3



* * *

Thus considerable progress has been achieved recently both in the search for new ways of converting one-carbon compounds and in the improvement of the traditional catalytic processes based on such compounds. It may be hoped that new processes using compounds with one carbon atom will be developed in the next few years and that those already introduced into industry will be significantly improved.

References

1. J M Tedder, A Nechtaval, A H Jubb *Basic Organic Chemistry, Part 5, Industrial Products* (Translated into Russian), Izd. Mir, Moscow, 1979, 700 pp
2. US P. 4 205 194
3. T Fang, C Yeh *J. Catal.*, 1981, **69** 227
4. T Fang, C Yeh *J. Chin. Chem. Soc.*, 1982, **29** 265
5. G E Keller, M M Bhasin *J. Catal.*, 1982, **73** 9
6. US P. 4 443 644
7. US P. 4 443 645
8. US P. 4 443 646
9. US P. 4 443 647
10. US P. 4 443 648
11. US P. 4 443 649
12. US P. 4 444 984
13. US P. 4 489 215
14. B.P. 2 156 842

15. US P. 4 495 374
16. US P. 4 499 324
17. US P. 4 517 398
18. US P. 4 544 786
19. US P. 4 544 787
20. US P. 4 547 607
21. US P. 4 547 608
22. US P. 4 547 611
23. US P. 4 523 049
24. US P. 4 523 050
25. US P. 4 547 610
26. W Hinsen, M Baerns, *Chem. Ztg.*, 1983, **107** 223
27. W Hinsen, W Bytyn, M Baerns *8th International Congress on Catalysis*, Weinheim, 1984, Vol. 3, p. 581
28. BRD P. 3 237 079
29. J A S P Carreiro, M Baerns *React. Kinet. Catal. Lett.*, 1987, **35** 349
30. BRD P. 35 345 306
31. A I Suleimanov, S M Aliev, V D Sokolovskii *Okislitel'naya Degidrodimerizatsiya Metana v Vysshie Uglevodorody na Mg-Soderzhashchikh Katalizatorakh* (Oxidative Dehydrodimerisation of Methane to Higher Hydrocarbons on Mg-containing Catalysts); Manuscript deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 11.10.85, No. 7220-V85
32. N P Kirik, A G Anshits, A S Ivanova *Vsesoyuznoe Soveshchanie 'Khimicheskii Sintez na Osnova Odnouglerodnykh Molekul': Tezisy Dokladov* (All-Union Conference on 'Chemical Synthesis based on One-Carbon Molecules': Abstracts of Reports), Izd. Nauka, Moscow, 1984, p. 75
33. T Ito, J H Lunsford *Nature*, 1985, **314** 721
34. T Ito, J H Lunsford *Shokybai* (Catalyst), 1985, **27** 443
35. T Ito, J -X Wang, C -H Lin, et al., *J. Amer. Chem. Soc.*, 1985, **107** 5062
36. I I A Emesh, Yo Amenomiya *J. Phys. Chem.*, 1986, **90** 4785
37. C -H Lin, K D Campbell, J -X Wang, J H Lunsford *J. Phys. Chem.*, 1986, **90** 534
38. T Moriyama, N Takasaki, E Iwamatsu, K Aika *Chem. Lett.*, 1986, 1165
39. K Asami, S Hashimoto, T Shikada, et al. *Chem. Lett.*, 1986, 1233
40. Kh M Minachev, N Ya Usachev, Yu S Khodakov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 1986
41. K Otsuka, K Jinno, A Morikawa *Chem. Lett.*, 1985, 499
42. K Otsuka, K Jinno, A Morikawa *J. Catal.*, 1986, **100** 353
43. K Otsuka, Q Liu, M Hatano, A Morikawa *Chem. Lett.*, 1986, 467
44. H Imai, T Tagawa *J. Chem. Soc., Chem. Comm.*, 1986, 52
45. H Imai, T Tagawa, N Kamide *Proceedings of 8th Japan–USSR Catalysis Seminar*, Tokyo, 1986, p. 139
46. US P. 4 544 784
47. US P. 4 544 785
48. K Otsuka, Q Liu, M Hatano, A Morikawa *Chem. Lett.*, 1986, 903
49. K Otsuka, Q Liu, A Morikawa *Inorg. Chim. Acta*, 1986, **118** L23
50. K Otsuka, M Hatano, Q Liu, A Morikawa *Proceedings of the 8th Japan–USSR Catalysis Seminar*, Tokyo, 1986, p. 1
51. K Otsuka, Q Liu, A Morikawa *J. Chem. Soc., Chem. Comm.*, 1986, 586
52. W Bytyn, M Baerns *Appl. Catal.*, 1986, **28** 199
53. D J Driscoll, W Martir, J -X Wang, J H Lunsford *J. Amer. Chem. Soc.*, 1985, **107** 58
54. D J Driscoll, W Martir, J -X Wang, J H Lunsford *Adsorption and Catalysis on Oxide Surfaces*, Proceedings of Symposium in Uxbridge, June 28–29, 1984., Elsevier, Amsterdam, 1985, p. 403
55. D J Driscoll, J H Lunsford *J. Phys. Chem.*, 1985, **89** 4415
56. C A Jones, J J Leonard, J A Sofranko *J. Catal.*, 1987, **103** 311
57. J A Sofranko, J J Leonard, C A Jones *J. Catal.*, 1987, **103** 302
58. M Yu Sinev, G A Vorob'eva, V N Korchak *Kinetika i Kataliz*, 1986, **27** 1164
59. M Yu Sinev, V N Korchak, O V Krylov *IV Vsesoyuznaya Konferentsiya po Mekhanizmu Kataliticheskikh Reaktsii: Tezisy Dokladov* (The IVth All-Union Conference on the Mechanisms of Catalytic Reactions: Abstracts of Reports), Izd. Inst. Khim. Fiz. Akad. Nauk SSSR, Moscow, 1986, Part 2 p. 27
60. O V Krylov *React. Kinet. Catal. Lett.*, 1987, **35** 315
61. M Yu Sinev *Abstract of Candidate's Thesis in Chemical Sciences*, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1987, 23 pp
62. M Yu Sinev, V N Korchak, O V Krylov *Kinetika i Kataliz*, 1986, **27** 1274
63. O V Buevskaya, A I Suleimanov, S M Aliev, V D Sokolovskii *React. Kinet. Catal. Lett.*, 1987, **33** 223
64. A I Suleimanov, E G Ismailov, S M Aliev, V D Sokolovskii *React. Kinet. Catal. Lett.*, 1987, **34** 51
65. V D Sokolovskii *Reakt. Kinet. Catal. Lett.*, 1987, **35** 337
66. V D Sokolovskii, N N Bulgakov *React. Kinet. Catal. Lett.*, 1977, **6** 65
67. L D Chang *Catal. Rev. -Sci. Eng.*, 1983, **25** 1
68. K G Ione *Polifunktsional'nyi Kataliz na Tseolitakh* (Polyfunctional Catalysis on Zeolites), Izd. Nauka, Novosibirsk, 1982, 268 pp
69. Kh M Minachev, D A Kondrat'ev *Uspekhi Khim.*, 1983, **52** 1921 [*Russ. Chem. Rev.*, 1983(12)]
70. K G Ione, L A Vostrikova *Uspekhi Khim.*, 1987, **56** 393 [*Russ. Chem. Rev.*, 1987(3)]
71. O V Bragin, T V Vasina, Ya I Isakov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 954
72. V V Tonkopryadchenko, M I Levinbuk *III Vsesoyuznaya Konferentsiya 'Primenenie Tseolitov v Katalize'; Tezisy Dokladov* (The IIIrd All-Union Conference on the 'Application of Zeolites in Catalyst'; Abstracts of Reports), Izd. Nauka, Moscow, 1985, p. 178
73. S S Shepelev, K G Ione *Kinetika i Kataliz*, 1984, **15** 347
74. S S Shepelev, K G Ione *V Neftekhimicheskii Simpozium Sotsialisticheskikh Stran: Tezisy Dokladov* (The Vth Petrochemical Symposium of Socialist Countries: Abstracts of Reports), Sofia, 1986, p. 94
75. USSR P. 950 707; *Byul. Izobret.*, 1982(30) 67
76. J R Anderson, P Tsai *Appl. Catal.*, 1985, **19** 141
77. G Lormand *Ind. Eng. Chem.*, 1925, **17** 430
78. V A Plotnikov, K N Ivanov *Zhur. Obshch. Khim.*, 1931, **1** 826
79. V A Plotnikov, K N Ivanov *Zhur. Prikl. Khim.*, 1931, **8** 119
80. J D Stroup *J. Amer. Chem. Soc.*, 1949, **71** 569
81. J Brihta, D Vranjagan, B Pend *Ark. Cemi.*, 1953, **25**(121) *Chem. Abs.*, 1954, **48**(11 166)
82. G Natta *Catalysis* (Edited by P H Emmet), Reinhold Publ. Corp., New York, 1955, Vol. 3, p. 349
83. P G Bondar', A S Markova, V E Leleka, I A Ryzhak *Kataliz i Katalizatory* (Catalysis and Catalysts), Izd. Naukova Dumka, Kiev, No. 17, p. 78

84. D S Shishkov, D A Stavrakeva, N A Kasabova *Kinetika i Kataliz,* 1980, **21** 1559
85. Polish P. 34 000; *Chem. Abs.,* 1949, **43** 8594h
86. T P Ivanovskii, T E Braude, T A Semenova, B G Lyudkovskaya *Problemy Kinetiki i Kataliza,* 1980, **10** 90
87. V V Kostrov, I P Kirillov, A M Alekseev *Khim. i Khim. Tekhnol.,* 1967, **10** 1027
88. R G Herman, G W Simmons, K Klier *Proceedings of 7th International Congress on Catalysis,* Tokyo, 1980, Prep. A-32
89. Japanese P. 52-120 264; *Ref. Zhur. Khim.,* 1986, 6L259P
90. L I Gvasaliya, M A Kusrashvili *Izv. Akad. Nauk Gruz. SSR, Ser. Khim.,* 1982, **8** 211
91. T A Semenova, M I Markina, B G Lyudkovskaya, et al., *Metody Issledovaniya Katalizatorov i Kataliticheskikh Reaktsii* (Methods for the Investigation of Catalysts and Catalytic Reactions), Izd. Nauka, Novosibirsk, 1965, Vol. 2, p. 346
92. H Uchida, N Tsogai, M Oba, J Hasegawa *Bull. Chem. Soc. Jap.,* 1967, **40** 1985
93. E M Tsybina, T S Petrishcheva, A S Chernysh, et al. *Khim. Prom.,* 1973(4) 257
94. G G Shchibrya, N P Maksimov, N G Dadugina, et al. *Kinetika i Kataliz,* 1975, **16** 979
95. Zh F Iovanovich, P S Putanov, R M Gerak, M Tsurik *Glasnik Khem. Drushtva Beograd,* 1978, **43**(4) 127
96. D S Shishkov, N A Kasabova, E M Gatev *Kinetika i Kataliz,* 1979, **20** 521
97. S P S Andrew *Plenary Lecture at the Post Congress Symposium of the 7th International Congress on Catalysis,* Osaka, 1980
98. T H Fleisch, R L Mieville *J. Catal.,* 1984, **90** 165
99. T A Semenova, B G Lyudkovskaya, M I Markina, et al. *Kinetika i Kataliz,* 1977, **18** 1014
100. D S Campbell *Ind. Eng. Chem., Process. Des. Dev.,* 1970, **9** 588
101. T A Semenova, Z V Komova, A A Vasilevich, V G Lyudkovskaya, *Khim. Prom.,* 1979(8) 505
102. A A Vasilevich, Z V Komova, I P Zrelova, T A Semenova *Kinetika i Kataliz,* 1978, **19** 1512
103. G Leherte, D Derie, P H Duvigneaud *Preparation of Catalysts* (Edited by B Delmon, et al.), Elsevier, Amsterdam, 1976, p. 303
104. G G Shchibrya, A M Alekseev, B G Lyudkovskaya, et al. *Kinetika i Kataliz,* 1980, **21** 231
105. T M Yur'eva, G K Boreskov, V Sh Gruver *Kinetika i Kataliz,* 1969, **10** 294
106. T M Yur'eva, G K Boreskov, V V Popovskii, et al. *Kinetika i Kataliz,* 1971, **12** 140
107. G K Boreskov, T M Yur'eva, V A Chigrina, A A Davydov *Kinetika i Kataliz,* 1978, **19** 915
108. S V Ketchik, L M Plyasova, T M Yur'eva, et al. *Izv. Sibir. Otd. Akad. Nauk SSSR, Ser. Khim.,* 1983, **6** 109
109. S V Ketchik, T P Minyukova, L I Kuznetsova, et al. *React. Kinet. Catal. Lett.,* 1982, **19** 345
110. T M Yurieva, T P Minyukova *React. Kinet. Catal. Lett.,* 1985, **29** 55
111. F Garbassi, G Petrinin *J. Catal.,* 1984, **90** 106
112. R G Herman, K Klier, G W Simmons, et al. *J. Catal.,* 1979, **56** 407
113. S V Ketchik, L M Plyasova, T M Yur'eva, et al. *Izv. Sibir. Otd. Akad. Nauk SSSR,* 1984, **1** 36
114. Y Okamoto, K Fukino, T Imanaka, S Teranishi *J. Phys. Chem.,* 1983, **87** 3740; 3748
115. S V Ketchik, L M Plyasova, T M Yur'eva, et al. *Izv. Sibir. Otd. Akad. Nauk SSSR,* 1984, **4** 37
116. A Andreev, P Schopov, P Schischkov *Z. Chem.,* 1980, **16** 457
117. L I Kuznetsova, T M Yurieva, T P Minyukova, et al. *React. Kinet. Catal. Lett.,* 1982, **19** 355
118. N A Toropov *Diagrammy Sostoyanii Silikatnykh Sistem* (Phase Diagrams of Silicate Systems), Izd. Nauka, Leningrad, 1969, No. 1 p. 138
119. S Menta, G W Simmons, K Klier, R G Herman *J. Catal.,* 1979, **57** 339
120. T M Yurieva *React. Kinet. Catal. Lett.,* 1983, **23** 267
121. BRD P. 1 366 367
122. G Busetto, G Del Piero, G Manara, et al. *J. Catal.,* 1984, **85** 260
123. P B Himerfarb, G W Simmons, K Klier, R G Herman *J. Catal.,* 1985, **93** 442
124. F S Hadzhieva, V F Anufrienko, T M Yurieva, et al. *React. Kinet. Catal. Lett.,* 1986, **30** 85
125. G S Litvak, T P Minyukova, M P Demeshkina, et al. *React. Kinet. Catal. Lett.,* 1986, **31** 403
126. M Boudart, E G Derovane, V Indovina, A B Walters *J. Catal.,* 1975, **39** 115
127. V G Shinkarenko, V F Anufrienko *Teor. Eksper. Khim.,* 1976, **12** 270
128. Y Okamoto, K Fukino, T Imanaka, S Teranishi *J. Chem. Soc., Chem. Comm.,* 1982, 1405
129. G Petrini, F Garbassi *J. Catal.,* 1984, **90** 113
130. G Apai, J R Monnier, D R Preuss *J. Catal.,* 1986, **98** 563
131. B S Clausen, B Lengeler, B S Rasmussen *J. Phys. Chem.,* 1985, **89** 2319
132. A L Turcheninov, E S Shpiro, N V Nekrasov, et al. *Dokl. Akad. Nauk SSSR,* 1987, **296** 165
133. A A Davydov, G K Boreskov, T M Yur'eva, N A Rubene *Dokl. Akad. Nauk SSSR,* 1977, **236** 1402
134. G I Salomatin, V S Sobolevskii, L I Lafer, V I Yakerson *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1980, 1988
135. H H Kung *Catal. Rev. -Sci. Eng.,* 1980, **20**(2) 235
136. K Klier *Adv. Catal.,* 1982, **31** 243
137. A B Fasman, M M Kalina, Kh M Minachev, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1979, 244
138. A B Fasman, M M Kalina, V M Ermolaev, Manuscript Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 1982, No. 921-82
139. J B Friedrich, M S Wainwright, D J Young *J. Catal.,* 1983, **80** 1
140. J B Friedrich, M S Wainwright, D J Young *J. Catal.,* 1983, **80** 14
141. Yu Sh Matros *Zhur. Vses. Khim. Obshch. im Mendeleeva,* 1977, **22** 576
142. G K Boreskov, Yu Sh Matros *Catal. Rev. -Sci. Eng.,* 1983, **25**(4) 551
143. Yu Sh Matros *Kataliticheskie Protsessy v Nestatsionarnykh Usloviyakh* (Catalytic Processes under Non-Stationary Conditions), Izd. Nauka, Novosibirsk, 1987, 230 pp
144. O V Kiselev, Yu Sh Matros *Matematicheskoe Modelirovanie Khimicheskikh Reaktorov* (Mathematical Modelling of Chemical Reactors), Izd. Nauka, Novosibirsk, 1984, p. 25
145. USSR P. 1 249 010; *Byul. Izobret.,* 1986(29) 97
146. V M Pomerantsev, V P Mukhlenov, D T Traber *Zhur. Prikl. Khim.,* 1963, **36** 754
147. M G Rozenfel'd, M T Rusov *Kataliz i Katalizatory* (Catalysis and Catalysts), Izd. Naukova Dumka, Kiev, 1972, No. 9 p. 59

148. Yu B Kagan, L G Liberov, E V Slivinskii, et al. *Dokl. Akad. Nauk SSSR*, 1975, **221** 1093
149. A Ya Rozovskii *Khim. Prom.*, 1980(11) 652
150. O A Malinovskaya, A Ya Rozovskii, I A Zolotarskii, et al. *Kinetika i Kataliz*, 1987, **28** 970
151. Yu Sh Matros *Nestatsionarnye Protssesy v Kataliticheskikh Reaktorakh* (Non-Stationary Processes in Catalytic Reactors), Izd. Nauka, Novosibirsk, 1982
152. G K Boreskov, Yu Sh Matros, V B Nakrokhin, et al. *Khim. Prom.*, 1977(1) 48
153. USSR P. 448 705; *Byul. Izobret.*, 1978(25) 231
154. V N Bibin, B I Popov, V S Beskov, et al. *Partsial'noe Okislenie Uglevodorodov. Metodicheskie i Matematicheskie Voprosy Kinetiki* (Partial Oxidation of Hydrocarbons; Methodological and Mathematical Problems of Kinetics), Izd. Inst. Katal. Sibir. Otd. Akad. Nauk SSSR, Novosibirsk, 1973, p. 56
155. V N Bibin, B I Popov *Kinetika i Kataliz*, 1969, **10** 1326
156. Yu Sh Matros *Katalizatory i Kataliticheskie Protsessy* (Catalysts and Catalytic Processes), Izd. Inst. Katal. Sibir. Otd. Akad. Nauk SSSR, Novosibirsk, 1977, p 111
157. Yu Sh Matros, V A Kirillov, M I Gavrilenko *Khim. Prom.*, 1974(9) 57
158. K I Zamaraev, V N Parmon (Editors) *Fotokataliticheskoe Preobrazovanie Solnechnoi Energii* (Photocatalytic Transformation of Solar Energy), Part 1 *Khimicheskie i Biologicheskie Metody* (Chemical and Biological Methods), Izd. Nauka, Novosibirsk, 1985, 195 pp
159. Yu I Aristov, V N Parmon, V A Anikeev, et al. *Gorizonty v Katalize* (Horizons in Catalysis), Izd. Inst. Katal. Sibir. Otd. Akad. Nauk SSSR, Novosibirsk, 1986, p. 16
160. V I Anikeev, V N Parmon, Yu I Aristov, et al. *Dokl. Akad. Nauk SSSR*, 1986, **289** 158
161. V I Anikeev, V A Kuz'min, V A Kirillov, et al. *Dokl. Akad. Nauk SSSR*, 1987, **293** 1427
162. M E Vol'pin, I I Moiseev, A E Shilov *Zhur. Vses. Khim. Obshch im. Mendeleeva*,1980, **25** 515
163. I I Moiseev *Zhur. Vses. Khim. Obshch. im. Mendeleeva*, 1982, **27** 69–86
164. I I Moiseev *π-Kompleksy v Zhidkofaznom Okislenii Olefinov* (π-Complexes in the Liquid-Phase Oxidation of Olefins), Izd. Nauka, Moscow, 1970, 240 pp
165. M E Vol'pin, V B Shur *Zhur. Vses. Khim. Obshch. im. Mendeleeva*, 1967, **12** 31
166. N M Zhavoronkov, I I Moiseev *Koord. Khim.*, 1978, **4** 803
167. A E Shilov *Zhur. Vses. Khim. Obshch. im. Mendeleeva*, 1977, **22** 521
168. B A Dolgoplosk *Kinetika i Kataliz*, 1981, **22** 807
169. M L Khidekel' *Kinetika i Kataliz*, 1980, **21** 53
170. V A Likholobov, Yu I Ermakov *Kinetika i Kataliz*, 1980, **21** 904
171. V A Likholobov, N K Eremenko, V N Zudin *Izv. Sibir. Otd. Akad. Nauk SSSR, Ser. Khim.*, 1976, **3** 102
172. V N Zudin, V A Likholobov, Yu I Ermakov *Kinetika i Kataliz*, 1977, **18** 921
173. V N Zudin, V A Likholobov, Yu I Ermakov, N K Eremenko *Kinetika i Kataliz*, 1977, **18** 524
174. W Hieber, F Leutert *Z. Anorg. Chem.*, 1932, **204** 145
175. N S Imyanitov, B E Kubaev, D M Rudkovskii *Zhur. Prikl. Khim.*, 1967, **40** 2871
176. C -H Cheng, R Eisenberg *J. Amer. Chem Soc.*, 1978, **100** 5968
177. E G Chepaikin, A P Bezruchenko, M L Khidekel' *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 2666
178. T Joshida, T Okano, J Ueda, S Otsuka *J. Amer. Chem. Soc.*, 1981, **103** 3411
179. I I Moiseev, M N Vargaftik, O I Gentosh, et al. *Dokl. Akad. Nauk SSSR*, 1977, **237** 645
180. V N Zudin, V A Likholobov, Yu I Ermakov *Kinetika i Kataliz*, 1979, **20** 1599
181. A S Danilyuk V A Likholobov, Yu I Ermakov *Kinetika i Kataliz*, 1977, **18** 252
182. V N Zudin, V A Likholobov, V M Mastikhin, et al. *Koord. Khim.*, 1979, **5** 432
183. V N Zudin, V D Chinakov, V A Likholobov, et al. *J. Organometal. Chem.*, 1985, **289** 425
184. V N Zudin, V A Likholobov, Yu I Ermakov *Kinetika i Kataliz*, 1979, **20** 805
185. US P. 3 059 031; *Chem. Abs.*, 1963, **58** 6698d
186. V N Zudin, G N Il'inich, V A Likholobov, Yu I Yermakov *J. Chem. Soc., Chem. Comm.*, 1984, 545
187. Yu I Ermakov, V A Likholobov *Kinetika i Kataliz*, 1980, **21** 1208
188. F E Paulic *Catal. Rev.*, 1972, **6** 49
189. P M Maitlis *The Organic Chemistry of Palladium*, Acad. Press, New York, 1971, Vol. 1 319 pp; Vol. 2 216 pp
190. B L Moroz, V A Semikolenov, V A Likholobov, Yu I Yermakov *J. Chem. Soc., Chem. Comm.*, 1982, 1286
191. B L Moroz, O N Shumilo, E A Paukshtis, et al. *Proceedings of the 5th International Symposium on Relations Between Homogeneous and Heterogeneous Catalysis, Novosibirsk, 1986* [Edited by Yu I Yermakov (Ermakov), V I Likholobov], VNU Sci. Press, Utrecht, 1986
192. B L Moroz, I L Mudrakovskii, L I Bulgakova, et al. *Proceedings of the 6th International Symposium on Relations Between Homogeneous and Heterogeneous Catalysis, Sofia, 1987* (Edited by D Shopov, A Andreev, A Palazov, L Petrov), PHBAS, Sofia, 1987, Part 2, p. 25
193. V A Likholobov, V A Zakharov *React. Kinet. Catal. Lett.*, 1987, **35** 153
194. R D Partridge, A H Weiss, D Todd *J. Carbohydr. Res.*, 1972, **24** 29
195. V A Likholobov, V A Semikolenov, Yu I Ermakov *Kataliz i Kataliticheskie Protsessy Proizvodstva Khimiko-Farmatsevticheskikh Perparatov: Sbornik Dokladov 1-oi Vsesoyuznoi Konferentsii, Tashkent, 17–18 Aprelya, 1985 g.* (Catalysis and Catalytic Processes in the Manufacture of Chemical-Pharmaceutical Preparations. Collected Reports at the 1st All-Union Conference, Tashkent, 17–18 April, 1985), Izd. TsBNTIMP, Moscow, 1985, Part 1, p. 15
196. *Fiziko-Khimicheskie i Prikladnye Problemy Fotosinteza: Sbornik Statei* (Physicochemical and Applied Problems of Photosynthesis: Collected Reports), Zhur. Vses. Khim. Obshch im. Mendeleeva, 1986, **31** 482(1–108)
197. Govindjee (Editor) *Photosynthesis* (Translated into Russian), Izd. Mir, Moscow, 1987, Vols. 1 and 2, 1500 p
198. M Halmann *Energy Resources Through Photochemistry and Catalysis* (Edited by M Graetzel), (Translated into Russian), Izd. Mir, Moscow, 1986, p. 549
199. V A Rabinovich, Z Ya Khavin *Kratkii Khimicheskii Spravochnik* (A Short Chemical Handbook), Izd. Khimiya, Moscow, 1978, p. 329
200. D P Summers, S Leach, K W Frese *J. Electroanal. Chem.*, 1986, **205** 219
201. F Haggin *Chem. Eng. News*, 1985, **63** 29

202. V A Benderskii, A G Krivenko *Dokl. Akad. Nauk SSSR,* 1986, **291** 1395
203. I V Stankevich, T V Lysyak, G G Aleksandrov, I S Kolomnikov *Zhur. Strukt. Khim.*, 1978, **19** 908
204. B R Egging, F McNeill *J. Electroanal. Chem.*, 1983, **148** 17
205. Y Hori, K Kikuchi, S Suzuki *Chem. Lett.*, 1985(11) 1695; 1986(6) 897
206. N A Maiorova, O A Khazova, Yu B Vasil'ev *Elektrokhimiya,* 1986, **22** 1196
207. I S Kolomnikov, V P Kukolev, M E Vol'pin *Uspekhi Khim.*, 1975, **44** 903 [*Russ. Chem. Rev.*, 1975(5)]
208. I S Kolomnikov, M Kh Grigoryan *Uspekhi Khim.*, 1978, **47** 603 [*Russ. Chem. Rev.*, 1978(4)]
209. D J Pearce, D Pletcher *J. Electroanal. Chem.*, 1986, **197** 317
210. M Beley, J -P Collin, R Ruppert, J -P Sauvage *J. Amer. Chem. Soc.*, 1986, **108** 7461
211. K Ogura *Shokybai* (Catalyst), 1986, **28** 9
212. K Ogura, M Takagi *J. Electroanal. Chem.*, 1986, **201** 359; **206** 209
213. K Ogura, I Yoshida *J. Mol. Catal.*, 1986, **34** 67; 309
214. K Ogura, K Takamagari *J Chem. Soc., Dalton Trans.*, 1986(8) 1519

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The mechanism of the partial oxidation of methane

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ABSTRACT. The principal characteristics of the homogeneous and heterogeneous-catalytic conversion of methane into condensation products (C_2 and C_3 hydrocarbons) and partial oxidation products (methanol and formaldehyde) are considered. Data are presented concerning the most effective catalysts and data relating to the mechanism of the activation of methane on oxide and oxide halide catalysts, the nature of the active centres, and the kinetics of the partial oxidation of methane are analysed. It is shown that the oxidative condensation of methane in the presence of the catalysts considered is a heterogeneous-homogeneous process, which imposes special requirements in its practical realisation.
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I. Introduction

The limited resources of petroleum and the constant increase in the cost of its extraction have brought to the fore the problem of the search for an alternative raw material for the chemical and petrochemical industry.

In the immediate future natural gas, and primarily its principal component (methane), may become such raw material.[1] Methane is also a side product in a whole series of reactions involved in the processing of organic raw material, including coal, which are likely to become the principal source of organic intermediate products and motor fuels.[2] This gives rise to the problem of devising effective processes for the conversion of methane into valuable products—methanol, formaldehyde, lower alkanes, etc.

Together with its practical importance, the problem of the processing of methane is of considerable theoretical interest, since it is associated with research into the possibility of activating an extremely stable molecule, whose reactivity is significantly lower than that of the target products.

Studies on the heterogeneous catalytic oxidation of methane to useful products can be arbitrarily divided into two parts. One of these is associated with the synthesis of valuable oxygen-containing compounds—methanol and formaldehyde. This aspect has been developing for a very long time and definite results concerning the understanding of the process mechanism and of the influence of the nature of the active centres of the catalysts on their activity and selectivity have been obtained. However, the yields of the useful products on stably operating catalysts do not exceed 3% for methanol and 5–8% for formaldehyde in the oxidation of methane by oxygen or air without the addition of various compounds (nitrogen oxides, halogeno-derivatives) as oxidants and initiators. Thus a significant increase in the yields of valuable oxygen-containing compounds has not so far been achieved in the heterogeneous-catalytic oxidation of methane compared with the homogeneous oxidation.

The second aspect—the catalytic oxidtive condensation of methane to higher hydrocarbons (mainly to ethane, ethylene, propene, and acetylene)—began to develop comparatively recently, about five years ago. Nevertheless, during this extremely brief period a considerable number of effective catalysts have been developed, which makes it possible, for example, to achieve a yield of C_2 hydrocarbons up to 30% relative to the methane passed through the system.

Definite progress has been made also in the understanding of the mechanism of the oxidative condensation of methane; multistage schemes and the simplest kinetic models have been proposed, permitting an explanation of the characteristics of the process including homogeneous stages in which the radicals $CH_3^{\cdot}$ and $CH_3O_2^{\cdot}$ participate.

We must emphasise that the oxidation of methane on the majority of catalysts apparently includes a stage involving the heterogeneous generation of $CH_3^{\cdot}$ radicals and stages in which they undergo further reactions both in the gas phase and on the surface. It therefore appears useful to carry out a brief survey of investigations into the gas-phase oxidation of methane, before proceeding to the consideration of studies on its heterogeneous-catalytic oxidation. Among the latter, most attention will be devoted to studies on oxidative condensation—in our view, the most promising aspect of the selective catalytic oxidation of methane.

II. Reactions of methane in the gas phase

Homogeneous reactions of methane in the gas phase have been studied in greatest detail at the present time; investigations on these lines have been prosecuted for many decades and their results have been surveyed in a number of reviews (see, for example, Refs. 3–5) and new data go on being added.

Owing to the high thermodynamic stability of methane, its conversion into, for example, hydrocarbons at a relatively low temperature is impossible because of the virtually complete shift of

the equilibrium towards methane.[6] With increase in temperature, the equilibrium is displaced and the possibility of the formation of appreciable amounts of hydrocarbons appears. It has been established[3] that the pyrolysis of methane takes place at temperatures above 700 °C in accordance with the scheme

$$CH_4 \xrightarrow{a} C_2H_6 \xrightarrow{b} C_2H_4 \xrightarrow{c} C_2H_2 \xrightarrow{d} \text{aromatic hydrocarbons, coke.} \quad (1)$$

The primary radical formed in the system is $CH_3^{\cdot}$:

$$CH_4 \rightarrow CH_3^{\cdot} + H^{\cdot}. \quad (2)$$

The activation energy for reaction (2) is 90–107 kcal mol^{-1}. Admixtures of other hydrocarbons as well as halogens and oxygen have an initiating effect.

The initiation stage (2) is followed by the chain propagation and termination stages, which can be represented in the following simplified form:

$$H^{\cdot} + CH_4 \rightarrow CH_3^{\cdot} + H_2, \quad (3)$$

$$2CH_3^{\cdot} \rightarrow C_2H_6, \quad (4)$$

$$CH_3^{\cdot} + H^{\cdot} \rightarrow CH_4. \quad (5)$$

The activation energies for the overall stages *b*, *c*, and *d* in Scheme (1) are respectively 64–90, 35–65, and 22–50 kcal mol^{-1}, which indicates a higher reactivity of the condensation products compared with the initial methane.

According to Roscoe and Thompson,[7] the C_2 and C_3 hydrocarbons are formed via a series of radical stages:

$$\begin{gathered} CH_3^{\cdot} + C_2H_6 \rightarrow C_2H_5^{\cdot} + CH_4;\ CH_3^{\cdot} + C_2H_4 \rightleftarrows n\text{-}C_3H_7^{\cdot}; \\ C_2H_5^{\cdot} \rightarrow C_2H_4 + H^{\cdot};\ n\text{-}C_3H_7^{\cdot} \rightarrow C_4H_8 + H^{\cdot}; \\ CH_3^{\cdot} + C_2H_4 \rightarrow C_2H_3^{\cdot} + CH_4;\ CH_3^{\cdot} + C_3H_5^{\cdot} \rightleftarrows C_3H_5^{\cdot} + CH_4; \\ C_2H_3^{\cdot} \rightarrow C_2H_2 + H^{\cdot};\ C_3H_5^{\cdot} \rightarrow CH_2{=}C{=}CH_2 + H^{\cdot}, \text{ etc.} \end{gathered} \quad (6)$$

It was shown in the same study by numerical calculation that the concentration of $CH_3^{\cdot}$ radicals exceeds by more than an order of magnitude the overall concentration of all other radicals. The calculated formation curves for the molecular products at 765 °C describe satisfactorily the experimental data:[8,9] for reaction times up to 500 s, the concentration of ethane is highest among all the hydrocarbon products, while for longer times that of ethylene is highest; if the reaction time exceeds 2290 s, the concentration of propene is higher than that of ethane and, whatever the reaction time, the concentration of propene is 3–4 times higher than that of acetylene. Alkanes heavier than ethane (propane, butane, etc.) are not formed.

The rate of conversion of methane increases significantly in the presence of a large surface area, apparently as a result of the acceleration of the initiation stage. On a carbon surface, and any surface becomes coated with carbon on pyrolysis with deposition of coke,[3] the effective activation energy for the initiation stage may fall to ~50 kcal mol^{-1}.[10] A change in the composition of the surface during the process can influence its rate and direction. Thus, in the presence of MgO [11] at 900 °C, the degree of conversion of methane falls from 22 to 8% during the first 6–7 h, after which it retains a stationary value; however, the yield of hydrocarbons increases from 0.8 to 2.4%. Whereas in an empty quartz reactor the formation of hydrocarbons is not observed for a contact time less than 3 s, with increase in contact time to 10 s the yields of hydrocarbons on the coke-saturated MgO and in the empty quartz reactor are similar.

It must be emphasised yet again that the attainment of high yields of hydrocarbon methane condensation products is limited by the unfavourable equilibrium position even at relatively high temperatures (700–900 °C). Thermodynamic prohibition of the conversion of methane is removed in oxidation processes which take place with a decrease in free energy.

The characteristic features of the homogeneous oxidation of methane have been studied most fully compared with other hydrocarbons.[12] This process is complex, proceeds via a branched chain mechanism, and includes several tens of stages. A whole series of kinetic models have now been proposed for the description of the homogeneous oxidation of methane (see for example, Refs. 13–17). Each of them corresponds to definite homogeneous oxidation reaction conditions (temperature and pressure range, concentration of the components of the reaction mixture, macrokinetic characteristics of the system).

In all the mechanisms proposed, it is assumed that chain initiation takes place in the following stage characterised by an activation energy of ~50 kcal mol^{-1}:[18]

$$CH_4 + O_2 \rightarrow CH_3^{\cdot} + HO_2^{\cdot}. \quad (7)$$

Chain propagation takes place in the following stages:

$$\begin{gathered} CH_3^{\cdot} + O_2 \rightleftarrows CH_3O_2^{\cdot};\qquad CH_3O^{\cdot} \rightarrow CH_2O + H^{\cdot}; \\ CH_3O_2^{\cdot} + CH_4 \rightarrow CH_3OOH + CH_3^{\cdot};\qquad H^{\cdot} + CH_4 \rightarrow H_2 + CH_3^{\cdot}; \\ CH_3O_2^{\cdot} + CH_3^{\cdot} \rightarrow 2CH_3O^{\cdot};\qquad CHO_3^{\cdot} + CH_2O \rightarrow CH_3OH + CHO^{\cdot}; \\ CH_3O_2^{\cdot} + CH_4 \rightarrow CH_3OH + CH_3O^{\cdot};\qquad CH_3O^{\cdot} + O_2 \rightarrow CH_2O + HO_2^{\cdot}; \\ HO_2^{\cdot} + CH_4 \rightarrow H_2O_2 + CH_3^{\cdot};\qquad CHO^{\cdot} + O_2 \rightarrow CO + HO_2^{\cdot}; \\ CH_3O_2^{\cdot} \rightarrow CH_2O + OH^{\cdot};\qquad CO + HO_2^{\cdot} \rightarrow CO_2 + OH^{\cdot}; \\ OH^{\cdot} + CH_4 \rightarrow CH_3^{\cdot} + H_2O;\qquad 2CH_3O_2^{\cdot} \rightarrow CH_3OH + CH_2O + O_2; \\ CH_2O + HO_2^{\cdot} \rightarrow CHO^{\cdot} + H_2O_2;\qquad 2CH_3O_2^{\cdot} \rightarrow 2CH_3O^{\cdot} + O_2, \text{ etc.} \end{gathered} \quad (8)$$

Chain branching occurs in the stages

$$H_2O_2 + M \rightarrow 2OH^{\cdot}, \quad (9)$$

$$CH_2O + O_2 \rightarrow HO_2^{\cdot} + CHO^{\cdot}, \quad (10)$$

$$CH_3OOH \rightarrow CH_3O^{\cdot} + OH^{\cdot}. \quad (11)$$

Chain termination can occur in stages (4) and (5) and also as a result of the destruction of active species ($HO_2^{\cdot}$, $CH_3O_2^{\cdot}$, $CH_3^{\cdot}$, OH, H_2O_2, CH_3OOH) on the reactor walls. The kinetic parameters of the radical destruction processes on the walls are frequently unknown and are estimated from the correspondence of the results of the numerical computation to the experimental data (see, for example, Vardanyan et al.[14]). The rate constants for the majority of the homogeneous stages found by different methods are available in the literature.[19–22]

The data accumulated for the homogeneous gas-phase methane oxidation processes show that the partial oxidation products formed (CH_2O, CH_3OH) exhibit a higher reactivity under the process conditions compared to methane and undergo further successive transformations into extensive oxidation products. As a result, the yield of formaldehyde at 500–600 °C cannot exceed 0.5% relative to the methane passed through the system.[13] The preparation of

methanol requires an increase in pressure to tens of atmospheres;[5,17,23] the yield of CH_3OH can then reach several per cent relative to the methane passed through the system at 400–600 °C.

III. Heterogeneous-catalytic oxidation of methane

The most realistic method of increasing the yield of target products may involve the oxidation of methane in the presence of heterogeneous catalysts. However, for a long time the attempts to create effective catalysts for the conversion of methane into valuable products on the basis of traditional catalytic systems were unsuccessful; in the presence of transition metals and their oxides (see, for example, Refs. 24–26), extensive oxidation of methane mainly takes place; the efficiency of zeolitic catalysts in relation to the partial oxidation in the presence of oxygen is also low.[27]

However, in recent years definite progress has been achieved in the search for catalysts and conditions for the process leading to the partial oxidation of methane.

1. Partial oxidation of methane to oxygen-containing compounds

It was noted above that at elevated pressures it is possible to drive the gas-phase methane oxidation process towards CH_3OH. The application of catalysts based on zinc, cadmium, and nickel oxides, which are solid solutions,[28] and the use of a high pressure (up to 100 atm)[29] make it possible to achieve a yield of CH_3OH up to 2% relative to the methane passed through the system for a selectivity of about 80%. Like other heterogeneous catalysts,[5] this system does not give rise to a significant increase in the yield of methanol compared with homogeneous oxidation.

A wide range of oxide and phosphate catalytic systems have been investigated in the reaction involving the oxidation of methane to formaldehyde.[30,31] Catalysts which are weakly reduced by hydrogen (SiO_2, BPO_4, $AlPO_4$) exhibit a high selectivity with respect to CH_2O. Highly passive catalysts are most active as regards CH_2O, which is attributed to the easier desorption of the products from their surfaces. In the series investigated, tin phosphate is the optimum catalyst[32] on which the yield of CH_2O can reach 16% under conditions with circulation of the reaction mixture and the freezing out of the product during the cycle. In the flow regime, the yield of CH_2O during one pass does not exceed 2%.[33]

When aluminosilicates (with an Al_2O_3 content of 10–11%), modified by the addition of metal (Fe, Zr, V, Ni, Mo, Cu, Cd, Bi, Cr) oxides,[34] are used as catalysts, it is also possible to increase the yield of CH_2O (1.9% relative to the methane passed through the system on aluminosilicate containing 1.5% of Fe_2O_3). The maximum yield of CH_2O (2.6%) was obtained on aluminosilicate with added 2% of cerium phosphate and 0.05–0.06% of P_2O_5 at 750 °C. In the presence of this catalyst, it is possible to reduce the reaction temperature approximately by 100 °C with simultaneous increase in the CH_2O yield to 5–5.5% as the result of the introduction of 0.2–0.5% of $(CH_3)_2O$ into the contact zone.[35]

The addition of halogen-containing compounds into the reactant stream also entails an increase in the yield of CH_2O. Catalysts containing deposited transition metal (Ce, Mo, V, Fe, Co) oxides have been described.[36] At 450–600 °C and after the addition of up to 1 mole of HCl per mole of CH_4 to the initial mixture, they make it possible to obtain a yield of CH_2O up to 15% relative to the methane passed through the system.

When a deposited palladium catalyst (0.5% of the oxide on Al_2O_3) is used,[37] the introduction of 5 mole % (relative to methane) of CH_2Cl_2 into the stream of the 5 : 1 mixture of air and methane lowers the degree of conversion of methane at 475 °C from 20 to 13% with a simultaneous increase in the CH_2O yield from 0 to 6%. Experiments involving the introduction of CH_2Cl_2 into the mixture of CH_2O with air showed that this entails the suppression of the subsequent oxidation of formaldehyde.

Detailed investigation of the partial oxidation of methane to CH_2O [38] by methods involving separate calorimetric measurements and EPR with the freezing out of radicals showed that, in the presence of KSK silica gel and γ-Al_2O_3, the process takes place partly in the bulk of the gas phase. Evidence was obtained for a heterogeneous-homogeneous mechanism of the oxidation of methane, according to which the gas-phase processes lower the selectivity with respect to CH_2O. The low process selectivity on Al_2O_3 can be explained by the high rate of successive conversion of formaldehyde into carbon oxides as a result of the additional oxidation and decomposition into CO and H_2. The influence of the modification of silica gel by the addition of ZnO, SrO, CdO, B_2O_3, Al_2O_3, CeO_2, Bi_2O_3, V_2O_5, MoO_3, and WO_3 on the yield of methane oxidation products has been investigated. The maximum yield of CH_2O (up to 3.6%) has been obtained on a specimen modified with ZnO.

A communication[39] describing the formation of a complex catalyst containing Fe, Mo, Ni, Mg, and Bi oxides on SiO_2, which makes it possible to obtain CH_2O at 650 °C by oxidising methane with a selectivity of 86.5% for a conversion of 8.9%, has been published recently.

A significant increase in the yield of oxygen-containing products of the partial oxidation of methane can be achieved using N_2O as the oxidising agent. The replacement of O_2 by N_2O leads to an increase in the degree of conversion of methane on the 2% MoO_3/SiO_2 catalyst[40,41] at 550 °C from 0.5 to 6%; the selectivities with respect to CH_3OH and CH_2O are then 38 and 55% respectively. The maximum yield of the partial methane oxidation products is observed when water is added to the initial mixture: at p_{H_2O} = 0.18 to 0.20 atm, the degree of conversion of methane is 26% for selectivities with respect to CH_3OH and CH_2O of 80 and 19% respectively, in the absence of water, the degree of conversion is approximately 4% for an overall selectivity of about 60%. Under the conditions of thermoprogrammed desorption, C_2H_6 and C_2H_4 are evolved at relatively low temperatures (100–200 °C) after the successive admission at 25 °C of N_2O and CH_4 to a specimen, containing molybdenum (V) ions,[41] which had been reduced beforehand; the maximum evolution of CH_3OH occurs at a temperature above 450 °C. Traces of C_2 hydrocarbons are present in the reaction mixture also under the conditions of the continuous supply of a mixture of CH_4 and N_2O.[40,41]

The proposed process mechanism includes the following stages leading to the formation of CH_3OH and CH_2O:[43]

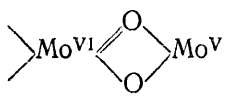
$$
\begin{aligned}
&Mo^{V} + N_2O \rightarrow Mo^{VI}O^{-} + N_2,\\
&Mo^{VI}O^{-} + CH_4 \rightarrow Mo^{VI}OH^{-} + CH_3^{\cdot},\\
&Mo^{VI}O^{2-} + CH_3^{\cdot} \rightarrow Mo^{V}OCH_3,\\
&Mo^{V}OCH_3^{-} + H_2O \rightarrow Mo^{V}OH^{-} + CH_3OH,\\
&Mo^{V}OH^{-} + Mo^{VI}OH \rightarrow Mo^{V} + Mo^{VI}O^{2-} + H_2O,\\
&Mo^{V}OCH_3^{-} + Mo^{VI}O^{2-} \rightarrow Mo^{VI} + Mo^{V}OH + CH_2O.
\end{aligned}
\qquad (12)
$$

The processes

$$8Mo^{VI} + 4O^{2-} + CH_4 \rightarrow 8Mo^{V} + 2H_2O + CO_2, \quad (13)$$

$$2Mo^{V} + N_2O \rightarrow 2Mo^{VI} + N_2 + O^{2-}, \quad (14)$$

can lead to non-selective oxidation. It has been suggested that the active centre has the structure



A difference in the behaviour of the surface CH_3O^- groups on deposited MoO_3, where they react in accordance with Scheme (12) as presented above, and on MgO where their only reaction pathway is decomposition into CO and H_2 [44] has been noted.[42] Nor can one exclude also the possibility of the formation of CH_3OH via the interaction of the $CH_3^{\cdot}$ radicals with water or Si—OH groups.[43]

It has been shown[45] that the mechanisms of the formation of CH_2O at temperatures below and above 540 °C on the 2% MoO_3/SiO_2 catalyst are different. There is a possibility of both the direct formation of CH_2O from the CH_3O^- groups and of the successive conversion of methanol into formaldehyde; the effective activation energies E_a for these two processes are respectively 82 ± 4 and 41 ± 4 kcal mol^{-1} (the latter value virtually agrees with E_a for the formation of CH_3OH, which is 40 ± 2 kcal mol^{-1}).

The 2% V_2O_5/SiO_2 catalyst, in which the deposited component is present as a submonolayer of isolated vanadium ions,[46] also exhibits activity in the formation of partial oxidation products of methane in the presence of N_2O.[47] This system operates at a lower temperture compared with MoO_3/SiO_2; the activation energies E_a for the formation of CH_3OH and CH_2O are respectively 40 ± 4 and 22 ± 2 kcal mol^{-1}. A difference between the mechanisms of the formation of CH_2O on the above systems has been noted: in the case of V_2O_5/SiO_2 there is no successive conversion of CH_3OH into CH_2O and formaldehyde is formed only in the course of the dehydrogenation of the surface CH_3O^- group occurring simultaneously.

The possibility of the conversion of the CH_3O^- group on $Bi_2O_3-SnO_2$ catalysts into both CH_2O (in the absence of water) and CH_3OH (in the presence of water), on the one hand, and into C_2H_6, on the other, has been postulated.[48] In the presence of N_2O at 550 °C, the selectivity with respect to CH_2O on these catalysts can reach 92.2% for a degree of conversion of methane of 2.6%. In the absence of N_2O, methane can be oxidised by the oxygen of the catalyst to CH_2O with a selectivity of about 80%, the activity falling gradually.

The increase in the yield of the methane partial oxidation products in the presence of N_2O as the oxidant has been attributed to the oxidation on the catalyst surfaces of the radical-ions $O^{\cdot-}$, which are capable of abstracting a hydrogen atom from the methane molecules.[49]

It is notable that the mode of the methane oxidation process can change when O_2 is replaced by N_2O. Thus mainly carbon oxides are formed on zeolitic catalysts when O_2 is used;[27] the replacement of O_2 by N_2O leads to the formation of aromatic hydrocarbons, the overall yield at 400 °C on a decationated zeolite with the ratio $Al_2O_3:SiO_2 = 1:68$ can reach 10% for a conversion of methane of 25%.[50] With decrease in the degree of cationation, the yield of hydrocarbons falls.[51]

As already mentioned, when O_2 is used as the oxidant, it is not possible to achieve an appreciable yield of the products of the partial oxidation of methane on oxide and zeolitic catalysts. However, recently major progress has been achieved in effecting another process—the oxidative condensation of methane with formation of C_2 and higher hydrocarbons.

2. Oxidative condensation of methane

(a) Alternate oxidation–reduction of oxide systems

The possibility of obtaining an appreciable yield of the products of the oxidative condensation of methane was apparently first demonstrated in a patent.[52] The process is carried out with methane supplied to solid catalysts containing 0.01–0.2% of a Group VIII or IB metal, chromium and molybdenum oxides, or tungsten, barium, lanthanum, and other oxides on the MgO, TiO_2, ZrO_2, and Al_2O_3 carriers. In particular, when methane is supplied at a temperature of about 700 °C to a specimen obtained by the successive treatment of γ-Al_2O_3 with solutions of magnesium, barium, and chromium nitrates, with an intermediate heat treatment, and then with a solution of H_2PtCl_6, it is possible to obtain 8% of C_2H_4, 3.2% of C_2H_6, 0.056% of C_4H_8, and 14.4% of benzene. Furthermore, 19.3% of methane is converted into condensation products, from which C_2H_4 and C_6H_6 are formed on treatment with water vapour or O_2. The proposed process mechanism involves the formation of dehydrogenated forms on the surface as far as coke and their subsequent interaction with CH_4 to form higher hydrocarbons.

Keller and Bhasin[53] investigated the formation of ethane and ethylene on alternate exposure of metal oxides deposited on α-Al_2O_3 to methane and air. The Mn, Cd, Sb, Tl, Pb, and Mg oxides proved to be the most active and selective at 800 °C. The overall yield of C_2 hydrocarbons on the best specimen, containing manganese, was 5% relative to the methane passed through the system for an 11% conversion. A mechanism was proposed for the formation of the oxidative condensation products:

$$\begin{gathered} CH_4 + M^{(2n)+}O_n^{2-} \rightarrow M^{(2n-2)+}O_{n-1}^{2-} + OH_{ads} + CH_{3,ads}, \\ 2CH_{3,ads} \rightarrow CH_3CH_{3,ads}, \\ 2OH_{ads} \rightarrow H_2O + O_{ads}, \\ 2M^{(2n-2)+}O_{n-1}^{2-} + O_2 \rightarrow 2M^{(2n)+}O_n^{2-}. \end{gathered} \quad (15)$$

Analogous processes leading to the formation of the products of the oxidative condensation of methane with separate supply of methane and oxygen to a solid catalyst have been described in the patent literature.[54–61] The active phase of the catalyst employed contains Mn, Sb, In, Ge, Pb, Sn, and Bi oxides with added alkali or alkaline earth metal cations and phosphate ions on carriers. The selectivity with respect to the sum of hydrocarbons in the first oxidation-reduction cycles can exceed 80% for a methane conversion of about 15%.[55] The Mn/γ-Al_2O_3 catalyst is characterised by a much lower selectivity than Mn/SiO_2.[62] In the latter case, 0.4 ± 0.05 of a gram-atom of oxygen per gram-atom of Mn can be removed reversibly from the catalyst. The increase in the selectivity and stability of the 15% Mn/SiO_2 catalyst when it is modified by the addition of 5% of $Na_4P_2O_7$ [63] has been explained by the decrease in acidity and a change in the phase composition. The introduction of halogen-containing compounds (for example, CH_3Cl) into the stream of methane makes it possible to increase the selectivity to 85–93% for conversions up to 29%.[60]

Although an appreciable yield of the products of the oxidative condensation of methane can be achieved in the processes described, they suffer from two significant disadvantages: the difficulty of achieving in practice an alternating supply of the reactants and a gradual (in many cases extremely rapid) loss of activity by the solid catalyst.

(b) The performance of the process in the continuous regime

After the communications in which the oxidative condensation of methane involving the use of the lattice oxygen of oxide systems was described, data were published on catalysts which made it possible to carry out the process in the continuous regime. For this purpose, use is made of systems which had been employed earlier as sources of lattice oxygen (Mn, Sn, In, Ge, Pb, Sb, Bi, Pr, Tl, Cd oxides on carriers promoted by alkali or alkaline earth metals and stabilised by phosphate ions).[64-67] For example, when a CH_4:air = 1:1 mixture is supplied to a catalyst containing 10% each of Mn (in the form of oxides) and $Na_4P_2O_7$ on SiO_2, the degree of conversion of methane can reach 24.1% for an overall selectivity with respect to C_2 hydrocarbons of 57%.[64]

If N_2O is used as the oxidant, then, for a methane conversion of 28.4%, the selectivity with respect to the sum of C_2 and higher hydrocarbons can reach 68% (800 °C, catalyst—12.5% $NaMnO_4$ on MgO).[65]

In the case of deposited catalysts containing PbO, the highest yield of hydrocarbons is obtained when Al_2O_3 is used as the carrier.[68] At 740 °C, CH_4 and O_2 pressures in the initial mixture of 0.7 and 0.07 atm respectively, and the virtually complete conversion of O_2, the selectivity of the PbO/Al_2O_3 catalysts increases with increase in the PbO content, reaching a maximum value of 57.7% (with respect to the sum of C_2 and C_3 hydrocarbons) for a PbO concentration of 36%. The introduction of 2% of Na_2O into the 6.5% PbO/Al_2O_3 catalyst increases the selectivity with respect to hydrocarbons from 12.9 to 35.4%. The selectivity of catalysts on different carriers decreases in the sequence SiO_2 > Al_2O_3 > aluminosilicates, but the activity of the systems based on SiO_2 is extremely low.

Catalysts obtained by depositing PbO on carriers with a high alkalinity (MgO, CaO, β-Al_2O_3) are even more effective.[69] The conversion of methane and the selectivity with respect to C_2 hydrocarbons on the 5% PbO/MgO catalyst at 750 °C are respectively 13 and 72%.[70] The influence of the basicity of the carrier on the efficiency of the oxidative condensation has been emphasised.[69,70]

After prolonged use of the PbO/Al_2O_3 catalysts at 800 °C (30 h), the selectivity falls from 40 to 7%,[71] which has been attributed to the possible entrainment of lead by the gas stream.

In the series of catalysts containing Ga, In, and Tl oxides on an aluminosilicate carrier (19 mole % SiO_2), the highest yield of C_2 hydrocarbon (2.3%) was observed for the thallium catalysts.[72] Catalysts on aluminomagnesium carriers (20-50 mole % MgO) have a higher activity.

Oxidation catalysts of a new type, not containing metal ions in a variable oxidation state, based on alkaline earth metal oxides modified by alkali metal cations with similar (or smaller) ionic radii were first described and investigated in detail by Lunsford and co-workers.[73-78] These catalysts possess a high activity and selectivity in the oxidative condensation of methane, which has been attributed to the possibility of the formation of substitutional defects in the cationic sublattice and to the appearance of centres of the type Li^+O^-, which can participate in the activation of methane molecules. Thus, on the 7% Li/MgO catalysts, obtained by impregnating MgO with a solution of Li_2O_3 and subsequent heat treatment at 720 °C, the yield of C_2 hydrocarbons, from an initial mixture in which the CH_4 and O_2 pressures were 58 and 36 mm Hg, reached 19.4% (the yield relative to MgO was 1%) and diminished with increase in the reactant concentrations in the initial mixture while their ratio remained constant.[73] With increase in the relative amount of CH_4, the selectivity increases and the degree of conversion falls. CH_3OH and CH_2O are formed in trace amounts. The 15% Na/CaO catalyst also exhibits a high efficiency (the selectivity with respect to hydrocarbons is 52% for a methane conversion of 22%). On the other hand, if the ionic radius of the alkali metal cation is greater than that of the alkaline earth metal cation, the catalytic properties of the system are much worse: on the 20% Na/MgO catalyst, the degree of conversion of methane is 12% and the selectivity with respect to hydrocarbons is 18%.[77]

However, it has been shown, that in the series of catalysts obtained by impregnating MgO with metal (alkali, alkaline earth, transition, etc.) nitrate solutions, specimens containing more than 10% of Na_2O are the most effective: the yield of C_2 hydrocarbons reaches 19.5-22.4% relative to the methane passed through the system at 750-800 °C for a methane concentration in the initial mixture of about 3% (CH_4:O_2 = 2:1).[79] When this method is used to introduce the additive, the lithium-containing catalysts are less effective (the yield of C_2 hydrocarbons at 750 °C is about 9%). The high efficiency of the sodium-containing catalysts has been explained by the influence of Na^+ on the MgO structure.

The study of a large number of metal oxides[80] has led to the conclusion that the highest selectivity is manifested by lanthanide metal oxides (with the exception of Ce, Pr, and Tb). Among them, the most effective is Sm_2O_3, in the presence of which the selectivity with respect to C_2H_6 at low O_2 concentrations (1.6%) can reach 100% at 700 °C.[81]

The modification of Sm_2O_3 by alkali metal ions, carried out by impregnating the catalyst with solutions of their carbonates and subsequent heat treatment, increases the yield of C_2 hydrocarbons.[82] The specimen containing 10 mole % of Li_2O, on which the yield of C_2 hydrocarbons reaches 21% compared with 12% for the unmodified Sm_2O_3 is optimal (750 °C, CH_4 and O_2 pressures in the initial mixture 50 and 20 mmHg respectively).

The modification of Sm_2O_3 with 20 mole % of LiCl instead of Li_2CO_3 [82] increases the yield of C_2H_4 by a factor of 1.5 (to 16.8%) with a slight decrease of the overall yield of the C_2 hydrocarbons. However, such a catalyst, as well as other Sm_2O_3-based systems, works most effectively at low CH_4 and O_2 concentrations: at 750 °C at an overall pressure of 1 atm, and with the ratio CH_4:O_2 = 5:2, the increase in the CH_4 concentration in the initial mixture from 5 to 40% lowers the yield of C_2 hydrocarbons from 15.6 to 7.2% as a result of the decrease in selectivity from 63.4 to 26.9%.

The oxides of other lanthanides also exhibit a higher efficiency at low reactant concentrations: in the presence of La_2O_3, a decrease in the methane pressure in the initial mixture from 313 to 132 mmHg (p_{O_2} = 8.4 and 15 mmHg respectively) increased the yield of C_2 hydrocarbons from 2.53 to 4.4%.[83]

In this respect, lanthanum aluminate, which works effectively in concentrated mixtures, is preferable:[84] at 710 °C in a 1:1 methane–air mixture, the yield of C_2 hydrocarbons was 12.5% for a methane conversion of 25.3%. A disadvantage of this catalyst is its low stability as regards temperature: it loses activity and selectivity even at 800 °C, which has been attributed to the loss of its amorphous structure.[85]

Interesting data have been obtained in studies on transition metal (Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn) oxides modified by alkali metal compounds.[86–88] Systems containing LiCl have the best catalytic properties: whereas the unmodified nickel oxide propagates only extensive oxidation, after the addition of LiCl the overall yield of C_2 hydrocarbons at 750 °C and initial CH_4 and O_2 concentrations of 5 and 2% respectively reaches 28.9% for a C_2H_4 yield of 26.2%. Under the same conditions, the yields of C_2H_4 and C_2H_6 on the 20% $LiCl/MnO_2$ catalyst are respectively 28.1 and 25%. With increase in the reactant concentrations in the initial mixture by a factor of 10, the yield of C_2 hydrocarbons falls approximately by a factor of 1.5.[85]

A serious disadvantage of the catalysts containing alkali metal halides is their rapid deactivation: LiCl containing specimens based on Sm, Ni, and Mn oxides are deactivated in several hours. There is a simultaneous decrease in the ratio C_2H_4/C_2H_6. The deactivation is attributed to the abstraction of chlorine from the catalysts, since CH_3Cl has been detected in the reaction mixture, its amount decreasing in parallel with the loss of activity.[87]

As already mentioned, in the presence of N_2O, the oxidative condensation of methane in the presence of zeolitic catalysts leads to the formation of aromatic hydrocarbons,[50,51] whereas oxidation with oxygen leads to the formation of carbon oxides.[27] Modification of zeolites with manganese promotes the manifestation by the latter of catalytic activity in the oxidative condensation of methane to C_2 hydrocarbons in the presence of O_2.[89,90] The best parameters are attained when manganese-containing catalysts based on the NaH-HSZ † ($SiO_2:Al_2O_3$ = 71) zeolite are used: at 750 °C and with the CH_4:air = 0.83 : 1 ratio, the yield of C_2 hydrocarbons is 9.5%.

Thus a whole series of catalytic systems active in the oxidative condensation of methane are now known. However, the known catalysts suffer from a number of disadvantages, which precludes their practical use:

(1) They all exhibit the optimum efficiency at high temperatures (> 700 °C), which complicates the apparatus needed for the process.

(2) The most effective catalysts work well in mixtures with low CH_4 and O_2 concentrations; as a result, even when the yields of the target products relative to the methane passed through the system are high, their concentration in the reaction mixture is low, which prevents their isolation by the known methods.[91]

(3) The activity and selectivity of many catalysts fall rapidly during their operation because of the entrainment of active components; other catalysts are unstable when overheated, which happens inevitably when the higher exothermic process considered (with a relatively low selectivity) is carried out in a large reactor.

The elucidation of the causes of the above disadvantages and the search for possible ways of eliminating them require the study of the process mechanism.

3. Hypotheses concerning the mechanism of the oxidative condensation of methane

The available literature data on the mechanism of the oxidative condensation of methane relate to the following questions: (1) the nature of the stages involving the activation of CH_4 molecules; (2) the mechanism of the formation of oxidative condensation products; (3) the nature of the active centres of the catalysts.

There exists apparently a unanimous view at the present time concerning the nature of the stage leading to the activation of the methane molecule: it involves the dissociation of a C–H bond with the simultaneous formation of a surface OH group and a methyl fragment. However, the ideas concerning the state of this fragment are different among different workers.

It has been suggested[53,67,92,93] that the CH_3 group bound to the surface is formed in the first stage. On the other hand, in a study of the interaction of CH_4-O_2 and CH_4-N_2O mixtures with catalysts of the oxidative condensation of methane at pressures less than 1 mmHg and temperatures below 450 °C, the liberation of $CH_3^{\cdot}$ radicals into the gas phase was detected by the freezing out method, which indicates the possibility of the formation of radicals not bound to the surface in this stage.[74–76,83]

The possibility of the oxidative condensation of methane via a heterogeneous-homogeneous mechanism was postulated already in one of the first studies on this process.[94] The formation of radicals under the conditions of the catalytic oxidation of methane over a wide temperature range (400–800 °C) at atmospheric pressure has been observed[95] and it has been shown that, in the presence of a more effective catalyst (10 mole % K_2O/Al_2O_3), the rate of formation of radicals is much higher than on a less effective catalyst (θ-Al_2O_3). The formation of radicals has been detected[63] by the lead mirror method in the reduction of the 15% Pb + 5% $Na_4P_2O_7/SiO_2$ system. The volume propagation of the methane oxidation process in the presence of Al_2O_3 and SiO_2 was observed even earlier by methods involving separate calorimetric measurements and the freezing out of radicals,[93] although the products in this study were oxygen-containing compounds.

If the question of pathways leading to the formation of the products of the oxidative condensation of methane in the presence of oxide systems with deposited platinum group metals is ignored,[52] then one must conclude that, according to the majority of investigators, the primary product is ethane. This is indicated by the dependence of the yield of hydrocarbons on temperature and contact time in the presence of MgO-based catalysts[77,96] and catalysts containing Bi_2O_3,[67] PbO,[68] and lanthanide oxides[81,83,84] and also by analogous data obtained in the reduction of Mn/SiO_2 systems with methane.[62,63] It has been noted[97] that the sequence in the formation of C_2 and C_3 hydrocarbons in accordance with the scheme $CH_4 \rightarrow C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_2$, C_3H_6 ($\rightarrow C_3H_4$) is a general feature of the oxidative condensation of methane on oxide catalysts of different chemical nature. Similar effective activation energies for the formation of ethane—the primary condensation product—have been observed for many catalysts. It amounts to 46.5 ± 1.5 kcal mol^{-1},[98] which is extremely close to the activation energy for the formation of methyl radicals in the presence of the MgO-based catalyst (42 ± 6 kcal mol^{-1} [74]).

The approximate identity of the proportions of the hydrocarbon products in the reduction of various oxide catalysts with methane[62,63] cannot apparently serve as evidence for a heterogeneous-homogeneous process mechanism. A more convincing argument is the closeness of the rates of formation of radicals and oxidative condensation products.[74,95] The homogeneous formation of C_3 and C_4 olefins as a result of the interaction of $CH_3^{\cdot}$ radicals with ethylene and propene respectively is indicated by the sharp increase in their yield when lower olefins are added to methane used to reduce the catalysts.[62,63]

On the other hand, data have been obtained by IR spectroscopy[71] showing the formation on the surfaces of the PbO/Al_2O_3 and Li/MgO catalysts of unidentified surface compounds which can serve, according to the authors, as sources or precursors of ethylene.

† HSZ = high-silica zeolite (Ed. of Translation).

This means that there can exist a parallel pathway leading to the formation of C_2H_4. There are also data according to which methane is converted into ethylene on certain catalysts (for example, $LiCl/Al_2O_3$ [88]) without the formation of appreciable amounts of ethane. The formation of adsorbed CH_3 and CH_2 fragments as well as ethane-like structures has also been observed by Raman spectroscopy in the adsorption of methane on oxidised metallic films at low temperatures.[99]

Thus there exist two views concerning the mechanism of the formation of the products of the oxidative condensation of methane.

(1) The heterogeneous mechanism. The activation of methane is accompanied by the formation of surface CH_3 groups bound to oxygen or metal ions, for example, in the form CH_3O^- [48] or $CH_3^{\delta-}M^{\delta+}$;[67] the interaction of these groups on the surface leads to the formation of ethane, which is successively converted into ethylene. There is a possibility of the parallel formation of ethylene from the surface compounds.[71]

(2) The heterogeneous-homogeneous mechanism. The activation of methane leads to the formation of the $CH_3^{\cdot}$ free radicals (either directly or via the intermediate formation of a CH_3 group bound to the surface[70]); the recombination of the $CH_3^{\cdot}$ radicals in the gas phase results in the formation of ethane, which is successively converted into ethylene as a result of oxidative dehydrogenation on the catalyst.

The choice between these two alternative schemes is of fundamental importance both from the standpoint of the determination of the true process mechanism and from the standpoint of the creation of effective catalysts. If the heterogeneous mechanism is valid, then the catalyst should have the optimum adsorption properties, ensuring the binding of the CH_3 fragments in the necessary form and the possibility of their interaction with formation of ethane (or of its adsorbed precursor). Furthermore, the oxygen present on the catalyst surface must not be too active, so that the bound hydrocarbon fragments are not oxidised to CO and CO_2. In this case, it appears important to examine the nature of the catalyst from the standpoint of its ability to convert the CH_3 groups into electron-deficient or neutral states or states with an electron excess.[70,100] Hence follows the concept of the selection of catalysts on the basis of their acid-base properties.[101] As already mentioned, in a whole series of cases a direct correlation has been observed between the efficiency of the catalysts and their basicity.

On the other hand, according to the heterogeneous-homogeneous mechanism, the efficiency of the catalyst is determined by its ability to generate $CH_3^{\cdot}$ radicals in the gas phase. The possible homogeneous reactions leading to the formation of both the target products (the combination of $CH_3^{\cdot}$ radicals) and of oxygen-containing compounds (the interaction of methyl radicals with O_2 to form the $CH_3O_2^{\cdot}$ radicals) then becomes important for the further course of the process.[77,83,95]

The heterogeneous-homogeneous process mechanism appears more probable at the present time. It is supported by the experimental detection of radicals, formed in the oxidation of methane in the presence of various oxide catalysts, with a direct correlation of the yield of radicals and the efficiency of the catalysts, and by the similarity of the rates of formation of radicals and hydrocarbon products.

The compounds and fragments on the surfaces of catalysts, whose presence has been demonstrated by spectroscopic methods, may not in fact be precursors of the oxidative condensation products but can lead to extensive oxidation. Nor is there reliable evidence of the occurrence of the parallel process involving the formation of ethylene, because in those cases where large amounts of C_2H_4 were formed on the catalysts for a low yield of C_2H_6 the dependence of the yield of products on temperature and contact time was not stated. For low conversions, the primary hydrocarbon product on all the specimens investigated is ethane,[97] as should in fact be the case according to the heterogeneous-homogeneous scheme.

This model can explain also another general feature—the increase in selectivity with increasing temperature for low conversions. In the initial stage of the process, where the only hydrocarbon product is ethane and its successive transformations can be neglected, the set of reactions occurring in the gas phase can be reduced to the following stages:[95]

$$[O] + CH_4 \xrightarrow{k_1} [OH] + CH_3^{\cdot}, \quad (16)$$

$$2CH_3^{\cdot} \xrightarrow{k_2} C_2H_6, \quad (17)$$

$$CH_3^{\cdot} + O_2 \xrightarrow{K_3} CH_3O_2^{\cdot}, \quad (18)$$

$$2CH_3O_2^{\cdot} \xrightarrow{k_4} \text{extensive oxidation products;} \quad (19)$$

$$CH_3^{\cdot} + CH_3O_2^{\cdot} \xrightarrow{k_5} \text{extensive oxidation products.} \quad (20)$$

Analysis of this scheme on the hypothesis that equilibrium has been attained in stage (18) and that the system is quasi-stationary with respect to the sum of the radicals $CH_3^{\cdot}$ and $CH_3O_2^{\cdot}$ makes it possible to obtain an expression for the limiting selectivity S_{lim} determined solely by the processes occurring in the gas phase, provided that the catalyst surface participates only in the radical generation stage (16) and that the parallel extensive oxidation process does not take place on it:

$$S_{lim} = \left[1 + K_3 p_{O_2}\left(\frac{k_4}{k_2} K_3 p_{O_2} + \frac{k_5}{k_2}\right)\right]^{-1},$$

where p_{O_2} is the partial pressure of oxygen, K_3 is the equilibrium constant of stage (18), and k_2, k_4, and k_5 are the rate constants for stages (17), (19), and (20) respectively.

The above expression describes also the temperature dependence of S_{lim}. Since the equilibrium stage (18) shifts to the left with increase in temperature, S_{lim} increases. Experimental data have shown[95] that, on all the catalysts investigated, the observed selectivity for low conversions is below S_{lim}. This indicates the existence of a parallel channel leading to heterogeneous extensive oxidation. Analysis demonstrates that the effective activation energy for the heterogeneous extensive oxidation is as a rule lower than the activation energy for the formation of ethane, which is an additional factor promoting an increase in selectivity with increasing temperature.

There is no unanimous view in the literature concerning the nature of the active centres of the catalysts, which reflects the absence of unanimity as regards the mechanism of the methane activation stage. If it is assumed that bound CH_3 groups, forming ultimately the target products, are present on the surface, then the catalysts should exhibit bifunctionality,[67,70] namely an oxidising capacity (for the dissociation of the C—H bond) and basicity (for the prevention of an electron density deficiency at the CH_3 group). The view has also been expressed[101] that the presence of nucleophilic

(basic) centres is essential for the stabilisation of the proton and the compensation for the energy expended on the heterolytic dissociation of the C–H bond in the stage involving the activation of a CH_4 molecule; in this case the oxidation surface centres should ensure the abstraction of an electron from the CH_3^- group and its transition to an electrically neutral state.

The investigators who adhere to the heterogeneous-homogeneous mechanism[73-77,81,102-104] consider only the nature of the oxidation centres promoting the homolytic dissociation of the C–H bond. Since the oxidation centres occur in both mechanisms, we shall indicate the types of such centres discussed in the literature:

Oxygen bound to readily reducible cations;[53] the participation of oxygen of this type in the process is indicated by the possibility of obtaining oxidative condensation products both under the conditions of alternate oxidation-reduction and under the conditions of continuous catalysis on the same systems.

Oxygen ions O^- existing in the form of the ion pairs M^+O^- (M^+ is an alkali metal ion) in catalysts based on alkaline earth metal oxides modified by alkali metal cations;[73-78] the formation of centres of this type becomes possible in alkaline earth metal oxides as a result of the thermally activated electron transfer from the oxygen anion to the metal cation or due to the presence of a vacancy at a neighbouring cationic site;[74,76] the presence of O^- centres has been postulated also in Sm_2O_3.[81]

O^{2-} ions with reduced coordination in lead, bismuth and magnesium oxide:[76] it may be that centres of this type are identical with the first two types both in PbO and Bi_2O_3,[53] on the one hand, and in the case of alkaline earth metal oxides,[105] on the other.

The peroxide ions O_2^{2-},[98,103,104] which may be stabilised in systems containing alkali and alkaline earth metal cations with large ionic radii.[106]

By analogy with the gas-phase process

$$O^- + CH_4 \rightarrow OH^- + CH_3^{\cdot}, \qquad (21)$$

which occurs at a high rate even at room temperature, it has been suggested that the activation energy for a reaction of this type with participation of the O^- ions of the Li/MgO catalyst surface is also low.[77] The high observed activation energy for the formation of ethane (55 ± 1.6 kcal mol^{-1}) and the increase in selectivity with increase in temperature associated with it have been explained by the difficulty of reactivating the surface centre via the scheme:

$$\begin{aligned} &2Li^+{-}OH^- \rightarrow Li^+{-}O^{2-} + Li^+{-}[*] + H_2O, \\ &Li^+{-}O^{2-} + Li^+{-}[*] + \tfrac{1}{2}O_2 \rightarrow 2Li^+{-}O^- \end{aligned} \qquad (22)$$

or

$$\begin{aligned} &2Li^+{-}OH^- \rightarrow Li^+{-}O^- + Li^+{-}[*]^- + H_2O, \\ &Li^+{-}[*]^- + \tfrac{1}{2}O_2 \rightarrow Li^+{-}O^-, \end{aligned} \qquad (23)$$

where [*] is an oxygen vacancy and $[*]^-$ an oxygen vacancy with a captured electron.

However, this scheme does not agree with the phenomenon, observed by the same workers,[74,75] of the decay of the radical formation process via reactions of types (16) when N_2O is used as the oxidant (in the presence of O_2, there is no decay), because the filling of the oxygen vacancies, formed as a result of the dehydroxylation via schemes (22) and (23), should occur in the presence of N_2O at least no less effectively than in the presence of O_2.

The difficulty of the reoxidation of N_2O is also indicated by the data of Otsuka and Hatano:[107] when O_2 as the oxidant is replaced by N_2O, the conversion of CH_4 in the presence of the Sm_2O_3 catalyst decreases significantly. At the same time, the selectivity at relatively low temperatures (below 680 °C) increases in the presence of N_2O, which is fully explicable within the framework of the heterogeneous-homogeneous mechanism, since the extensive oxidation processes in the gas phase proceed via the $CH_3O_2^{\cdot}$ radicals whose formation is impossible in the absence of molecular oxygen.

As regards the basicity of the catalyst, an alternative explanation of its influence on their efficiency in the oxidative condensation of methane is apparently possible. It has been shown[108] that one of the pathways leading to the formation of the extensive oxidation products may be the decomposition of formaldehyde via the reaction

$$CH_2O \rightarrow CO + H_2. \qquad (24)$$

As already mentioned, the formation of CH_2O in the oxidation of methane takes place most effectively on catalysts with a high acidity.[30-33] The increase in selectivity with respect to hydrocarbons after the introduction of alkaline additives can then be attributed to the decreased contribution of this extensive oxidation channel as a result of the suppression of the acid centres.[68]

Together with the increase in selectivity, after the introduction of alkali and alkaline earth metal cations, an increase in the rate of formation of the products of the oxidative condensation of methane is also observed.[72,98,102] This is associated with the increase in the amount of the active forms of oxygen, for example O^- (in alkaline earth metal oxides with alkali metal additives[73-78]) or O_2^{2-} (in the M_2O/Al_2O_3 [97] and BaO [103,104] systems). Whereas the efficiency of the M_2O/Al_2O_3 catalysts increases under these conditions with increase in the ionic radius of the alkali metal cation,[97,102] the opposite variation is observed for the M_2O/MgO and M_2O/CaO systems,[77,102] which can be readily explained by the influence of the alkali metal cation on the properties of the oxygen of the catalysts. Thus the observed relation between basicity and catalyst efficiency can be purely superficial and may not be determined by the involvement of the basic centres directly in the stage involving the activation of CH_4 molecules. The final elucidation of this question requires additional research.

4. Kinetics of the oxidative condensation of methane

Some light may be thrown on the mechanism of the process by studying its kinetics. Unfortunately, one should note that, on the majority of the catalysts described in the literature, the kinetics of the oxidative condensation of methane have not been studied. The 7% Bi_2O_3–9% K_2CO_3/Al_2O_3 [67] and 34% PbO/Al_2O_3 [68] systems are an exception. Formal power equations of the following type were used for the kinetic description in both cases:

$$r_i = k_i p_{hc}^m p_{O_2}^n, \qquad (25)$$

where r_i is the rate of the ith process, k_i the observed rate constant, p_{hc} and p_{O_2} are the hydrocarbon and oxygen pressures respectively, and m and n are the effective reaction orders with respect to carbon and oxygen respectively.

The kinetic parameters obtained in the above studies[67,68] are listed in Table 1.

The kinetic parameters quoted in these studies[67,68] have been scarcely discussed apparently because of their formal character and low information content. The activation energies for the formation of CO, determined by Hinsen et al.,[68] illustrate qualitatively the observed increase in selectivity in the temperature range up to 700–750 °C without, however, any explanation of this finding.

Table 1. Kinetic parameters of the overall stages of the oxidative condensation of methane on the 7% $Bi_2O_3-K_2CO_3/Al_2O_3$ (I) [67] and 20% PbO/Al_2O_3 (II) [68] catalysts.

Stage	Catalyst					
	I				II	
	m	n	m	n	E, kcal mol^{-1}	k_i
$CH_4 \rightarrow C_2H_6$	2	1	1.1±0.3	0.8±0.2	24	$6.0\cdot10^4$
$CH_4 \rightarrow CO_2$	0.3	1	1.5±0.3	0.4±0.1	12	$1.5\cdot10^6$
$C_2H_6 \rightarrow C_2H_4$	1	2.5	1±0.2	0.8±0.1	1.5	$1\cdot10^2$
$C_2H_6 \rightarrow CO_2$	0	1.4	—	—	—	—
$C_2H_4 \rightarrow CO_2$	0	0.6	1.6±0.3	0.8±0.3	−52	$1\cdot10^{-10}$

The kinetics of the oxidation of methane on the 20% PbO/Al_2O_3 catalyst have been studied in detail.[95,104] For low conversions, taking into account the contribution of the homogeneous stages, the rate of the process in the ethane formation pathway is described by the kinetic equation characteristic of processes occurring via an oxidation-reduction mechanism:

$$r_1 = \frac{k_r p_{CH_4} k_{ox} p_{O_2}}{k_r p_{CH_4} + k_{ox} p_{O_2}}, \quad (26)$$

where k_r and k_{ox} are the rate constants for the reduction of the active centres by methane and for their reoxidation by oxygen respectively and p_{CH_4} and p_{O_2} are the methane and oxygen pressures respectively.

The kinetics of the conversion of ethane into ethylene on this catalyst are described by an analogous equation, which can be obtained on the assumption that two oxidised centres participate in the process:

$$r_2 = \frac{4k'_r p_{C_2H_6} k_{ox}^2 p_{O_2}^2}{(k_{ox} p_{O_2} + (k_{ox}^2 p_{O_2}^2 + 8k'_r p_{C_2H_6} k_{ox} p_{O_2})^{-1/2})^2}, \quad (27)$$

while k'_r is the rate constant for the reduction of the active centres by ethane and $p_{C_2H_6}$ is the ethane pressure.

The reoxidation rate constants, found in experiments with methane and ethane, proved to be extremely close, from which it was concluded that the same active centres are involved in both processes. The rate constants for the interaction of ethane with oxidised active centres were 10–20 times higher at identical temperatures than the corresponding constants for methane. From the pre-exponential factor for the constant k_r (assuming the impact character of the reduction stage), it was found that the surface concentration of the active centres is 0.3% of a monolayer on the catalyst surface.

Analysis of Eqn. (26) made it possible to explain the similarity of the effective activation energies E_{eff} for the formation of ethane on different catalysts.[95] It was shown that the following expression is valid for E_{eff}:

$$E_{eff} = \frac{\kappa E_r + E_{ox}}{1 + \kappa} \quad (28)$$

where E_r and E_{ox} are the activation energies for reduction and reoxidation respectively and $\kappa = k_{ox} p_{O_2} / k_r p_{CH_4}$.

For κ not differing greatly from unity, E_{eff} is close to half the sum of E_r and E_{ox}. On the other hand, if E_{ox} increases linearly with decrease in E_r, then E_{eff} is approximately constant in the series of catalysts. When one of the processes—reduction or reoxidation—takes place at a significantly lower rate than the other, the rate of the overall process is naturally determined by the kinetic parameters of the slower stage. Thus it has been shown[104] that in the case of BaO the reoxidation stage is slow which induces an increase in E_{eff} to a value in excess of 60 kcal mol^{-1}.

According to Sinev et al.,[98] the rates of the extensive oxidation of methane and ethane on the 20% PbO/Al_2O_3 catalyst are described by kinetic equations of the Langmuir type, which indicates the involvement of adsorbed forms in the reaction. This means that the mechanisms of the oxidative condensation and extensive oxidation differs significantly.

5. Reactions of methane on photoactivated and mechanically activated oxides

Additional information about the mechanism of the process considered has been obtained in studies on oxide systems subjected to photochemical[109–114] and mechanochemical[115–118] activation.

The action of radiation (in the visible, UV, X-ray, and γ-ray ranges) on TiO_2 [109–111] and other simple oxides[112,114] and also on SiO_2 and Al_2O_3 modified by vanadium and molybdenum ions[109,113] leads to the photosorption of methane. When the system is heated, C_2 and C_3 hydrocarbons as well as CH_3OH and C_2H_5OH appear in considerable amounts in the thermal desorption spectrum in addition to methane and carbon oxides. A certain amount of other hydrocarbons can be collected in a cooled trap even when methane is passed over photoactivated specimens at room temperature,[110] which indicates an extremely low activation energy for their formation. The principal characteristics of the photostimulated condensation of methane have been formulated by Kotova.[114]

(1) In the photoreactions of methane on oxides, two competing processes occur simultaneously: the formation of hydrocarbons and the formation of oxygen-containing compounds. On irradiation in the region of the intrinsic absorption by the oxide, the second process predominates, while outside this region (in the region where the defects absorb) the first process is dominant.

(2) The first stage of the process is homolytic dissociation of the C–H bond; the dissociative adsorption of hydrocarbons is accompanied by the formation of excited surface OH groups.

(3) After a time, the surface is poisoned by the reaction products and the efficiency of the photoconversion of methane decreases; the surface can be regenerated by a high-temperature treatment in oxygen.

(4) The presence of H_2 and O_2 in the system decreases the yield of hydrocarbons.

(5) There exist analogous dark reactions of methane, which may indicate the similarity of the mechanisms of the dark conversion and photoconversion of methane. It has been suggested that weakly coordinated oxygen ions in a charged state close to −1, whose properties are analogous to those of photoinduced hole O^- centres, participate in the dark process.

Thus data on the photoreactions of methane also indicate the involvement of weakly coordinated oxygen of the oxides and centres of type O^- in its activation. The direct use of these data for the description of the mechanism of the catalytic oxidative condensation of methane is precluded by the fact that, among the systems investigated in photostimulated processes, only La_2O_3 is effective in the usual catalytic reaction.[83] The dark reactions of methane leading to its conversion into other hydrocarbons have been observed on Ga_2O_3, SnO_2, and α- and η-Al_2O_3,[114] which are poor catalysts of oxidative condensation. Furthermore, the postulated intermediate carbon-containing compounds have not been detected experimentally and the mechanisms discussed are hypothetical.

The study of the centres formed on oxides surfaces disordered by mechanical activation (in the first place on SiO_2 and GeO_2 [115–118]) has shown that some of them are very highly reactive in relation to molecule such as those of H_2 and lower paraffins and are capable of inducing the dissociation of H−H and C−H bonds. Such centres include strained Si−O−Si bridges, the radical centres $-\overset{\diagdown}{\underset{\diagup}{\dot{S}i}}$, $-\overset{\diagdown}{\underset{\diagup}{Si}}\dot{O}$, and $-\overset{\diagdown}{\underset{\diagup}{Si}}O\dot{O}$,[117] as well as groups of the peroxide type $-\overset{\diagdown}{\underset{\diagup}{Si}}-O-O-\overset{\diagup}{\underset{\diagdown}{Si}}-$.[118] The interaction of methane with these centres proceeds via reactions of type (16), the oxy-radicals $SiO^\cdot$ and $-\overset{\diagdown}{\underset{\diagup}{Ge}}O^\cdot$ (in the case of GeO_2) being most active. The $CH_3^\cdot$ radicals are formed on them with an exothermic effect of 14–17 kcal mol^{-1} and an activation energy close to.[117] The methyl fragments formed are bound to centres of different types, present in a large amount on the mechanically activated surface (=Si:, $-\overset{\diagdown}{\underset{\diagup}{Si}}O\dot{O}$, $-\overset{\diagdown}{\underset{\diagup}{Si}}-O-\overset{\diagup}{\underset{\diagdown}{Si}}-$, $-\overset{\diagdown}{\underset{\diagup}{Si}}-O-O-\overset{\diagup}{\underset{\diagdown}{Si}}-$) and undergo further reactions (more far reaching dehydrogenation and decomposition accompanied by isomerisation[117]). It is notable that methyl radicals have also not been detected in these investigations, although the authors identified by EPR a series of paramagnetic products of their interaction with various surface centres (=$SiCH^\cdot$, $-\overset{\diagdown}{\underset{\diagup}{Si}}CH_2^\cdot$, $-\overset{\diagdown}{\underset{\diagup}{Si}}OCH_2^\cdot$).

Unfortunately the centres formed on mechanically disordered surfaces are thermally unstable (because of their non-equilibrium nature) and are annealed at lower temperatures than those at which oxidative condensation of methane takes place. This factor as well as the absence of information in the relevant communications[115–118] about the hydrocarbon methane conversion products necessitates some caution in using the above data for the description of the mechanism of the oxidative condensation.

The mechanism of the formation of C_2 hydrocarbons in the presence of oxides modified by alkali metal halides apparently appears to be somewhat different.[82,86–88] However, in this case too a heterogeneous-homogeneous process is most likely with the participation of an atomic halogen, for example chlorine, in the initiation stages:

$$Cl + CH_4 \rightarrow HCl + CH_3^\cdot, \quad (29)$$

$$Cl + C_2H_6 \rightarrow HCl + C_2H_5^\cdot. \quad (30)$$

Chlorine atoms can be formed both in the decomposition of Cl_2 molecules formed via the Deacon reaction

$$2HCl + O_2 \rightarrow H_2O + Cl_2, \quad (31)$$

and in the direct oxidation of the alkali metal chloride melt on the oxide surface. The possibility of the oxidative condensation of methane via the oxidation of halides analogously to the hydroxychlorination of hydrocarbons is indicated by the high efficiency of the same transition metal oxides with added alkali metal halid salts in both reactions.

At high temperatures and appreciable concentrations of water in the reaction mixture, the reversible hydrolysis of the halides (for example, LiCl), i.e.

$$2LiCl + H_2O \rightleftharpoons Li_2O + 2HCl \quad (32)$$

can maintain the optimum concentration of HCl in the system, ensuring both its supply to the gas phase in order to effect reaction (31) and its binding, which precludes its being carried away from the reaction zone. However, at high concentrations of the $CH_3^\cdot$ radicals and $Cl^\cdot$ atoms, there is a high probability of the reaction

$$CH_3^\cdot + Cl^\cdot \rightarrow CH_3Cl, \quad (33)$$

which leads to the active component being carried away and to the loss of catalytic activity.[88]

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The available literature data on the reactions leading to the conversion of methane into methanol, formaldehyde, and hydrocarbons, including unsaturated and aromatic hydrocarbons, show that heterogeneous-catalytic processes constitute the most promising method for the conversion of methane into intermediate products of organic and petrochemical synthesis.

Many oxide systems exhibit catalytic activity in the oxidative condensation of methane to other hydrocarbons. However, virtually all the known catalysts suffer from the same disadvantages, which preclude the practical realisation of the process. The most effective catalysts afford the maximum yield of the target products at 700–750 °C, i.e. at an extremely high temperature.

According to its nature, the process is heterogeneous-homogeneous, which may lead to an appreciable influence of the reactor material and its parameters, especially at high temperatures. The highest yields of C_2 hydrocarbons have been observed, as a rule, in quartz reactors. The practical realisation of the process necessitates the use of metallic reactors and it is to be expected that at temperatures of 600 °C and above the rate of the extensive oxidation of methane will increase under the influence of the reactor material and hence selectivity will fall appreciably.[53]

This difficulty can be overcome, on the one hand, by creating highly efficient catalysts capable of propagating the process at lower temperatures and, on the other hand, by suppressing the activity of the reactor walls with respect to the extensive oxidation of methane.

The problem of the increase in the volume concentration of the products of the oxidative condensation of methane, which would greatly facilitate the task of their isolation and would increase the economic effectiveness of the process, is no less important. It is therefore necessary to achieve the stable operation of the catalyst at a high concentration of the reactant in the initial mixture.

The use of oxide systems, in which lattice oxygen exhibits a high mobility and activity, may prove promising. The oxidative condensation of methane on such catalysts under the conditions of alternate reduction-oxidation would permit the attainment of the maximum possible volume concentrations of useful products.

Despite the complexity of the catalytic activation of methane, the advances achieved in this field, especially as regards the oxidative condensation of methane, permit one to hope that practical solution to the problem will be found in the near future. This will be assisted by broadening the research into the mechanism and kinetics of the catalytic oxidation of methane.

References

1. V A Legasov, A L Buchachenko *Uspekhi Khim.*, 1986, **61**(11) 1937 [*Russ. Chem. Rev.*, 1986(11)]
2. B N Kuznetsov *Izv. Sibir. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1987, (4) 117
3. S F Evanlov, N V Lavrov *Nauchnye Osnovy Kataliticheskoi Konversii Uglevodorov* (Scientific Principles of the Catalytic Conversion of Hydrocarbons), Izd. Naukova Dumka, Kiev, 1977, p. 210
4. R Z Magaril *Mekhanizm i Kinetika Gomogennykh Termicheskikh Prevrashchenii Uglevodorodov* (The Mechanisms and Kinetics of the Homogeneous Thermal Reactions of Hydrocarbons), Izd. Khimiya, Moscow, 1970
5. H D Gesser, N R Hunter, C B Prakash *Chem. Rev.*, 1985, **85** 235
6. Yu M Zhorov *Termodinamika Khimicheskikh Protsessov* (Thermodynamics of Chemical Processes), Izd. Khimiya, Moscow, 1985
7. J M Roscoe, M J Thompson *Int. J. Chem. Kinet.*, 1985, **17** 967
8. C-J Chen, M H Back, R A Back *Canad. J. Chem.*, 1975, **53** 3580
9. C-J Chen, M H Back, R A Back *Canad. J. Chem.*, 1976, **54** 3175
10. N M Emanuel' *Promezhutochnye Produkty Slozhnykh Gazovykh Reaktsii* (Intermediates in Complex Gas Reactions), Izd. Akad. Nauk SSSR, Moscow, 1946
11. A I Suleimanov, S M Aliev, V D Sokolovskii *React. Kinet. Catal. Lett.*, 1986, **31** 285
12. N N Semenov *O Nekotorykh Problemakh Khimicheskoi Kinetiki i Reaktsionnoi Sposobnosti* (Some Problems of Chemical Kinetics and Reactivity), Izd. Akad. Nauk SSSR, Moscow, 1958
13. L V Karmilova, N S Enikolopyan, A B Nalbandyan, N N Semenov *Zhur. Fiz Khim.*, 1960, **34**(6) 1176 [*Russ. J. Phys. Chem.*, 1960(6)]
14. I A Vardanyan, S Yan, A B Naldandyan *Kinetika i Kataliz*, 1981, **22** 845
15. V Ya Basevich, S M Kogarko *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, (12) 2658
16. A A Borisov, E V Dragalova, V M Zamanskii, et al. *Kinetika i Kataliz*, 1981, **22** 305
17. D J Huckal *Chemistry of Hydrocarbons Combustion*, Chapman and Hall, London–New York, 1985
18. A A Mantashyan, A B Nalbandyan *Zhur. Fiz. Khim.*, 1972, **46**(12) 3030 [*Russ. J. Phys. Chem.*, 1972(12)]
19. V N Kondrat'ev *Konstanty Skorosti Gazofaznykh Reaktsii* (The Rate Constants for Gas-phase Reactions), Izd. Nauka, Moscow, 1970
20. K Hoyerman, H G Wagner *Oxid. Comm.*, 1982, **2** 259
21. W B Demore, J J Magiton, M J Molina, et al *Int. J. Chem. Kinet.*, 1985, **17** 1135
22. W Tsang, R F Hampson *J. Phys. Chem., Ref. Data*, 1986, **15** 1086
23. V E Leonov, V E Limonov, A D Khaitun, I V Krupnik *Khim. Prom. za Rubezhom*, 1976, (5) 33
24. L F Marek, D A Gan *Kataliticheskoe Okislenie Organicheskikh Soedinenii* (Catalytic Oxidation of Organic Compounds), Izd. ONTI, Moscow, 1936
25. V A Roiter (Editor), Handbook *Kataliticheskie Svoistva Veshchestv* (Catalytic Properties of Substances), Izd. Naukova Dumka, Kiev, 1968
26. G K Boreskov, V A Sazonov, V V Popovskii *Dokl. Akad. Nauk SSSR*, 1967, 176
27. S S Shepelev, K G Ione *React. Kinet. Catal. Lett.*, 1983, **23** 323
28. Yu L Vysotskii, L E Semikina, Ya A Shuster, et al. *Kataliz i Katalizatory*, 1979, (17) 82
29. V E Leonov, L M Kalinichenko, Yu V Shulyakov, et al. *Kataliz i Katalizatory*, 1977, (15) 6
30. V A Borko, V I Gomonai, K Yu Sekeresh *Soobshch. po Kinetike i Katalizu*, 1980, **14** 439
31. B M Ershov, K Yu Sekeresh, I I Gusinka, M A Pueva *Izuchenie Protsessa Okisleniya Metana na Kislotno-Osnovnykh Katalizatorakh* (The Oxidations of Methane on Acid–Base Catalysts), Deposited at the ONIITEKhIM, Cherkassy, 1.12.82, No. 1273KhP-D82
32. USSR P. 958 407; *Byul. Izobret.*, 1982, (7)
33. V I Gomonai, D I Mel'nik, and K Yu Sekeresh *Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Mekhanizmu Kataliticheskikh Reaktsii* (Abstracts of Reports of the IVth All-Union Conference on the Mechanisms of Catalytic Reactions), Moscow, 1986, Part 2, p. 72
34. A Ya Averbukh, N Yu Pavlova *Geterogennye Kataliticheskie Protsessy* (Heterogeneous Catalytic Processes), Leningrad, 1979, p. 94
35. Yu A Ivanov, A Ya Averbukh, I P Mukhlenov, L I Musienko *Tezisy Dokladov IV Respublikanskoi Konferentsii po Okislitel'nomu Geterogennomu Katalizu* (Abstracts of Reports at the IVth Republican Conference on Oxidative Heterogeneous Catalysis), Baku, 1978, Part 2, p.56
36. USSR P. 366 178; *Byul. Izobret.*, 1973, (7)
37. R S Mann, M K Dosi *J. Chem. Techn. Biotechnol*, 1979, **29** 467
38. L A Nersesyan, Candidate's Thesis in Chemical Sciences, Institute of Chemical Physics, Academy of Sciences of the Armenian SSSR, Erevan, 1979
39. *Appl. Catal.*, **26** 408
40. M Iwamoto, S Kagawa, J H Lunsford *Shokubai (Catalyst)*, 1981, **23** 278
41. M Iwamoto *MOL*, 1982, 79
42. H-P Liu, R-S Liu, K J Liew, et al. *J. Amer. Chem. Soc.*, 1984, **106** 4117
43. R-S Liu, M Iwamoto, J H Lunsford *J. Chem. Soc., Chem. Comm.*, 1982, 78

44. K Aika, J H Lunsford *J. Phys. Chem.*, 1977, **84** 1393
45. M M Khan, G A Somorjai *J. Catal.*, 1985, **91** 263
46. M Inokawa, K Mori, A Miyamoto, Y Murakami, *J Phys. Chem.*, 1983, **87** 761
47. K J Zhen, M M Khan, S H Mak, et al. *J. Catal.*, 1985, **94** 501
48. F Solymosi, I Tombacz, G Kutsan *J. Chem. Soc., Chem. Comm.*, 1985, (20) 1455
49. T S Seiyama *Oxid. Comm.*, 1982, **2** 239
50. S S Shepelev, Abstract of Candidate's Thesis in Chemical Sciences, Institute of Kinetics [and Organic Synthesis], Siberian Division of the USSR Academy of Sciences, Novosibirsk, 1987
51. S S Shepelev, K G Ione *React. Kinet. Catal. Lett.*, 1983, **23** 319
52. US P. 4 205 194, 1980
53. G F Keller, M M Bhasin *J. Catal.*, 1982, **73** 9
54. US P. 4 554 395, 1985
55. US P. 4 544 786, 1985
56. US P. 4 547 608, 1985
57. US P. 4 547 607, 1985
58. US P. 4 547 611, 1985
59. B. P. 2 156 842, 1985
60. US P. 4 544 784, 1985
61. US P. 4 517 398, 1985
62. J A Sofranko, J J Leonard, C A Jones *J. Catal.*, 1987, **103** 302
63. C A Jones, J J Leonard, J A Sofranko *J. Catal.*, 1987, **103** 311
64. US P. 4 523 049, 1985
65. US P. 4 547 610, 1985
66. *Appl. Catal.*, 1986, **27** 410
67. I T Ali Emesh, Y Amenomiya *J. Phys. Chem.*, 1986, **90** 4785
68. W Hinsen, W Bytyn, M Baerns *Proceedings of VIIIth International Congress on Catalysis*, Verlag Chemie, West Berlin, 1984, Vol. III, p. 581
69. K Asami, S Hashimoto, T Shikada, et al. *Chem. Lett.*, 1986, 1233
70. K Asami, S Hashimoto, T Shikada, et al. *Ind. Eng. Chem. Res.*, 1986, **26** 1485
71. J A Roos, A G Bakker, H Bosch, et al. *Catalysis Today*, 1987, **1** 133
72. N P Kirik, A G Anshits, A S Ivanova *Khimicheskii Sintez na Osnove Odnouglerodnykh Molekul. Tezisy Dokladov Vsesoyusnogo Soveshchaniya* (Chemical Synthesis Based on One-carbon Molecules. Abstracts of Reports at an All-Union Conference), Izd. Nauka, Moscow, 1984, p. 75
73. T Ito, J H Lunsford *Nature (London)*, 1985, **314** 721
74. D J Driscoll, W. Martir, J-X Wang, J H Lunsford *J. Amer. Chem. Soc.*, 1985, **107** 48
75. D J Driscoll, W Martir, J-X Wang, J H Lunsford *Adsorption and Catalysis on Oxide Surfaces*, Amsterdam, 1985, p. 403
76. D J Driscoll, J H Lunsford *J. Phys. Chem.*, 1985, **89** 4415
77. T Ito, J-X Wang, C-X Lin, J H Lunsford *J. Amer. Chem. Soc.*, 1985, **107**
78. J-X Wang, J H Lunsford *J. Phys. Chem.*, 1986, **90** 5883
79. T Moriyama, N Takasaki, E Iwamatsu, K Aika *Chem. Lett.*, 1986, 1165
80. K Otsuka, K Jinno, A Morikawa *Chem. Lett.*, 1985, 499
81. K Otsuka, K Jinno, A Morikawa *J. Catal.*, 1986, **100** 353
82. K Otsuka, Q Liu, M Hatano, A Morikawa *Chem. Lett.*, 1986, 467
83. C-H Lin, K D Campbell, J-X Wang, J H Lunsford *J Phys. Chem.*, 1986, **90**
84. H Imai, T Tagawa *J Chem. Soc., Chem. Comm.*, 1986, (1) 52
85. H Imai, T Tagawa, N Kamide *Proceedings of VIIIth Japan–USSR Catalysis Seminar*, Tokyo, 1986, p. 139
86. K Otsuka, Q Liu, M Hatano, A Morikawa *Chem. Lett.*, 1986, 903
87. K Otsuka, Q Liu, A Morikawa *Inorg. Chim. Acta*, 1986, **118** L23
88. K Otsuka, M Hatano, Q Liu, A Morikawa *Proceedings of VIIIth Japan–USSR Catalysis Seminar*, Tokyo, 1986, p. 1
89. Kh M Minachev, N Ya Usachev, Yu S Khodakov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, (7) 1686
90. Kh M Minachev, N Ya Usachev, Yu S Khodakov, et al. *Izv. Akad Nauk SSSR, Ser. Khim.*, 1987, (3) 504
91. R Scholler, U Muller *Chem. Techn. (DDR)*, 1986, **38** 19
92. W Bytyn, M. Baerns *Appl. Catal.*, 1986, **28** 199
93. L A Nersesyan, I A Vardanyan, E N Kegeyan, et al. *Dokl. Akad. Nauk SSSR*, 1975., **220** 605
94. T Fang, C Yeh *J. Catal.*, 1981, **69** 227
95. M Yu Sinev, Candidate's Thesis in Chemical Sciences, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1987
96. A I Suleinmanov, S M Aliev, V D Sokolovskii *Okislitel'naya Degidromerizatsiya Metana v Vysshie Uglevodorody na Mg-soderzhashchikh Katalizatorakh* (Oxidative Dehydrodimerisation of Methane to Higher Hydrocarbons on Mg-containing Catalysts), Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 11.10.85, No. 7220-V85
97. M Yu Sinev *Tezisy Dokladov III Vsesoyuznoi Konferentsii Molodykh Uchenykh po Fizicheskoi Khimii* (Abstracts of Reports at the IIIrd All-Union Conference of Young Scientists of Physical Chemistry), Moscow, 1986, p. 121
98. M Yu Sinev, V N Korchak, O V Krylov *Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Meckanizmu Kataliticheskikh Reaktsii* (Abstracts of Reports at the IVth All-Union Conference on the Mechanisms of Catalytic Reactions), Moscow, 1986, Part 2, p. 27
99. S E Plate, A V Bobrov, A A Kadushin, Ya M Kimmel'fel'd *Kinetika i Kataliz*, 1986, **27** 495
100. E A Mamedov, V P Vislovskii, R G Rizaev *Kinetika i Kataliz*, 1986, **27**
101. V D Sokolovskii *React. Kinet. Catal. Lett.*, 1986, **32** 159
102. M Yu Sinev, P A Shiryaev, V N Korchak, O D Krylov *V Neftekhimicheskii Simpozium Sotsialisticheskikh Stran. Burgas (NRB)* [The Vth Petrochemical Symposium of Socialist Countries, Burgas, Bulgaria], 1986, p. 101
103. M Yu Sinev, V N Korchak, O V Krylov *Kinetika i Kataliz*, 1986, **27**
104. M Yu Sinev, V N Korchak, O V Krylov *Proceedings of the VIth International Symposium on Heterogeneous Catalysis*, Sofia, 1987, Part 1, p. 450
105. H Hattori *Adsorption and Catalysis on Oxide Surfaces* Amsterdam, 1985, p. 319
106. V I Vol'nov *Perekisnye Soedineniya Shchelochnozemel'nykh Metallov* (Peroxide Compounds of Alkaline Earth Metals), Izd. Nauka, Moscow, 1982
107. K Otsuka, M Hatano *J. Chem. Soc., Faraday Trans. I*, 1987, **83** 1315
108. M Yu Sinev, G A Vorob'eva, V N Korchak *Kinetika i Kataliz*, 1986, **27**
109. S L Kaliaguine, B N Shelimov, V B Kazansky *J. Catal.*, 1978, **55** 384

110. G N Kuz'min, M V Knatko, S V Kurganov *Tezisy Dokladov I Vsesoyuznoi Konferentsii po Kataliticheskomu Preobrazovaniyu Solnechnoi Energii* (Abstracts of Reports at the Ist All-Union Conference on the Catalytic Transformation of Solar Energy), Novosibirsk, 1983, p. 120
111. G E Kuzmin, M V Knatko, S V Kurganov *React. Kinet. Catal. Lett.*, 1983, **23**
112. V M Yurkin, Abstract of Candidate's Thesis in Physical-mathematical Sciences, Leningrad State University, Leningrad, 1985
113. S F Gerasimov, Abstract of Candidate's Thesis in Physical-mathematical Sciences, Leningrad State University, Leningrad, 1986
114. O D Kotova, Abstract of Candidate's Thesis in Physical-mathematical Sciences, Leningrad State University, Leningrad, 1986
115. V A Radtsig *Kinetika i Kataliz*, 1979, **20**, 450
116. A V Bystrikov, A N Streletskii, P Yu Butyagin *Kinetika i Kataliz*, 1980, **21** 1013
117. A A Bobyshev, V A Radtsig *Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Mechanizu Kataliticheskikh Reaktsii* (Abstracts of Reports at the IVth All-Union Conference on the Mechanisms of Catalytic Reactions), Moscow, 1986, Part 2, p. 425
118. A A Bobyshev, V A Radtsig *Khim. Fiz.*, 1986, **5** 517

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The role of the adsorbed forms of hydrogen and oxygen in the reaction of oxygen-containing one-carbon molecules on membrane catalysts

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ABSTRACT. The role of various adsorbed forms of hydrogen and oxygen in hydrogenation and oxidation reactions respectively on palladium alloy and silver membrane catalysts is examined. The possibility of altering the ratio of the concentrations of hydrogen and oxygen on the working surface and in the layer near the surface of the catalyst after the introduction of these substances into the reaction zone, either by means of diffusion through the bulk of the metal or as part of a mixture with oxygen-containing one-carbon molecules, is demonstrated. When the above ratio is altered, there is a change in the selectivity and activity of the corresponding catalysts.
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I. Introduction

The interaction of diatomic gases with the surface of a metal can be accompanied by their molecular adsorption, subsequent dissociation of the adsorbed molecules, and also surface diffusion of the adsorbed atoms and in certain cases their dissolution in the bulk of the metal. The last phenomenon is manifested most strikingly in the hydrogen–palladium and oxygen–silver systems. The high solubility and mobility of the hydrogen and oxygen atoms in palladium and silver respectively, combined with the catalytic activity of palladium in hydrogenation and dehydrogenation reactions and of silver in oxidation reactions, made it possible to create on the basis of these metals membrane catalysts which permit the introduction of one of the reactants into the reaction zone by diffusion through the metal.[1,2] Depending on the thickness of the membrane, the state of its entry and exit surfaces as regards the permeating gas, and the nature of the gases in contact with these surfaces, the rate of transfer of the gas through the metal may be limited[3] both by one of the stages indicated above and by the release of the diffuse species from the bulk of the metal onto the surface, surface diffusion, the recombination of atoms to molecules, and the desorption of the latter to the gas phase.

Thus, when a diatomic gas is introduced, it is possible to generate on the catalyst surface concentrations of adsorbed species which differ from the concentrations of the same species when hydrogen or oxygen are introduced in a mixture with substances to be hydrogenated or oxidised respectively.

The catalytic hydrogenation of carbon oxides is of interest in connection with the search for the possible replacement of the petroleum raw material, while the oxidation of methanol is an important industrial process requiring detailed investigation. When these reactions are carried out, the different ways of supplying hydrogen or oxygen to the catalyst surface can provide new information about the influence of the type of adsorbed forms on the catalytic reactions.

II. Diffusion of hydrogen through palladium membranes

For thick membranes at fairly high temperatures and hydrogen pressures, the rate-limiting stage is the diffusion of hydrogen through the bulk of the metal.[4] In the case of thin membranes at lower temperatures and low hydrogen pressures, the processes occurring at the gas–metal interface are rate-limiting.

The study of the interaction of hydrogen with the (110) and (111) faces of a palladium single crystal by the slow electron diffraction method[5] showed that the dissociative adsorption of hydrogen does not require an activation energy, while the presence of the hydrogen dissolved in palladium does not influence the structure of its adsorption layer. Moreover, it has been shown that the removal of the adsorbed hydrogen promotes its inflow to the surface from the bulk of the metal. On the other hand, the desorption of hydrogen at 368–413 K requires an activation energy of about 80 kJ mol^{-1} and takes place via the recombination of two adsorbed atoms, the adsorption centres being located in hollows between the surface palladium atoms.[6]

Data concerning the influence of the adsorbed hydrogen on the electronic work function[7–9] show that the sign of the charge on the adsorbed structures depends on the degree of surface coverage of palladium. At low coverages (up to 0.05), predominantly the negatively charged form $H^{\delta-}$ is formed, while with increasing coverage a layer of the positively charged form $H^{\delta+}$ is produced. The same result has been observed also on the exit surface of a palladium membrane in the diffusion of hydrogen. According to Cattania et al.,[10] the study of thermal desorption from the surface of palladium makes it possible to observe four different states of

hydrogen: two of these are the states of the surface chemisorbed forms and two others refer to hydrogen under the external layer of metal and are associated with the dissolution of hydrogen. According to Dus,[7] one of the surface forms of hydrogen, namely the positively charged form, can dissolve in palladium.

Thus one can postulate that the positively charged atomic form of hydrogen, which exists in the layer at the surface in a state subsequently designated by $H_b^{\delta+}$, participates in its transport through the palladium membrane. When thin palladium membranes are used, the transport process in the bulk of the metal can be fairly rapid, while the release from the surface layer onto the surface encounters certain difficulties. The concentration of the $H_b^{\delta+}$ species in the surface layer is then greater than under conditions where the exit surface of the membrane comes into contact with hydrogen at the same partial pressure in the absence of the diffusion flux. Probably, when the hydrogen pressure at the exit surface of the membrane is high and the degree of coverage of this surface by hydrogen is therefore considerable, the hydrogen is adsorbed mainly in the positively charged form which can be designated by $H_a^{\delta+}$.

III. The influence of the method of introduction of hydrogen into the reaction zone on the hydrogenation of carbon monoxide in the presence of palladium alloys

Since the permeation of hydrogen through thin membranes is limited by stages recurring at the gas–metal interface, the ratio of the concentrations of the hydrogen forms $H_a^{\delta+}$ and $H_b^{\delta+}$ depends on the composition of the membrane catalyst, the state of its surface, temperature, the partial pressures of the reactants, their adsorption capacities, and also on the method of introduction of the initial substances into the reaction zone. If hydrogen enters the reaction zone as a result of diffusion through the membrane catalyst, then the ratio $H_a^{\delta+}/H_b^{\delta+}$ is smaller than in the case where hydrogen is supplied to the working surface of the membrane catalyst in a mixture with the substance to be hydrogenated. This has been confirmed by data[11,12] obtained in a study of the hydrogenation of carbon oxides on a palladium alloy in membrane catalysts, where the method of supplying hydrogen to the working surface was varied.

The catalysts were foils and thin-walled tubes made of binary palladium alloys. In experiments with tubes when hydrogen was supplied to the reaction zone via diffusion, the inner surface of the tubes served as the entry side, while the substance to be hydrogenated was supplied to the outer side of the tube. In experiments on the hydrogenation of a mixture of the given substance with hydrogen, the gas having a specified composition passed to the outer surface of the tube while an inert gas was present inside the tube in a closed volume. The catalysts in the form of foil were placed in a stainless steel reactor and were fixed so that two identical chambers were formed. In order to carry out experiments under diffusion conditions, hydrogen was supplied to one of the chambers, while the substance to be hydrogenated was introduced into the other. The mixture was made to react in one of the chambers, while the other contained helium.

In the hydrogenation of carbon monoxide on binary palladium alloy membrane catalysts with 10 wt.% of ruthenium or with 6 wt.% of nickel[11] in the temperature range 523–683 K, methane, ethane, ethylene, water, and carbon dioxide were detected among the reaction products. The method of introduction of hydrogen into the reaction zone and the catalyst composition did not alter the nature of the products, but they did influence the rate of their formation (Tables 1 and 2).

Table 1. The rates of formation of hydrocarbons (10^3 mol h^{-1} m^{-2}) in the hydrogenation of CO on palladium–ruthenium and palladium–nickel alloys at different temperatures with hydrogen supplied to the reaction zone via diffusion through the catalyst (1) or in a mixture with CO (2).[11]

Alloy	T, K	CH_4		C_2H_6		C_2H_4	
		1	2	1	2	1	2
Pd—Ru	523	6.2	70.0	1.0	10.2	3.4	1.1
	583	7.5	80.4	2.3	10.1	6.2	1.4
	633	58.1	130.1	4.4	10.1	9.5	2.4
	683	83.4	310.4	3.4	30.5	7.6	2.7
Pd—Ni	523	2.6	2.4	1.4	0.6	0.8	0.2
	583	21.2	23.5	2.2	1.33	1.6	0.3
	633	49.7	41.1	3.8	2.9	3.4	0.4
	683	183.5	131.8	6.5	5.8	4.3	0.7

Table 2. The rates of formation of carbon dioxide (10^3 mol h^{-1} m^{-2}) on palladium–ruthenium and palladium–nickel alloys in the interaction of CO with hydrogen arriving in the reaction zone via diffusion through the catalyst (1) or in a mixture with CO (2) and also on contact of the working surface with CO alone (3).[11]

Alloy	T, K	1	2	3
Pd—Ru	523	29.4	65.1	98.2
	583	37.2	83.5	125.3
	633	48.6	125.2	263.9
	683	98.3	267.1	362.1
Pd—Ni	523	7.5	15.2	30.2
	583	21.2	27.6	37.1
	633	30.2	39.2	45.2
	683	42.0	47.1	53.1

The rate of formation of ethane and methane in the reaction of carbon monoxide with hydrogen diffusing through a palladium–ruthenium membrane catalyst was appreciably lower than in the hydrogenation of CO in a mixture with hydrogen (Table 1). Conversely, the rate of formation of ethylene when the reaction was carried out under diffusion conditions was much higher than in the hydrogenation of the mixture. It is quite likely that the $H_b^{\delta+}$ form present under the layer of surface atoms participates in the formation of the olefin, the amount of this form being greater when hydrogen is introduced into the reaction zone via diffusion through the membrane catalyst, while in the formation of alkanes the main role is assumed by hydrogen in the $H_a^{\delta+}$ form, the amount of which on the surface is greater in the hydrogenation of CO in a mixture with hydrogen. The fact that, regardless of the method of introduction of hydrogen into the reaction zone, the rate of formation of ethane is always lower than the rate of formation of methane evidently demonstrates that the addition of atomic hydrogen to the CH_3

radicals is faster than the dimerisation of the latter if it is assumed that CH_x radicals are formed via the hydrogenation of the surface carbon.

The differences between the hydrogen permeabilities of the palladium–ruthenium and palladium–nickel alloys[13] affect the concentrations of the adsorbed forms of hydrogen and their ratios. The activation energy for the permeation of hydrogen through a palladium–nickel alloy is greater than through a palladium–ruthenium alloy. This is apparently one of the main reasons why the rate of formation of methane when hydrogen is supplied via diffusion through a palladium–nickel alloy increases with increase in temperature to a greater extent than under analogous conditions on a palladium–ruthenium alloy (Table 1) and at 683 K exceeds the rate of formation of methane under the same conditions in the reaction of a mixture of CO and H_2.

The rates of formation of ethylene in the hydrogenation of carbon monoxide by diffusing hydrogen are higher on both catalysts over the entire experimental temperature range than in the case where a mixture of CO and H_2 is supplied. An analogous dependence of the rate of formation of ethane on the way in which the reaction is carried out on the palladium–nickel catalyst is probably due to the fact that the ethane is formed from ethylene via the hydrogenation of the latter.

Table 2 shows that the highest rates of formation of carbon dioxide were observed when carbon monoxide came into contact with palladium alloys in the absence of hydrogen. The latter suppressed the disproportionation of CO most effectively when it was introduced into the reaction zone via diffusion. The decrease in the rate of formation of carbon dioxide in the presence of hydrogen is apparently associated with the occurrence of a process in which the adsorbed oxygen species, formed on dissociation of CO, react with the hydrogen atoms to form water. The dependence of the rate of disproportionation of the way in which hydrogen is introduced into the contact zone also indicates a change in the ratio of the different adsorbed forms of hydrogen on the working surface. In all probability, adsorbed hydrogen atoms, localised in the surface layer of the alloy ($H_b^{\delta+}$), interact preferentially with the adsorbed atomic forms of oxygen.

The formation of carbon dioxide in the interaction of CO with palladium alloys in the absence of hydrogen indicates the dissociation of carbon monoxide. One can therefore postulate that hydrocarbons are formed from CO and H_2 on palladium alloys via the hydrogenation of the surface carbon formed on dissociation of carbon monoxide, which agrees with literature data.[14]. As shown above, the rate of formation of a particular hydrocarbon depends on the relative amounts of the different forms of hydrogen adsorbed on the working surface of the catalyst, which interact with the carbon monoxide dissociation products.

A study has been made to elucidate the role of the hydrogen entering the surface of the catalyst from its bulk phase.[15] A palladium–nickel foil was treated with hydrogen, after which its supply was stopped and CO was brought up to the working surface. Methane, ethane, ethylene, carbon dioxide, and water were found among the reaction products. As can be seen from Figure 1, a decrease in the rate of formation of methane and ethane begins immediately after the supply of carbon monoxide is begun, while the rate of formation of ethylene remains constant for almost 1.5 h and only then diminishes. This confirms the hypothesis that the $H_b^{\delta+}$ form of hydrogen participates in the formation of ethylene from carbon monoxide on the palladium–nickel catalyst. The decrease in the rate of formation of methane from the very beginning of the reaction indicates its involvement in the synthesis of the $H_a^{\delta+}$ form of hydrogen. The content of the latter on the surface diminishes rapidly after a time, since the $H_a^{\delta+}$ form is produced as a result of the transfer of the hydrogen dissolved in the metal onto the surface, which is in all probability the rate-limiting stage of the hydrogen transfer through a thin palladium–nickel membrane under the given conditions. The analogy in the character of the variation of the rates of formation of ethane and methane may be attributed to the fact that hydrogen adsorbed in the $H_a^{\delta+}$ form also participates in the formation of ethane from ethylene under the conditions investigated.

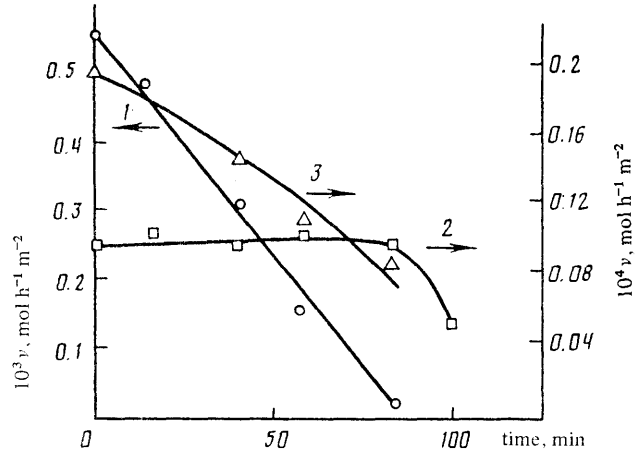


Figure 1. Time variation of the rates v of formation of methane (curve *1*), ethane (curve *2*), and ethylene (curve *3*) in the hydrogenation of carbon monoxide with hydrogen, dissolved beforehand in a palladium–nickel alloy, at 593 K.[15]

Table 3. Catalytic activity* of palladium–ruthenium and palladium–nickel alloys (10^3 mol h^{-1} m^{-2}) in the interaction of CO with hydrogen supplied to the reaction zone via diffusion through the catalyst (1) and in a mixture with CO (2).[11]

Alloy	T, K	1	2
Pd—Ru	523	73.1	222.8
	583	99.4	270.4
	633	182.9	406.4
	683	301.0	911.5
Pd—Ni	523	20.9	34.2
	583	70.9	80.6
	633	124.2	123.8
	683	288.7	238.7

*The activity was calculated from the sum of the rates of formation of the carbon-containing reaction products.

The overall catalytic activities of the binary palladium–ruthenium and palladium–nickel alloys (Table 3) can be calculated from the data presented in Tables 1 and 2. The overall activity of the palladium–nickel alloys depends only slightly on the way in which

hydrogen is introduced into the reaction zone, while the palladium–ruthenium catalyst is much more active in the hydrogenation of CO in a mixture with hydrogen than in its hydrogenation by the diffusing hydrogen, mainly as a result of the higher rate of formation of CO_2 and methane. In the reaction of a mixture of carbon monoxide and hydrogen, the activity of the palladium–nickel catalyst is much lower than that of the palladium–ruthenium alloy because of the lower rates of formation of carbon dioxide and methane in the presence of the former catalyst. When hydrogen is supplied into the reaction zone via diffusion, the activities of the palladium–nickel and palladium–ruthenium catalysts differ only slightly at 583–683 K.

The influence of the second component of the palladium alloy on its catalytic activity can be attributed both to a change in the concentrations of the different forms of adsorbed hydrogen and to the character of the adsorption of CO, which is indicated by data on the disproportionation of carbon monoxide in the absence of hydrogen (Table 2).

IV. Hydrogenation of carbon dioxide on membrane catalysts

The change in the ratio of the atomic forms of hydrogen on the working surface of the catalyst also affects the yield of the carbon dioxide hydrogenation products. It has been shown[16] that the maximum yield of methane when hydrogen is supplied via a palladium–ruthenium alloy membrane coated electrochemically by ruthenium is twice as high as in the hydrogenation of carbon dioxide in a mixture with hydrogen under the same conditions.

The state of the working surface of the catalyst and its chemical composition also influence the activity of the membrane catalyst. The study of the interaction of carbon dioxide with hydrogen which has diffused through a palladium–ruthenium alloy membrane catalyst showed that the activity of the latter is low in the hydrogenation of carbon dioxide to methane. The electrochemical deposition of a ruthenium layer[16] on the hydrogen exit surface of the palladium–ruthenium membrane catalyst increased sharply (by three orders of magnitude) the yield of the carbon dioxide hydrogenation products, among which ethane, carbon monoxide, and water were detected. Over the entire temperature range from 523 to 773 K, the rate of formation of methane increases with increase in the amount of hydrogen supplied through the membrane, which is consistent with literature data,[17] according to which the conversion of carbon dioxide into methane proceeds more vigorously on a ruthenium surface saturated beforehand with atomic hydrogen than on a clean ruthenium surface.

Thus the deposition of a layer of substance catalytically active in a specific reaction on a hydrogen-permeable membrane extends the possibilities of membrane catalysts. Nickel as well as ruthenium belongs to the group of the most active methane formation catalysts. The electrochemical deposition of a nickel layer 5×10^{-7} m thick on the exit surface of a palladium–ruthenium membrane catalyst[18] did not alter its permeability to hydrogen or the activation energy for the diffusion of hydrogen, which indicates a porous structure of the nickel layer and an insignificant influence of the latter on the transfer of hydrogen through the palladium–ruthenium alloy. During the hydrogenation of carbon dioxide with hydrogen, diffusing through such a catalyst, at 553 K and above, methane is formed, while an increase of temperature by a further 100 K leads to the appearance of carbon monoxide and small amounts of C_2–C_4 hydrocarbons. The rate of formation of methane in the hydrogenation of a mixture of carbon dioxide and hydrogen is always lower than the values obtained under the same conditions when hydrogen is supplied by diffusion.

The study of the temperature variation of the rate of formation of methane has shown[18] that the experimental activation energy for the reaction changes at 578 K, which may be due to a transition from the ferromagnetic to the paramagnetic state of the Ni–Pd–Ru layers formed near the nickel grains on the palladium–ruthenium foil as a consequence of the diffusion of the metal atoms. The change in activation energy may be associated with a magnetic transformation in pure nickel. Thus the presence of a thin layer of disperse nickel leads to magnetocatalytic effects without affecting the permeability of the palladium–ruthenium alloy to hydrogen.

The deposition of a lanthanum-containing nickel coating on the hydrogen exit surface of a palladium–ruthenium membrane catalyst[19] increased the rate of hydrogenation of carbon dioxide to methane compared with the rate of formation of methane on the same catalyst without the modifying element. However, the rate of reaction in the presence of lanthanum increased only in the temperature range from 573 to 663 K. Further increase of temperature resulted in a sharp fall of the rate of formation of methane, probably as a consequence of the formation of the catalytically inert lanthanum carbonate. The high stability of the latter precludes the regeneration of the catalyst.

As a result of the electrochemical deposition of a rhodium coating on a palladium–ruthenium membrane catalyst,[20] methane did not begin to form until 688 K, and although its content in the reaction products did increase with increase in temperature, it was appreciably (almost by a factor of four) smaller than the amount of carbon monoxide formed, traces of which were observed already at 473 K. An increase in the partial pressure of hydrogen at the hydrogen exit surface of the membrane catalyst from 200 to 725 mmHg increased somewhat the yield of methane and did not affect the yield of carbon monoxide. The formation of hydrocarbons with higher molecular weights was not observed.

Thus the method of introduction of hydrogen into the reaction zone as well as the deposition of dispersed layers of active metals on the hydrogen exit surface of the membrane catalyst influence the ratio of the concentrations of different forms of adsorbed hydrogen, which alters the selectivity and activity in the carbon dioxide hydrogenation process.

V. The role of adsorbed oxygen in the oxidation of methanol

Silver foil, which makes it possible to introduce oxygen into the reaction zone via diffusion through the metal, may be used as a membrane oxidation catalyst. The process involving oxygen transfer through silver membranes may include the same series of stages as the adsorption of oxygen on silver, in the forward and reverse sequences.[21] The adsorption of oxygen on silver in the temperature range from 453 to 623 K is known[22] to proceed in accordance with the scheme

$$O_{2\,gas} \rightarrow O_{2\,ads}^{-} \rightarrow 2O_{ads}^{-} \rightarrow 2O_{lat}^{2-}.$$

However, the rate-limiting stage in the transfer of oxygen through silver may not be the same as in the adsorption of oxygen from the gas phase.

The study of the permeability of silver tubes with walls 10^{-4} m thick to oxygen showed[23] that it is proportional to the square root of the oxygen pressure at the oxygen entry surface of the tube. This indicates the involvement of oxygen atoms in the rate-limiting stage of the transfer of oxygen through silver. The electrochemical deposition of a layer of silver on the oxygen exit surface of a silver membrane increases its permeability to oxygen by more than an order of magnitude,[24] but the linear dependence of this parameter on the square root of the oxygen pressure at the entry surface of the membrane is retained. All these factors show that the rate-limiting stage in the transfer of oxygen through thin silver membranes is the process occurring on the oxygen exit surface in which oxygen atoms participate.

The states of the oxygen, arriving via diffusion through membranes or as a result of adsorption from the gas phase, on the exit surface of the membrane have been investigated mass-spectrometrically[25] using a modernised ion source. In the immediate vicinity of the mass spectrometer ion source, a silver tube with walls 10^{-4} m thick was placed and the composition of the gas phase in contact with its outer surface was investigated. Furthermore, an additional cathode and potential-carrying grids were introduced into the ion source, which made it possible to investigate the species adsorbed on the outer surface of the silver tube by the method of the electron-stimulated desorption of ions (ESDI). Two peaks can be observed in the mass spectrum of gaseous oxygen: the molecular (O_2^+) peak with a mass number of 32 and a fragment (O^+) peak with a mass number of 16. The ratio of the intensities of these two peaks (I_{32}/I_{16}) was found to be close to 20 by the usual gas analysis. As can be seen from Table 4, approximately this value has been recorded when oxygen was admitted directly onto the outer surface of the silver membrane in the ionisation chamber. A similar value was also obtained when oxygen was supplied by diffusion through a silver tube at 665 K. However, in this case the decrease in the temperature of the membrane was accompanied by a decrease in the I_{32}/I_{16} ratio, which indicates the appearance in the gas phase of an additional source of oxygen atoms. These may be the atoms desorbed from the surface. The proximity of the membrane to the ionisation region makes it possible to record them. An analogous effect has been observed in a study by the ESDI method, which is probably associated with the enrichment of the exit surface of the silver membrane during the diffusion of oxygen through it in adsorbed forms, which on electron bombardment of the surface are capable of being desorbed to the gas phase in the form of the positively charged O^+ ions.

Since the entire oxygen which has diffused through the silver membrane passes to the ionisation chamber, the intensities of the molecular (O_2^+) and fragment (O^+) oxygen peaks are proportional to the permeability of the given silver membrane to oxygen under stationary conditions.

The activation energy calculated from the temperature variation of the intensity of the peak with a mass number of 32 exceeds the corresponding value found by measuring the height of the peak, with a mass number of 16, the same effect being observed for both methods of analysis. Presumably, in the diffusion of oxygen into a vacuum through a thin silver membrane, its exit surface is enriched in atoms capable of being desorbed into the gas phase on electron impact, the number of such species increasing with decrease in temperature. Furthermore, at low temperatures the surface diffusion process as a result of which the lattice oxygen passes to the adsorbed state, preceding the recombination stage, is hindered and the release of atoms into the gas phase becomes possible which, as already stated above, is the cause of the decrease in the ratio I_{32}/I_{16} (Table 4) and also of the lower activation energy calculated from the variation of the intensity of the peak with a mass number of 16.

Table 4. The ratios of the intensities of the mass spectrometric peaks with mass numbers 32 and 16 (I_{32}/I_{16}) for different methods of supplying oxygen to the exit surface of a silver membrane and at different temperatures.[25]

Method of introduction of oxygen	Analytical method	T, K						
		525	548	570	591	613	634	665
Diffusion through silver	analysis of gas phase	2	3	7	11	14	—	18
Direct injection	ditto	19	—	—	16	16	18	18
Diffusion through silver	ESDI	0.01	0.02	0.03	0.04	0.06	0.09	0.1
Direct injection	ditto	0.66	0.62	0.57	0.54	0.49	0.47	0.47

Methanol was oxidised[21] on the outer surface of a silver tube with walls 1×10^{-4} m thick. When a mixture of methanol and oxygen was supplied to the outer surface, the inner part of the tube was evacuated.

The permeability of silver to oxygen under the conditions of the oxidation of methanol by diffusing oxygen exceeded its permeability to oxygen in the diffusion of the latter into a vacuum under the same conditions to a greater extent the lower was the experimental temperature. In the interaction of methanol vapour with diffusing oxygen on the exit surface of the silver membrane catalyst, oxygen did not appear in the gas phase until 619 K. On further increase in temperature, its amount also rose and the permeability of the silver membrane catalyst to oxygen diminished, approaching the value obtained for the diffusion of oxygen into a vacuum. The activation energy for the transfer of oxygen through a silver membrane catalyst during the oxidation of methanol is smaller by 25 kJ g-atom^{-1} than in the diffusion of oxygen into a vaccum. This is in fact the difference between the activation energies calculated from the intensities of the O_2^+ and O^+ peaks in the analysis of the gas phase near the exit surface of the silver membrane.[25] The decrease in the activation energy for the transfer of oxygen through silver under methanol oxidation conditions can be due to the interaction of the substances being oxidised on the exit surface of the silver with oxygen species which participate in the stage preceding the rate-limiting stage of the transfer of oxygen to a vacuum. According to the scheme presented above, this form may be the lattice oxygen O_{lat}^{2-}.

The supply of oxygen by diffusion through a silver membrane catalyst evidently creates on the working surface, at temperatures below 619 K, a higher concentration of this form than in the adsorption of oxygen from the gas phase. Thus, in the oxidation of methanol by diffusing oxygen, the yield of formaldehyde at 619 K reached 85%, while in the case where a mixture of methanol with oxygen was used under the same conditions, the maximum yield of formaldehyde was 23 %. Apart from formaldehyde, carbon monoxide and dioxide as well as water were formed in the reaction.

The amount of carbon monoxide formed per unit time was independent of temperature, while the rate of formation of carbon dioxide increased on heating. However, the yield of carbon dioxide did not exceed 22% even at the highest experimental temperature (673 K).

Thus the ratio of different forms of oxygen on the silver surface depends on the method of supplying oxygen through the surface of the membrane catalyst and this affects the process selectivity, since oxygen species dissolved in the surface layer of the metal participate in all probability in the formation of formaldehyde from methanol on silver.

References

1. V M Gryaznov, V S Smirnov *Uspekhi Khim.*, 1974, **43** 1716 [*Russ. Chem. Rev.*, 1974(10)]
2. V M Gryaznov, V I Vedernikov, S G Gul'yanova *Kinetika i Kataliz*, 1986, **27** 142
3. R M Barrer *Diffusion in and through Solids* (Translated into Russian), Moscow, 1948, 504 pp
4. V A Gol'tsov *Voprosy Atomnoi Nauki i Tekhniki. Ser. Atomno-Vodorodnaya Energetika* (Problems of Atomic Science and Engineering. The Atomic-Hydrogen Power Engineering Series), Atomizdat, Moscow, 1977, No.1(2), p. 65
5. H Conrad, G Ertl, E E Latta *Surface Sci.*, 1974, **41** 435
6. H Alefeld et al. (Editors) *Hydrogen in Metals* (Translated into Russian), Izd. Mir, Moscow, 1981, Vol. 2, p.103
7. R Dus *Surface Sci.*, 1973, **42** 324
8. Yu A Zubarev, O K Samuilova, V D Yagodovskii *Metally i Splavy kak Membrannye Katalizatory* (Metals and Alloys as Membrane Catalysts), Izd. Nauka, Moscow, 1981, p. 139
9. Yu A Zubarev, N N Mikhalenko, V D Yagodovskii *Kinetika i Kataliz*, 1988, **24** 194
10. M G Cattania, V Penka, R T Behm, et al. *Surface Sci.*, 1983, **126** 382
11. Yu M Serov, S G Gul'yanova, O S Gur'yanova *Membrannye Katalizatory Pronitsaemye dlya Vodoroda i Kisloroda* (Membrane Catalysts Permeable to Hydrogen and Oxygen), Izd. Nauka, Moscow, 1985, p. 129
12. Yu M Serov, Candidate's Thesis in Chemical Sciences, Patrice Lumumba University of Friendship Among Nations, Moscow, 1981
13. A P Mishchenko *Metally i Splavy kak Membrannye Katalizatory* (Metals and Alloys as Membrane Catalysts), Izd. Nauka, Moscow, 1981, p. 56
14. A T Bell *Catal. Rev. Sci. Eng.*, 1981, **23** 203
15. Yu M Serov, O S Gur'yanova, S G Gul'yanova, V M Gryaznov, *Zhur. Fiz. Khim.*, 1986, **60**, 206 [*Russ. J. Phys. Chem.*, 1986(1)]
16. V M Gryaznov, Yu M Serov, S G Gul'yanova, M V Palishkin, *Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol*, 1980, **23** 593
17. C A Luengo, A L Cabrera, H B MacKay, M B Maple *J. Catal.*, 1977, **47** 1
18. V M Gryaznov, S G Gul'yanova, Yu M Serov, V D Yagodovskii *Zhur. Fiz. Khim.*, 1981, **55** 1306 [*Russ. J. Phys. Chem.*, 1981(5)]
19. Yu M Serov, S G Gul'yanova, V M Gryaznov *Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol.*, 1983, **26** 882
20. Yu M Serov, S G Gul'yanova, V M Gryaznov *Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol.*, 1983, **26** 1140
21. V M Gryaznov, V I Vedernikov, S G Gul'yanova *Kinetika i Kataliz*, 1986, **27** 142
22. L Ya Margolis *Okislenie Uglevodorodov na Geterogennykh Katalizatorakh* (Oxidation of Hydrocarbons on Heterogeneous Catalysts), Izd. Khimiya, Moscow, 1972, 327 pp
23. V M Gryaznov, S G Gul'yanova, S Kanizius *Zhur. Fiz. Khim.*, 1973, **47** 2694 [*Russ. J. Phys. Chem.*, 1973(10)]
24. S G Gul'yanova, V M Vedernikov, V M Gryaznov *Zhur. Fiz. Khim.*, 1977, **51** 179 [*Russ. J. Phys. Chem.*, 1977(1)]
25. V M Gryaznov, S G Gul'yanova, E N Kolosov, N I Starkovskii *Dokl. Akad. Nauk SSSR*, 1987, **293** 872
26. V I Vedernikov, S G Gul'yanova *Membrannye Katlaizatory Pronitsaemye dlya Vodoroda i Kisloroda* (Membrane Catalysts Permeable to Hydrogen and Oxygen), Izd. Nauka, Moscow, 1985, p. 165

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The role of the adsorbed forms of hydrogen and oxygen in the reaction of oxygen-containing one-carbon molecules on membrane catalysts

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ABSTRACT. The role of various adsorbed forms of hydrogen and oxygen in hydrogenation and oxidation reactions respectively on palladium alloy and silver membrane catalysts is examined. The possibility of altering the ratio of the concentrations of hydrogen and oxygen on the working surface and in the layer near the surface of the catalyst after the introduction of these substances into the reaction zone, either by means of diffusion through the bulk of the metal or as part of a mixture with oxygen-containing one-carbon molecules, is demonstrated. When the above ratio is altered, there is a change in the selectivity and activity of the corresponding catalysts.
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I. Introduction

The interaction of diatomic gases with the surface of a metal can be accompanied by their molecular adsorption, subsequent dissociation of the adsorbed molecules, and also surface diffusion of the adsorbed atoms and in certain cases their dissolution in the bulk of the metal. The last phenomenon is manifested most strikingly in the hydrogen–palladium and oxygen–silver systems. The high solubility and mobility of the hydrogen and oxygen atoms in palladium and silver respectively, combined with the catalytic activity of palladium in hydrogenation and dehydrogenation reactions and of silver in oxidation reactions, made it possible to create on the basis of these metals membrane catalysts which permit the introduction of one of the reactants into the reaction zone by diffusion through the metal.[1,2] Depending on the thickness of the membrane, the state of its entry and exit surfaces as regards the permeating gas, and the nature of the gases in contact with these surfaces, the rate of transfer of the gas through the metal may be limited[3] both by one of the stages indicated above and by the release of the diffuse species from the bulk of the metal onto the surface, surface diffusion, the recombination of atoms to molecules, and the desorption of the latter to the gas phase.

Thus, when a diatomic gas is introduced, it is possible to generate on the catalyst surface concentrations of adsorbed species which differ from the concentrations of the same species when hydrogen or oxygen are introduced in a mixture with substances to be hydrogenated or oxidised respectively.

The catalytic hydrogenation of carbon oxides is of interest in connection with the search for the possible replacement of the petroleum raw material, while the oxidation of methanol is an important industrial process requiring detailed investigation. When these reactions are carried out, the different ways of supplying hydrogen or oxygen to the catalyst surface can provide new information about the influence of the type of adsorbed forms on the catalytic reactions.

II. Diffusion of hydrogen through palladium membranes

For thick membranes at fairly high temperatures and hydrogen pressures, the rate-limiting stage is the diffusion of hydrogen through the bulk of the metal.[4] In the case of thin membranes at lower temperatures and low hydrogen pressures, the processes occurring at the gas–metal interface are rate-limiting.

The study of the interaction of hydrogen with the (110) and (111) faces of a palladium single crystal by the slow electron diffraction method[5] showed that the dissociative adsorption of hydrogen does not require an activation energy, while the presence of the hydrogen dissolved in palladium does not influence the structure of its adsorption layer. Moreover, it has been shown that the removal of the adsorbed hydrogen promotes its inflow to the surface from the bulk of the metal. On the other hand, the desorption of hydrogen at 368–413 K requires an activation energy of about 80 kJ mol^{-1} and takes place via the recombination of two adsorbed atoms, the adsorption centres being located in hollows between the surface palladium atoms.[6]

Data concerning the influence of the adsorbed hydrogen on the electronic work function[7–9] show that the sign of the charge on the adsorbed structures depends on the degree of surface coverage of palladium. At low coverages (up to 0.05), predominantly the negatively charged form $H^{\delta-}$ is formed, while with increasing coverage a layer of the positively charged form $H^{\delta+}$ is produced. The same result has been observed also on the exit surface of a palladium membrane in the diffusion of hydrogen. According to Cattania et al.,[10] the study of thermal desorption from the surface of palladium makes it possible to observe four different states of

hydrogen: two of these are the states of the surface chemisorbed forms and two others refer to hydrogen under the external layer of metal and are associated with the dissolution of hydrogen. According to Dus,[7] one of the surface forms of hydrogen, namely the positively charged form, can dissolve in palladium.

Thus one can postulate that the positively charged atomic form of hydrogen, which exists in the layer at the surface in a state subsequently designated by $H_b^{\delta+}$, participates in its transport through the palladium membrane. When thin palladium membranes are used, the transport process in the bulk of the metal can be fairly rapid, while the release from the surface layer onto the surface encounters certain difficulties. The concentration of the $H_b^{\delta+}$ species in the surface layer is then greater than under conditions where the exit surface of the membrane comes into contact with hydrogen at the same partial pressure in the absence of the diffusion flux. Probably, when the hydrogen pressure at the exit surface of the membrane is high and the degree of coverage of this surface by hydrogen is therefore considerable, the hydrogen is adsorbed mainly in the positively charged form which can be designated by $H_a^{\delta+}$.

III. The influence of the method of introduction of hydrogen into the reaction zone on the hydrogenation of carbon monoxide in the presence of palladium alloys

Since the permeation of hydrogen through thin membranes is limited by stages recurring at the gas–metal interface, the ratio of the concentrations of the hydrogen forms $H_a^{\delta+}$ and $H_b^{\delta+}$ depends on the composition of the membrane catalyst, the state of its surface, temperature, the partial pressures of the reactants, their adsorption capacities, and also on the method of introduction of the initial substances into the reaction zone. If hydrogen enters the reaction zone as a result of diffusion through the membrane catalyst, then the ratio $H_a^{\delta+}/H_b^{\delta+}$ is smaller than in the case where hydrogen is supplied to the working surface of the membrane catalyst in a mixture with the substance to be hydrogenated. This has been confirmed by data[11,12] obtained in a study of the hydrogenation of carbon oxides on a palladium alloy in membrane catalysts, where the method of supplying hydrogen to the working surface was varied.

The catalysts were foils and thin-walled tubes made of binary palladium alloys. In experiments with tubes when hydrogen was supplied to the reaction zone via diffusion, the inner surface of the tubes served as the entry side, while the substance to be hydrogenated was supplied to the outer side of the tube. In experiments on the hydrogenation of a mixture of the given substance with hydrogen, the gas having a specified composition passed to the outer surface of the tube while an inert gas was present inside the tube in a closed volume. The catalysts in the form of foil were placed in a stainless steel reactor and were fixed so that two identical chambers were formed. In order to carry out experiments under diffusion conditions, hydrogen was supplied to one of the chambers, while the substance to be hydrogenated was introduced into the other. The mixture was made to react in one of the chambers, while the other contained helium.

In the hydrogenation of carbon monoxide on binary palladium alloy membrane catalysts with 10 wt.% of ruthenium or with 6 wt.% of nickel[11] in the temperature range 523–683 K, methane, ethane, ethylene, water, and carbon dioxide were detected among the reaction products. The method of introduction of hydrogen into the reaction zone and the catalyst composition did not alter the nature of the products, but they did influence the rate of their formation (Tables 1 and 2).

Table 1. The rates of formation of hydrocarbons (10^3 mol h^{-1} m^{-2}) in the hydrogenation of CO on palladium–ruthenium and palladium–nickel alloys at different temperatures with hydrogen supplied to the reaction zone via diffusion through the catalyst (1) or in a mixture with CO (2).[11]

Alloy	T, K	CH_4		C_2H_6		C_2H_4	
		1	2	1	2	1	2
Pd—Ru	523	6.2	70.0	1.0	10.2	3.4	1.1
	583	7.5	80.4	2.3	10.1	6.2	1.4
	633	58.1	130.1	4.4	10.1	9.5	2.4
	683	83.4	310.4	3.4	30.5	7.6	2.7
Pd—Ni	523	2.6	2.4	1.4	0.6	0.8	0.2
	583	21.2	23.5	2.2	1.33	1.6	0.3
	633	49.7	41.1	3.8	2.9	3.4	0.4
	683	183.5	131.8	6.5	5.8	4.3	0.7

Table 2. The rates of formation of carbon dioxide (10^3 mol h^{-1} m^{-2}) on palladium–ruthenium and palladium–nickel alloys in the interaction of CO with hydrogen arriving in the reaction zone via diffusion through the catalyst (1) or in a mixture with CO (2) and also on contact of the working surface with CO alone (3).[11]

Alloy	T, K	1	2	3
Pd—Ru	523	29.4	65.1	98.2
	583	37.2	83.5	125.3
	633	48.6	125.2	263.9
	683	98.3	267.1	362.1
Pd—Ni	523	7.5	15.2	30.2
	583	21.2	27.6	37.1
	633	30.2	39.2	45.2
	683	42.0	47.1	53.1

The rate of formation of ethane and methane in the reaction of carbon monoxide with hydrogen diffusing through a palladium–ruthenium membrane catalyst was appreciably lower than in the hydrogenation of CO in a mixture with hydrogen (Table 1). Conversely, the rate of formation of ethylene when the reaction was carried out under diffusion conditions was much higher than in the hydrogenation of the mixture. It is quite likely that the $H_b^{\delta+}$ form present under the layer of surface atoms participates in the formation of the olefin, the amount of this form being greater when hydrogen is introduced into the reaction zone via diffusion through the membrane catalyst, while in the formation of alkanes the main role is assumed by hydrogen in the $H_a^{\delta+}$ form, the amount of which on the surface is greater in the hydrogenation of CO in a mixture with hydrogen. The fact that, regardless of the method of introduction of hydrogen into the reaction zone, the rate of formation of ethane is always lower than the rate of formation of methane evidently demonstrates that the addition of atomic hydrogen to the CH_3

radicals is faster than the dimerisation of the latter if it is assumed that CH_x radicals are formed via the hydrogenation of the surface carbon.

The differences between the hydrogen permeabilities of the palladium–ruthenium and palladium–nickel alloys[13] affect the concentrations of the adsorbed forms of hydrogen and their ratios. The activation energy for the permeation of hydrogen through a palladium–nickel alloy is greater than through a palladium–ruthenium alloy. This is apparently one of the main reasons why the rate of formation of methane when hydrogen is supplied via diffusion through a palladium–nickel alloy increases with increase in temperature to a greater extent than under analogous conditions on a palladium–ruthenium alloy (Table 1) and at 683 K exceeds the rate of formation of methane under the same conditions in the reaction of a mixture of CO and H_2.

The rates of formation of ethylene in the hydrogenation of carbon monoxide by diffusing hydrogen are higher on both catalysts over the entire experimental temperature range than in the case where a mixture of CO and H_2 is supplied. An analogous dependence of the rate of formation of ethane on the way in which the reaction is carried out on the palladium–nickel catalyst is probably due to the fact that the ethane is formed from ethylene via the hydrogenation of the latter.

Table 2 shows that the highest rates of formation of carbon dioxide were observed when carbon monoxide came into contact with palladium alloys in the absence of hydrogen. The latter suppressed the disproportionation of CO most effectively when it was introduced into the reaction zone via diffusion. The decrease in the rate of formation of carbon dioxide in the presence of hydrogen is apparently associated with the occurrence of a process in which the adsorbed oxygen species, formed on dissociation of CO, react with the hydrogen atoms to form water. The dependence of the rate of disproportionation of the way in which hydrogen is introduced into the contact zone also indicates a change in the ratio of the different adsorbed forms of hydrogen on the working surface. In all probability, adsorbed hydrogen atoms, localised in the surface layer of the alloy ($H_b^{\delta+}$), interact preferentially with the adsorbed atomic forms of oxygen.

The formation of carbon dioxide in the interaction of CO with palladium alloys in the absence of hydrogen indicates the dissociation of carbon monoxide. One can therefore postulate that hydrocarbons are formed from CO and H_2 on palladium alloys via the hydrogenation of the surface carbon formed on dissociation of carbon monoxide, which agrees with literature data.[14]. As shown above, the rate of formation of a particular hydrocarbon depends on the relative amounts of the different forms of hydrogen adsorbed on the working surface of the catalyst, which interact with the carbon monoxide dissociation products.

A study has been made to elucidate the role of the hydrogen entering the surface of the catalyst from its bulk phase.[15] A palladium–nickel foil was treated with hydrogen, after which its supply was stopped and CO was brought up to the working surface. Methane, ethane, ethylene, carbon dioxide, and water were found among the reaction products. As can be seen from Figure 1, a decrease in the rate of formation of methane and ethane begins immediately after the supply of carbon monoxide is begun, while the rate of formation of ethylene remains constant for almost 1.5 h and only then diminishes. This confirms the hypothesis that the $H_b^{\delta+}$ form of hydrogen participates in the formation of ethylene from carbon monoxide on the palladium–nickel catalyst. The decrease in the rate of formation of methane from the very beginning of the reaction indicates its involvement in the synthesis of the $H_a^{\delta+}$ form of hydrogen. The content of the latter on the surface diminishes rapidly after a time, since the $H_a^{\delta+}$ form is produced as a result of the transfer of the hydrogen dissolved in the metal onto the surface, which is in all probability the rate-limiting stage of the hydrogen transfer through a thin palladium–nickel membrane under the given conditions. The analogy in the character of the variation of the rates of formation of ethane and methane may be attributed to the fact that hydrogen adsorbed in the $H_a^{\delta+}$ form also participates in the formation of ethane from ethylene under the conditions investigated.

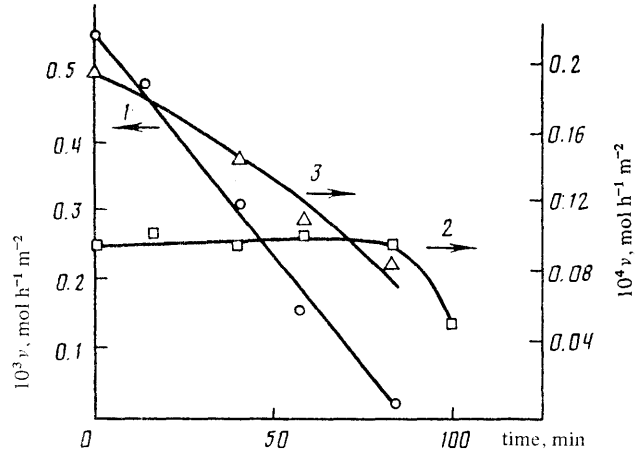


Figure 1. Time variation of the rates v of formation of methane (curve *1*), ethane (curve *2*), and ethylene (curve *3*) in the hydrogenation of carbon monoxide with hydrogen, dissolved beforehand in a palladium–nickel alloy, at 593 K.[15]

Table 3. Catalytic activity* of palladium–ruthenium and palladium–nickel alloys (10^3 mol h^{-1} m^{-2}) in the interaction of CO with hydrogen supplied to the reaction zone via diffusion through the catalyst (1) and in a mixture with CO (2).[11]

Alloy	T, K	1	2
Pd—Ru	523	73.1	222.8
	583	99.4	270.4
	633	182.9	406.4
	683	301.0	911.5
Pd—Ni	523	20.9	34.2
	583	70.9	80.6
	633	124.2	123.8
	683	288.7	238.7

*The activity was calculated from the sum of the rates of formation of the carbon-containing reaction products.

The overall catalytic activities of the binary palladium–ruthenium and palladium–nickel alloys (Table 3) can be calculated from the data presented in Tables 1 and 2. The overall activity of the palladium–nickel alloys depends only slightly on the way in which

hydrogen is introduced into the reaction zone, while the palladium–ruthenium catalyst is much more active in the hydrogenation of CO in a mixture with hydrogen than in its hydrogenation by the diffusing hydrogen, mainly as a result of the higher rate of formation of CO_2 and methane. In the reaction of a mixture of carbon monoxide and hydrogen, the activity of the palladium–nickel catalyst is much lower than that of the palladium–ruthenium alloy because of the lower rates of formation of carbon dioxide and methane in the presence of the former catalyst. When hydrogen is supplied into the reaction zone via diffusion, the activities of the palladium–nickel and palladium–ruthenium catalysts differ only slightly at 583–683 K.

The influence of the second component of the palladium alloy on its catalytic activity can be attributed both to a change in the concentrations of the different forms of adsorbed hydrogen and to the character of the adsorption of CO, which is indicated by data on the disproportionation of carbon monoxide in the absence of hydrogen (Table 2).

IV. Hydrogenation of carbon dioxide on membrane catalysts

The change in the ratio of the atomic forms of hydrogen on the working surface of the catalyst also affects the yield of the carbon dioxide hydrogenation products. It has been shown[16] that the maximum yield of methane when hydrogen is supplied via a palladium–ruthenium alloy membrane coated electrochemically by ruthenium is twice as high as in the hydrogenation of carbon dioxide in a mixture with hydrogen under the same conditions.

The state of the working surface of the catalyst and its chemical composition also influence the activity of the membrane catalyst. The study of the interaction of carbon dioxide with hydrogen which has diffused through a palladium–ruthenium alloy membrane catalyst showed that the activity of the latter is low in the hydrogenation of carbon dioxide to methane. The electrochemical deposition of a ruthenium layer[16] on the hydrogen exit surface of the palladium–ruthenium membrane catalyst increased sharply (by three orders of magnitude) the yield of the carbon dioxide hydrogenation products, among which ethane, carbon monoxide, and water were detected. Over the entire temperature range from 523 to 773 K, the rate of formation of methane increases with increase in the amount of hydrogen supplied through the membrane, which is consistent with literature data,[17] according to which the conversion of carbon dioxide into methane proceeds more vigorously on a ruthenium surface saturated beforehand with atomic hydrogen than on a clean ruthenium surface.

Thus the deposition of a layer of substance catalytically active in a specific reaction on a hydrogen-permeable membrane extends the possibilities of membrane catalysts. Nickel as well as ruthenium belongs to the group of the most active methane formation catalysts. The electrochemical deposition of a nickel layer 5×10^{-7} m thick on the exit surface of a palladium–ruthenium membrane catalyst[18] did not alter its permeability to hydrogen or the activation energy for the diffusion of hydrogen, which indicates a porous structure of the nickel layer and an insignificant influence of the latter on the transfer of hydrogen through the palladium–ruthenium alloy. During the hydrogenation of carbon dioxide with hydrogen, diffusing through such a catalyst, at 553 K and above, methane is formed, while an increase of temperature by a further 100 K leads to the appearance of carbon monoxide and small amounts of C_2–C_4 hydrocarbons. The rate of formation of methane in the hydrogenation of a mixture of carbon dioxide and hydrogen is always lower than the values obtained under the same conditions when hydrogen is supplied by diffusion.

The study of the temperature variation of the rate of formation of methane has shown[18] that the experimental activation energy for the reaction changes at 578 K, which may be due to a transition from the ferromagnetic to the paramagnetic state of the Ni–Pd–Ru layers formed near the nickel grains on the palladium–ruthenium foil as a consequence of the diffusion of the metal atoms. The change in activation energy may be associated with a magnetic transformation in pure nickel. Thus the presence of a thin layer of disperse nickel leads to magnetocatalytic effects without affecting the permeability of the palladium–ruthenium alloy to hydrogen.

The deposition of a lanthanum-containing nickel coating on the hydrogen exit surface of a palladium–ruthenium membrane catalyst[19] increased the rate of hydrogenation of carbon dioxide to methane compared with the rate of formation of methane on the same catalyst without the modifying element. However, the rate of reaction in the presence of lanthanum increased only in the temperature range from 573 to 663 K. Further increase of temperature resulted in a sharp fall of the rate of formation of methane, probably as a consequence of the formation of the catalytically inert lanthanum carbonate. The high stability of the latter precludes the regeneration of the catalyst.

As a result of the electrochemical deposition of a rhodium coating on a palladium–ruthenium membrane catalyst,[20] methane did not begin to form until 688 K, and although its content in the reaction products did increase with increase in temperature, it was appreciably (almost by a factor of four) smaller than the amount of carbon monoxide formed, traces of which were observed already at 473 K. An increase in the partial pressure of hydrogen at the hydrogen exit surface of the membrane catalyst from 200 to 725 mmHg increased somewhat the yield of methane and did not affect the yield of carbon monoxide. The formation of hydrocarbons with higher molecular weights was not observed.

Thus the method of introduction of hydrogen into the reaction zone as well as the deposition of dispersed layers of active metals on the hydrogen exit surface of the membrane catalyst influence the ratio of the concentrations of different forms of adsorbed hydrogen, which alters the selectivity and activity in the carbon dioxide hydrogenation process.

V. The role of adsorbed oxygen in the oxidation of methanol

Silver foil, which makes it possible to introduce oxygen into the reaction zone via diffusion through the metal, may be used as a membrane oxidation catalyst. The process involving oxygen transfer through silver membranes may include the same series of stages as the adsorption of oxygen on silver, in the forward and reverse sequences.[21] The adsorption of oxygen on silver in the temperature range from 453 to 623 K is known[22] to proceed in accordance with the scheme

$$O_{2\,gas} \rightarrow O_{2\,ads}^{-} \rightarrow 2O_{ads}^{-} \rightarrow 2O_{lat}^{2-}.$$

However, the rate-limiting stage in the transfer of oxygen through silver may not be the same as in the adsorption of oxygen from the gas phase.

The study of the permeability of silver tubes with walls 10^{-4} m thick to oxygen showed[23] that it is proportional to the square root of the oxygen pressure at the oxygen entry surface of the tube. This indicates the involvement of oxygen atoms in the rate-limiting stage of the transfer of oxygen through silver. The electrochemical deposition of a layer of silver on the oxygen exit surface of a silver membrane increases its permeability to oxygen by more than an order of magnitude,[24] but the linear dependence of this parameter on the square root of the oxygen pressure at the entry surface of the membrane is retained. All these factors show that the rate-limiting stage in the transfer of oxygen through thin silver membranes is the process occurring on the oxygen exit surface in which oxygen atoms participate.

The states of the oxygen, arriving via diffusion through membranes or as a result of adsorption from the gas phase, on the exit surface of the membrane have been investigated mass-spectrometrically[25] using a modernised ion source. In the immediate vicinity of the mass spectrometer ion source, a silver tube with walls 10^{-4} m thick was placed and the composition of the gas phase in contact with its outer surface was investigated. Furthermore, an additional cathode and potential-carrying grids were introduced into the ion source, which made it possible to investigate the species adsorbed on the outer surface of the silver tube by the method of the electron-stimulated desorption of ions (ESDI). Two peaks can be observed in the mass spectrum of gaseous oxygen: the molecular (O_2^+) peak with a mass number of 32 and a fragment (O^+) peak with a mass number of 16. The ratio of the intensities of these two peaks (I_{32}/I_{16}) was found to be close to 20 by the usual gas analysis. As can be seen from Table 4, approximately this value has been recorded when oxygen was admitted directly onto the outer surface of the silver membrane in the ionisation chamber. A similar value was also obtained when oxygen was supplied by diffusion through a silver tube at 665 K. However, in this case the decrease in the temperature of the membrane was accompanied by a decrease in the I_{32}/I_{16} ratio, which indicates the appearance in the gas phase of an additional source of oxygen atoms. These may be the atoms desorbed from the surface. The proximity of the membrane to the ionisation region makes it possible to record them. An analogous effect has been observed in a study by the ESDI method, which is probably associated with the enrichment of the exit surface of the silver membrane during the diffusion of oxygen through it in adsorbed forms, which on electron bombardment of the surface are capable of being desorbed to the gas phase in the form of the positively charged O^+ ions.

Since the entire oxygen which has diffused through the silver membrane passes to the ionisation chamber, the intensities of the molecular (O_2^+) and fragment (O^+) oxygen peaks are proportional to the permeability of the given silver membrane to oxygen under stationary conditions.

The activation energy calculated from the temperature variation of the intensity of the peak with a mass number of 32 exceeds the corresponding value found by measuring the height of the peak, with a mass number of 16, the same effect being observed for both methods of analysis. Presumably, in the diffusion of oxygen into a vacuum through a thin silver membrane, its exit surface is enriched in atoms capable of being desorbed into the gas phase on electron impact, the number of such species increasing with decrease in temperature. Furthermore, at low temperatures the surface diffusion process as a result of which the lattice oxygen passes to the adsorbed state, preceding the recombination stage, is hindered and the release of atoms into the gas phase becomes possible which, as already stated above, is the cause of the decrease in the ratio I_{32}/I_{16} (Table 4) and also of the lower activation energy calculated from the variation of the intensity of the peak with a mass number of 16.

Table 4. The ratios of the intensities of the mass spectrometric peaks with mass numbers 32 and 16 (I_{32}/I_{16}) for different methods of supplying oxygen to the exit surface of a silver membrane and at different temperatures.[25]

Method of introduction of oxygen	Analytical method	T, K						
		525	548	570	591	613	634	665
Diffusion through silver	analysis of gas phase	2	3	7	11	14	—	18
Direct injection	ditto	19	—	—	16	16	18	18
Diffusion through silver	ESDI	0.01	0.02	0.03	0.04	0.06	0.09	0.1
Direct injection	ditto	0.66	0.62	0.57	0.54	0.49	0.47	0.47

Methanol was oxidised[21] on the outer surface of a silver tube with walls 1×10^{-4} m thick. When a mixture of methanol and oxygen was supplied to the outer surface, the inner part of the tube was evacuated.

The permeability of silver to oxygen under the conditions of the oxidation of methanol by diffusing oxygen exceeded its permeability to oxygen in the diffusion of the latter into a vacuum under the same conditions to a greater extent the lower was the experimental temperature. In the interaction of methanol vapour with diffusing oxygen on the exit surface of the silver membrane catalyst, oxygen did not appear in the gas phase until 619 K. On further increase in temperature, its amount also rose and the permeability of the silver membrane catalyst to oxygen diminished, approaching the value obtained for the diffusion of oxygen into a vacuum. The activation energy for the transfer of oxygen through a silver membrane catalyst during the oxidation of methanol is smaller by 25 kJ g-atom^{-1} than in the diffusion of oxygen into a vaccum. This is in fact the difference between the activation energies calculated from the intensities of the O_2^+ and O^+ peaks in the analysis of the gas phase near the exit surface of the silver membrane.[25] The decrease in the activation energy for the transfer of oxygen through silver under methanol oxidation conditions can be due to the interaction of the substances being oxidised on the exit surface of the silver with oxygen species which participate in the stage preceding the rate-limiting stage of the transfer of oxygen to a vacuum. According to the scheme presented above, this form may be the lattice oxygen O_{lat}^{2-}.

The supply of oxygen by diffusion through a silver membrane catalyst evidently creates on the working surface, at temperatures below 619 K, a higher concentration of this form than in the adsorption of oxygen from the gas phase. Thus, in the oxidation of methanol by diffusing oxygen, the yield of formaldehyde at 619 K reached 85%, while in the case where a mixture of methanol with oxygen was used under the same conditions, the maximum yield of formaldehyde was 23 %. Apart from formaldehyde, carbon monoxide and dioxide as well as water were formed in the reaction.

The amount of carbon monoxide formed per unit time was independent of temperature, while the rate of formation of carbon dioxide increased on heating. However, the yield of carbon dioxide did not exceed 22% even at the highest experimental temperature (673 K).

Thus the ratio of different forms of oxygen on the silver surface depends on the method of supplying oxygen through the surface of the membrane catalyst and this affects the process selectivity, since oxygen species dissolved in the surface layer of the metal participate in all probability in the formation of formaldehyde from methanol on silver.

References

1. V M Gryaznov, V S Smirnov *Uspekhi Khim.*, 1974, **43** 1716 [*Russ. Chem. Rev.*, 1974(10)]
2. V M Gryaznov, V I Vedernikov, S G Gul'yanova *Kinetika i Kataliz*, 1986, **27** 142
3. R M Barrer *Diffusion in and through Solids* (Translated into Russian), Moscow, 1948, 504 pp
4. V A Gol'tsov *Voprosy Atomnoi Nauki i Tekhniki. Ser. Atomno-Vodorodnaya Energetika* (Problems of Atomic Science and Engineering. The Atomic-Hydrogen Power Engineering Series), Atomizdat, Moscow, 1977, No.1(2), p. 65
5. H Conrad, G Ertl, E E Latta *Surface Sci.*, 1974, **41** 435
6. H Alefeld et al. (Editors) *Hydrogen in Metals* (Translated into Russian), Izd. Mir, Moscow, 1981, Vol. 2, p.103
7. R Dus *Surface Sci.*, 1973, **42** 324
8. Yu A Zubarev, O K Samuilova, V D Yagodovskii *Metally i Splavy kak Membrannye Katalizatory* (Metals and Alloys as Membrane Catalysts), Izd. Nauka, Moscow, 1981, p. 139
9. Yu A Zubarev, N N Mikhalenko, V D Yagodovskii *Kinetika i Kataliz*, 1988, **24** 194
10. M G Cattania, V Penka, R T Behm, et al. *Surface Sci.*, 1983, **126** 382
11. Yu M Serov, S G Gul'yanova, O S Gur'yanova *Membrannye Katalizatory Pronitsaemye dlya Vodoroda i Kisloroda* (Membrane Catalysts Permeable to Hydrogen and Oxygen), Izd. Nauka, Moscow, 1985, p. 129
12. Yu M Serov, Candidate's Thesis in Chemical Sciences, Patrice Lumumba University of Friendship Among Nations, Moscow, 1981
13. A P Mishchenko *Metally i Splavy kak Membrannye Katalizatory* (Metals and Alloys as Membrane Catalysts), Izd. Nauka, Moscow, 1981, p. 56
14. A T Bell *Catal. Rev. Sci. Eng.*, 1981, **23** 203
15. Yu M Serov, O S Gur'yanova, S G Gul'yanova, V M Gryaznov, *Zhur. Fiz. Khim.*, 1986, **60**, 206 [*Russ. J. Phys. Chem.*, 1986(1)]
16. V M Gryaznov, Yu M Serov, S G Gul'yanova, M V Palishkin, *Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol*, 1980, **23** 593
17. C A Luengo, A L Cabrera, H B MacKay, M B Maple *J. Catal.*, 1977, **47** 1
18. V M Gryaznov, S G Gul'yanova, Yu M Serov, V D Yagodovskii *Zhur. Fiz. Khim.*, 1981, **55** 1306 [*Russ. J. Phys. Chem.*, 1981(5)]
19. Yu M Serov, S G Gul'yanova, V M Gryaznov *Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol.*, 1983, **26** 882
20. Yu M Serov, S G Gul'yanova, V M Gryaznov *Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol.*, 1983, **26** 1140
21. V M Gryaznov, V I Vedernikov, S G Gul'yanova *Kinetika i Kataliz*, 1986, **27** 142
22. L Ya Margolis *Okislenie Uglevodorodov na Geterogennykh Katalizatorakh* (Oxidation of Hydrocarbons on Heterogeneous Catalysts), Izd. Khimiya, Moscow, 1972, 327 pp
23. V M Gryaznov, S G Gul'yanova, S Kanizius *Zhur. Fiz. Khim.*, 1973, **47** 2694 [*Russ. J. Phys. Chem.*, 1973(10)]
24. S G Gul'yanova, V M Vedernikov, V M Gryaznov *Zhur. Fiz. Khim.*, 1977, **51** 179 [*Russ. J. Phys. Chem.*, 1977(1)]
25. V M Gryaznov, S G Gul'yanova, E N Kolosov, N I Starkovskii *Dokl. Akad. Nauk SSSR*, 1987, **293** 872
26. V I Vedernikov, S G Gul'yanova *Membrannye Katlaizatory Pronitsaemye dlya Vodoroda i Kisloroda* (Membrane Catalysts Permeable to Hydrogen and Oxygen), Izd. Nauka, Moscow, 1985, p. 165

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Development of ideas concerning the mechanism of the Fischer–Tropsch synthesis

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ABSTRACT. The principal stages in the development of ideas concerning the mechanism of the Fischer–Tropsch synthesis and its modifications are examined and the available literature data about the synthesis are surveyed. Attention has been concentrated on the analysis of modern ideas concerning the mechanism of the interaction of CO and H_2 on the basis of the latest advances in metal complex catalysis. The possibility of the existence of the postulated intermediates and of the occurrence of suggested elementary steps has been demonstrated in relation to model organometallic systems.

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I. Introduction

At the beginning of the 20th century Sabatier[1] and then Fischer and Tropsch[2,3] first achieved the catalytic synthesis of organic compounds from CO and H_2. Apart from the synthesis of methane[1] and aliphatic hydrocarbons, mainly having the normal structure,[2,3] from the synthesis gas (a mixture of CO and H_2), during the last decades other organic compounds have been synthesised, including methanol,[4] lower alkanes,[5] polymethylenes,[6] isoalkanes,[7] olefins,[8] high alcohols,[9] acids,[10,11] and polyols.[12] With the exception of certain compounds such as acetylene and formaldehyde, there are no thermodynamic limitations to the preparation of a wide range of organic products by this procedure.[13]

At the present time the term Fischer–Tropsch synthesis is given to the set of reactions involving the direct conversion of CO + H_2 into a mixture of aliphatic hydrocarbons and oxygen-containing compounds in which the number of carbon atoms ranges from two upwards. Typical catalysts of these reactions are Ni, Co, Fe, and Ru.[14,15] Under certain conditions, the predominating products of the conversion of the synthesis gas are oxygen-containing compounds in the presence of iron catalysts and hydrocarbons in the presence of cobalt catalysts. Nickel catalysts are known to effect the selective synthesis of methane,[15] although it has been recently reported[16] that the coprecipitated Ni–Ti–Mg catalysts, promoted with Na and Cu, are effective in the synthesis of higher aliphatic alcohols. A distinctive feature of the ruthenium catalyst is its capacity to effect the formation of high-molecular-weight polymethylenes from CO and H_2. Other Group VIII metals (Ir, Pd, Pt, Os, and Rh) exhibit an insignificant activity in the Fischer–Tropsch (FT) synthesis.

As a consequence of the increased interest in the FT synthesis after the petroleum embargo in 1973, there was a sharp increase in the number of publications on this question. Among them, mention must be made of certain monographs[14,17,18] and reviews.[15,19–31]

However, the latest complete review devoted directly to the mechanism of the FT synthesis in the Soviet periodical literature dates back to 1967,[32] although this topic has been briefly discussed in a number of communications by Soviet authors.[33–37]

II. The carbide mechanism

The first version of the carbide mechanism was proposed by Fischer and Tropsch. They suggested that this mechanism involves the formation of metal carbides and their hydrogenation to oxygen-free intermediates (for example, methylene species), whose polymerisation leads to the formation of the set of products observed.[2,3,88] In the course of the development of these views, a more detailed mechanism, supported by certain kinetic studies, was proposed.[39,40]

After this hypothesis had been forgotten for many years, there has been an appreciable growth of interest in it during the last 8–10 years. Furthermore, at the present time this is regarded as one of the main hypotheses.

The "neocarbide" theory originated from the studies by Wentercek et al.[41] and Araki and Ponec.[42] The elegant study by Goodman and Yates,[43] using doubly labelled CO, also confirmed the presence of a carbon monoxide dissociation stage in the FT synthesis. The formation of the following intermediate species on the (111) surface of nickel has been established by secondary ion mass spectrometry (SIMS):[44] C^+, CH^+, CH_2^+, CH_3^+, O^+, CD^+, CD_2^+, CD_3^+, $NiCO^+$, $NiOH^+$, $NiCH_2^+$, $NiCH_3^+$, $NiCH^+$, and NiC^+. It has been shown that surface oxygen-free species of the type CH_x (x = 0–3), formed via the CO dissociation stage, are intermediates on the Ni, Co, and Ru catalysts deposited on SiO_2.[45] In the study quoted, the Ni, Co, and Ru catalysts were first converted into the carbide form with the aid of ^{13}CO. The subsequent interaction of ^{13}CO and H_2 on their surface led to the formation of $^{13}CH_4$ methane and a number of normal alkanes containing several ^{13}C atoms in a single molecule, i.e. the carbide carbon participates in the formation of hydrocarbons.

The possibility of the rapid dissociative adsorption of CO on typical metallic catalysts of the FT synthesis and the presence of this stage, as the initial stage, in the mechanism of such synthesis have been confirmed by a series of experimental data and a large group of supporters.[46-53]

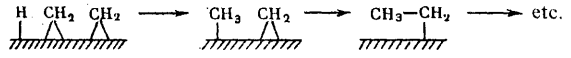
A significant confirmation of the carbide hypothesis was obtained in two investigations.[54,55] In the decomposition of diazomethane in the presence of hydrogen over a typical FT synthesis catalyst (Ru, Co, Fe), a mixture of mainly linear alkanes and alkenes was formed. The proportions of the products obeyed the Schulz–Flory equation and was typical for syntheses from CO and H_2. For practical purposes, it is convenient to express this equation in the logarithmic form

$$\lg(m_P/P) = \lg(\ln^2\alpha) + (\lg\alpha)P,$$

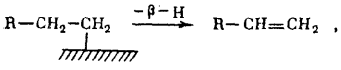
where P is the number of carbon atoms in the product molecule, m_p the weight fraction relative to the overall product, of the hydrocarbon (or the oxygen-containing compound) in which the number of carbon atoms is P, α is the probability of chain propagation defined as $\alpha = r_p/(r_p + \Sigma r_{tr})$, where r_p and r_{tr} are the rates of chain propagation and transfer respectively. If the molecular weight distribution obeys this equation, then the plot of $\lg(m_p/P)$ against P should be represented by a straight line. Furthermore, in this equation there is an "internal control", since α is determined both by the slope ($\lg\alpha$) and the intercept on the ordinate axis [$\lg(\ln^2\alpha)$]; the two values obtained should be identical.

C_1-C_{18} hydrocarbons have been obtained from $CH_2N_2 + H_2$ and $CO + H_2$ mixtures over Co and Fe, the selectivity of their formation depending in both cases to equal extents on the reaction conditions. Thus the increase in the H_2 partial pressure led to an increase in the alkane : alkene ratio and to a decrease of the average molecular weight. High molecular-weight polymethylenes were formed over Ru in both cases, which is typical of catalysts of this kind.[6] On the other hand, the decomposition of diazomethane in the presence of H_2 over Ni and Pd yielded not only methane but also higher hydrocarbons, although nickel is known to be a typical methane formation catalyst. However, at a pressure of 68 atm, the proportions of the products of the synthesis from CO and H_2 in the presence of this catalyst proved to be close to those obtained in experiments involving the treatment of the nickel catalyst with hydrogen for 1 atm after the decomposition of diazomethane over it. In the decomposition of the $CH_2N_2 + H_2$ mixture over Cu, only methane and ethylene were detected in the reaction products.

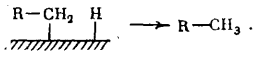
The gas-phase decomposition of diazomethane itself over metallic catalysts at 200 °C under the conditions used led in all cses to the formation of only one product–ethylene. Hence it follows that, in the absence of H_2, the methylene intermediates formed only dimerise with subsequent desorption of ethylene as the final product; the oligomerisation of the intermediate has not been observed. On the basis of the similarity of the proportions of the products of the conversion of $CO + H_2$ mixtures, on the one hand, and $H_2 + CH_2N_2$ mixtures, on the other, it has been concluded[54,55] that the mechanisms of the two processes are identical and that the methylene intermediates may polymerise, the polymerisation being initiated by the presence of the M–H bond on the catalyst surface. Although the authors[54,55] did not investigate the possible ways of the generation of CH_2 fragments on the catalyst surface, it had been noted earlier that the CH_x fragments on typical catalysts of the FT synthesis can be formed as a result of the hydrogenation of the carbides produced on the surface in the dissociative adsorption of CO. In their view, the data presented confirm the carbide hypothesis[23,38] and make it possible to justify the following mechanism proposed initially by Biloen et al.:[45]



Chain termination takes place either as a result of the elimination of β-hydrogen atoms with formation of α-olefins, i.e.



or as a consequence of the reduction of the M–C bond and the formation of alkanes:



We may note that in the studies quoted[54,55] only one feature of the carbide mechanism was demonstrated—the ability of the methylene intermediates to form hydrocarbons on polymerisation, but the question of the ways in which these intermediates arise under the conditions of the real synthesis from CO and H_2 in the absence of diazomethane remained unresolved.

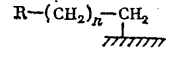
As regards the question of the origin of the CH_2 fragments on the catalyst surface, we may note that they may be formed both on the metal carbide (as a result of the interaction of hydrogen with the M–C intermediate arising in the dissociative adsorption of CO) and via the stepwise hydrogenation of the non-dissociatively chemisorbed CO. The answer to this question actually determines whether the carbide mechanism operates in a particular catalytic system.

Since the involvement of the CH_2 intermediates both in the chain initiation and chain propagation stages is postulated only in the carbide mechanism of the FT synthesis, the experimental data quoted by Brady and Pettit[54] concerning the influence of the additional $^{12}CH_2$ groups obtained by the preliminary decomposition of diazomethane on the proportions of the products in the synthesis from ^{13}CO and H_2 in the presence of a cobalt catalyst are consistent solely with the carbide hypothesis. Furthermore, in the experiment on the Co catalyst using mixtures of ^{13}CO, H_2, and $^{12}CH_2N_2$, the distribution of ^{13}C and ^{12}C in the propane formed also corresponds only to the carbide mechanism.

Analogous conclusions have also been reached in a study[56] where CH_xCl_{4-x} (x = 1–3) was used as the source of the surface CH_x intermediates.

However, the possibility of the formation of different forms of carbon in the dissociative adsorption of CO[57-60] very greatly complicates the question of the mechanism of the formation of methylene intermediates on the catalyst surfaces.

The carbide hypothesis presupposes that different alkyl fragments of the type

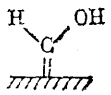


are present on the surface as intermediates in the chain propagation stage. Use of the novel method of the so called "chemical trapping agents" (pyridine, cyclohexene)[61-63] made it possible to demonstrate that alkyl intermediates are precursors of the hydrocarbons obtained.

Thus the set of experimental data available at present makes it possible to regard methylidyne, methylene, methyl, and R-alkyl species bound to the surface as possible intermediates in the FT synthesis. The carbide mechanism explains satisfactorily the formation of different hydrocarbons. On the other hand, the appearance of oxygen-containing products, which are known to be capable of predominating in the overall products under certain conditions, is inexplicable in terms of this mechanism. The explanation of the presence of oxygen-containing compounds in the reaction products by postulating a chain termination stage as a result of the insertion of CO in the M–C(Alk) bond in the carbide mechanism[25,64] is rather unconvincing, since this chain termination pathway does not explain the entire wide variety of the oxygen-containing reaction products formed.

III. The condensation mechanism

In the 1950's Stroch et al.[65] and independently Eidus[32] put forward the hypothesis that hydroxymethylene groups are formed on the surface of the metal from the adsorbed CO and the chemisorbed atomic hydrogen and that C–C bonds arise as a result of condensation with elimination of water. The following arguments have been quoted in support of this hypothesis: (1) the experimentally established fact that an adsorbed complex with the CH_2O stoichiometry is formed;[66–68] (2) the fact that the amount of CO and H_2 adsorbed from the mixture exceeds the overall amount of these substances adsorbed separately; (3) the detection of compounds having the composition CH_2O and other oxygen-containing intermediates[69] by gas-phase mass-spectrometry; (4) identification of oxygen-containing compounds on the surfaces of iron catalysts;[70] (5) evidence for the stability of chemisorbed complexes of the type[71]



based on quantum-chemical calculations.

However, it has been shown convincingly[37,72,73] that the possible contribution by processes involving the condensation of both methylene and hydroxycarbene intermediates is extremely insignificant, at least on iron catalysts. So far the condensation mechanism of chain propagation has not been widely recognised. Despite the major advances in organometallic chemistry, the occurrence of a condensation reaction of the type[22]

$$M{=}CHOH + M{=}CHOH \rightleftarrows M{=}CHCOH{=}M + H_2O$$

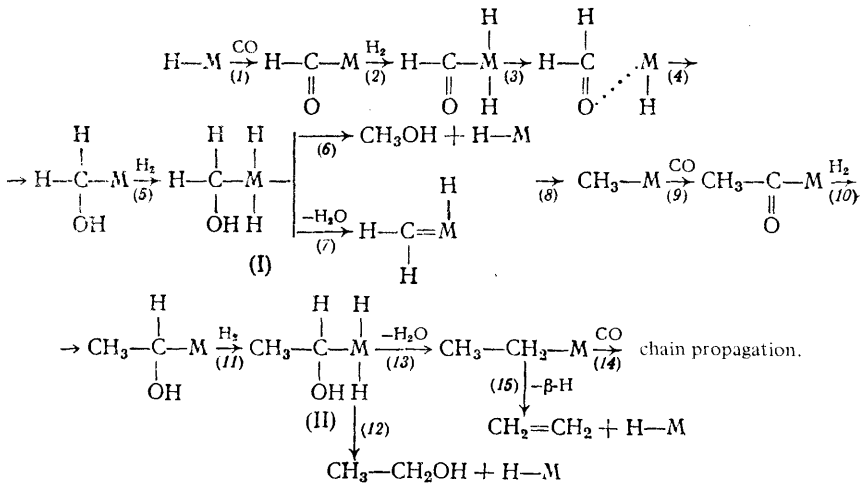
has not been established. However, the formation of oxygen-containing intermediates in the FT synthesis, which is at present the subject of vigorous discussion, has served as the basis of mechanisms which constitute an alternative to the condensation mechanism

IV. The mechanism based on the insertion of CO

The mechanisms of the FT synthesis according to which chain propagation is a result of the insertion of activated CO in the M–C bonds have been proposed by Schulz and co-workers[74,75] and later by Henrici-Olive and Olive.[76] Pichler and Schulz[74] postulate the formation of two-centre intermediate compounds, while Henrici-Olive and Olive[76] assume the possibility of a whole cycle of reactions on a mononuclear active centre. The mechanism proposed by Henrici-Olive and Olive (Scheme 1), most frequently discussed recently, is presented below:

In the first stage, CO is inserted into the M–H bond of the surface hydride and a primary formyl complex is formed. This is followed by stages involving the oxidative addition of H_2 [stage (2)] and the reductive elimination of the formyl ligand [stage (3)], leading to the formation of formaldehyde and a metal hydride. However, the formaldehyde does not leave the coordination sphere of the metal and remains bound to the active centre via the CO group. The interaction of the metal hydride with the aldehyde [stage (4)] with subsequent oxidative addition of hydrogen [stage(5)] entails the

Scheme 1



appearance of the intermediate (I). The intermediate can be converted via two pathways: either as a result of reductive elimination [stage (6)], which leads to the formation of methanol and a metal hydride as the kinetic chain transferring agent, or as a result of the elimination of water [stage (7)] with formation of a carbene intermediate, which is converted into a σ-bonded methyl complex after rearrangement [stage (8)]. The next CO molecule is coordinated to the active centre and is inserted in the $M-CH_3$ bond [stage (9)], which leads to an acyl intermediate. Stage (10) corresponds to the sum of stages (2)–(4), but differs by the fact that the hydrocarbon chain becomes longer by one carbon atom. The oxidative addition of hydrogen [stage (11)] results in the formation of the intermediate (II), which is converted via reactions of type (6), (7), and (8) into either ethanol and a metal hydride [stage (12)] or into a metal alkyl [stage (13)]. The metal alkyl is either subjected to the insertion of the next CO molecule [stage (14)] and then propagates the growing chain or affords, after β-elimination of a hydrogen atom [chain termination—stage (15)], the final product—an α-olefin (ethylene in the given stage). According to the authors, the metal hydride is responsible for the occurrence of secondary hydrogenation and isomerisation reactions [reactions (16) and (17)]:

$$R-CH=CH_2 + H-M \begin{cases} \xrightarrow{(16)} R-\underset{\displaystyle M}{\underset{|}{CH}}-CH_3, \\ \xrightarrow{(17)} R-CH_2-CH_2-M. \end{cases}$$

Since α-olefins are the primary products of the synthesis, the predominance of methyl-substituted structures among the isomeric products becomes understandable.

The main evidence in support of this mechanism is its analogy with metal complex catalysis.[77–83] Thus the formation of alkylbenzenes in the presence of the $W(CO)_6.AlCl_3$ catalytic system has been considered as one of the decisive pieces of evidence:[78]

$$C_6H_6 + nCO + H_2 \rightarrow C_6H_5(CH_2)_nH + H_2O,$$
$$n = 1-5,$$

the proportions of the alkylbenzenes obeying the Schulz–Flory relation. However, it has been shown that [84] the side chain in alkylbenzenes is formed with participation of the carbon atoms of the benzene ring: when carbon-labelled benzene was used, alkylbenzenes with the carbon label in the side chain were obtained.

Nevertheless, the migration insertion of CO in the M–C bond is a well known reaction in the chemistry of carbonyl complexes.[85] In fact, this involves the migration of the alkyl group to the carbonyl ligand coordinated to the metal, which has been demonstrated for the reaction[86,87]

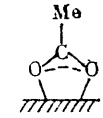
$$CH_3Mn(CO)_5 \underset{-CO}{\overset{+CO}{\rightleftarrows}} CH_3COMn(CO)_5.$$

There is also significant evidence that chain propagation in the FT synthesis takes place as a result of the insertion of CO in the M–C bond.[88,89] The interaction of CO, H_2, and $C_6H_5C\equiv CH$ in the presence of a premelted iron catalyst yielded aromatic alcohols with C_3-C_8 side chains whose proportions obey the Schulz–Flory statistics. The introduction of phenylacetylene made it possible to synthesise aromatic alcohols at temperatures in the range 110–130 °C, but the reaction proper between CO and H_2 is not observed and the C–C bonds can therefore be formed only as a result of the incorporation of CO in the chain without its preliminary interaction with H_2 and without dissociation (the mechanisms of the CO + H_2 + alkyne reactions will be considered below).

Attempts have been made[90,91] to detect on the surface of the working catalyst the structures postulated in the mechanism described. Convincing evidence for the existence of the acyl group



and the acetate



as precursors of the oxygen-containing C_2 compounds has been obtained by IR spectroscopy *in situ* on the surfaces of the Rh/SiO_2 and $Rh-Mn/SiO_2$ catalysts.[91] An attempt has also been made to detect structures of the acyl type on the Fe/SiO_2 surface using diethylamine as the chemical trapping agent. The reaction between the acyl carbon of the postulated oxygen-containing intermediate and diethylamine in the presence of hydrogen should have led to the formation of either *NN*-diethylamides or *N*-alkyldiethylamines. Among the reaction products, *NN*-diethylformamide, *NN*-diethylacetamide, and C_1-C_4 *N*-alkyldiethylamines were found in the experiment. However, this is not unambiguous evidence for the presence of oxygen-containing intermediates on the surface of the working catalyst, because the above products might have been formed via other pathways.

We may also note studies, [80–83] in which the latest experimental data confirming the carbide mechanism have been analysed.[80–83] It was shown that data[45,54,55] interpreted within the framework of the carbid theory do not nevertheless constitute unambiguous proof of the absence of the CO insertion stage as the chain propagation stage and that they are fully consistent with the mechanism proposed by Henrici-Olive and Olive.[76]

Kagan et al.,[37] who regard the synthesis of compounds from CO and H_2 as a heterogeneous-catalytic chain reaction initiated, as a result of the interaction of CO and H_2, by an oxygen-containing intermediate (chain initiation step), hold a similar view on the mechanism of the FT synthesis. Chain propagation takes place as a result of the successive addition of CO and H_2 to a hydroxymethylene complex of this kind or its homologues without a preliminary interaction between them. In the course of chain propagation, the complex undergoes intermediate dehydration and is lengthened by one CH_2 group with migration of the active centre to the end of the growing chain.

Aliphatic[92,93] and aromatic[89,94] alcohols, and α ω-diols or their monoethers[95] have been synthesised using respectively acetylene, phenylacetylene, and propargyl alcohol and its ethers as the third component.

Thus the possibility of a large series of syntheses based on CO and H_2 via the initiated hydrocondensation of CO was established. This method makes it possible to obtain compounds belonging to a wide variety of classes using the corresponding initiator (by varying the group R in the terminal alkyne $R-C\equiv CH$):

$$R-C\equiv CH + CO + H_2 \rightarrow R(CH_2)_nOH,$$
$$R = H;\ Ph,\ CH_2OH,\ CH_2OMe,\ CH_2OBu\text{-}t;\ n \geqslant 3.$$

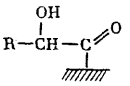
The presence of the $(CH_2)_nOH$ fragment is common to all these compounds.

Comparison of the syntheses of higher aliphatic alcohols from CO and H_2 [37] with the initiated syntheses showed that the mechanisms of these reactions are similar and probably differ solely by the chain initiation stage, i.e. by the way in which the primary complex is formed.

Detailed investigation of the mechanism of initiated syntheses by comparison with the available literature data suggested a mechanism of this process which accounts for the origin of the products detected (Scheme 2).†

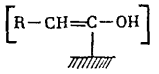
The studies published by Kline et al.[96] indicate the possibility of the formation of π-bonded acetylene $Fe_2(C_2H_2)$ when it interacts with the active centre of an iron catalyst. The idea that the chain initiation step involves the catalytic interaction of the alkyne with CO and H_2 is confirmed by the fact that the alkyne is in all cases incorporated only once in each molecule of the reaction product; its inclusion in the growing chain has not been observed.[88,97-99] This follows from the constancy of the molar radioactivity of C_3-C_9 alcohols in experiments with mixtures of CO, H_2, and $HC\equiv{}^{14}CH$.[97] Chain initiation takes place much more readily when alkynes are introduced into the mixture of CO and H_2. The syntheses with participation of these complexes can be achieved under conditions which are non-traditionally mild for the FT process: at temperatures in the range 110–130 °C and pressures in the range 25–50 atm. The products of the CO and H_2 interaction proper were not then detected. This agrees with the claim that the insertion of CO in the M–H bond is energetically more favourable than its insertion in the M–C bond.[100] The possibility of achieving initiated syntheses under mild conditions shows that the insertion of CO in the M–C bond is in fact the only possible way in which chain propagation can take place because the formation of intermediates as a result of the interaction of CO with H_2 or of reactions of CO itself would have naturally led to the appearance of the products of the interaction of CO and H_2.

The formation of the primary complex from CO, H_2, and the alkyne in the first stage of initiated hydrocondensation was confirmed by carrying out the homogeneous model synthesis of aromatic alcohols from CO, H_2, and iron carbonyl complexes of phenylacetylene. The set of products formed proved to be analogous to that obtained in the synthesis of aromatic alcohols from CO and H_2 with participation of phenylacetylene in the presence of a premelted iron catalyst.[99] In this case, chain propagation also proceeds via the insertion of CO in the Fe–C bond, as in the mechanisms considered previously in this Section.[74-76] This hypothesis is supported by the results of studies[101,102] in which the formation of hydroxyacyl complexes of the type



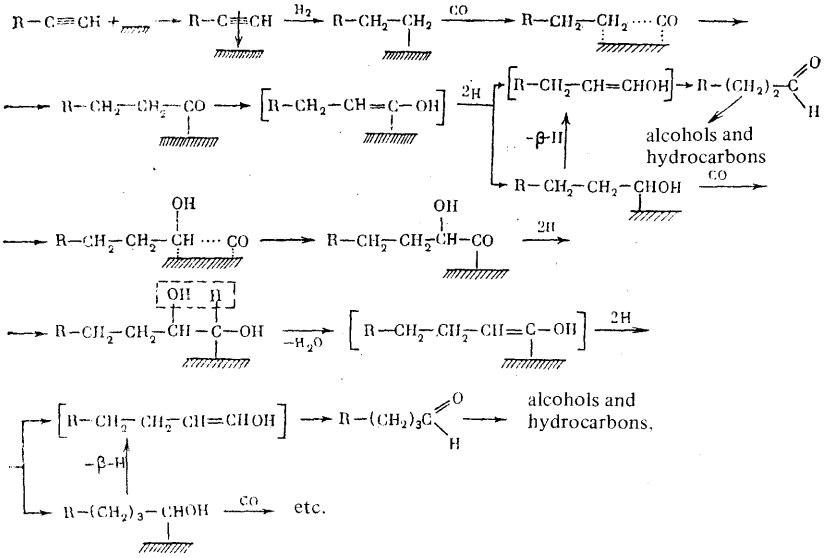
was established and the reaction involving the insertion of CO in the M–C bond in the hydroxyalkyl complex was achieved.

Surface enolic intermediates of the type



have been detected in the hydrogenation of ketones on the surface of premelted iron catalysts.[103]

Scheme 2



†See E V Slyvinsky, Yu P Voitsechovsky, and S M Loktev *Proceedings of the 9th International Congress on Catalysis, Calgary, 1988*, Vol. 2, p. 729

The possibility of the dehydration of diol structures with formation of surface enolic intermediates has been confirmed by carrying out the model reaction involving the dehydration of ethylene glycol to the expected acetaldehyde in the presence of the same catalyst.[104]

The detection of the R and CH_2OH groups in the reaction products in the α- and ω-positions respectively supports the hypothesis that, after the chain initiation step, the alkyne incorporated in the hydrocarbon chain moves away from the active centre without participating in the chain propagation stages. Comparison of the relative selectivities[105,106] shows that the primary products of the initiated syntheses are aldehydes, while alcohols and hydrocarbons are formed as a result of secondary hydrogenation reactions (probably via independent pathways).

Chain termination apparently occurs as a result of the β-elimination of hydrogen and its oxidative addition.

Although the majority of the reactions representing the individual stages of the mechanism based on the insertion of CO are known in organometallic chemistry, nevertheless for a long time it was not possible to achieve the homogeneous version of the FT synthesis. The advances in organometallic catalysts in recent years made it possible to obtain numerous pieces of evidence in support of these mechanisms (see Section VI).

V. Other mechanisms

The so called "hybrid mechanisms", in which the individual elements of different mechanisms are combined, have been considered recently in a number of studies. In their investigation of the influence of the Ni–Cu catalysts on the selectivity of the hydrogenation of CO, van Barneveld and Ponec[107] suggested that carbon monoxide is capable of dissociating on the surface, generating carbide carbon atoms, which are hydrogenated to hydrocarbon intermediates (for example, methylene species):

$$\left.\begin{array}{l} CO \rightarrow C + O \quad (a) \\ C + xH \rightarrow CH_x \quad (b) \end{array}\right\} \text{chain initiation.}$$

If a dual character of the adsorption of CO (with and without dissociation) is postulated, then chain propagation can proceed via the insertion of non-dissociatively adsorbed CO in the M–alkyl bond formed in the chain initiation stage with subsequent hydrogenation of the oxygen-containing intermediate:

$$\left.\begin{array}{l} CH_x + CO_{ads} \rightarrow (CH_xCO) \quad (c) \\ CH_xCO + nH \rightarrow H_2O + (CH_xCH_{n-2}) \quad (d) \\ CH_xCH_{n-2} + CO \rightarrow (C_2H_{(x+n-2)}CO) \quad (e) \end{array}\right\} \text{chain propagation.}$$

The oxidative addition of hydrogen to the intermediate surface complex leads to chain termination:

$$CH_xCH_{n-2} + yH \rightarrow \text{hydrocarbons} \} \text{ chain termination.}$$

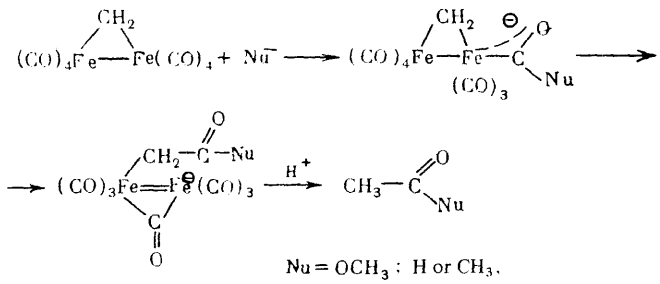
However, it had been shown earlier[108] that the only product obtained from carbide carbon on a premelted iron catalyst is methane.

A similar mechanism, combining the features of the carbide mechanism and the mechanism based on the insertion of CO, has also been adopted by Matsumoto and Benett.[109]

In a study of the Ru/SiO_2 and Co/kieselguhr systems, it was shown that only the conversion into methane takes place via the carbide mechanism, while C_n ($n \geqslant 2$) products are formed with participation of non-carbide intermediates.[110] A mechanism has been proposed for chain propagation, on the basis of the experimental data, via the condensation of hydroxylated intermediates:

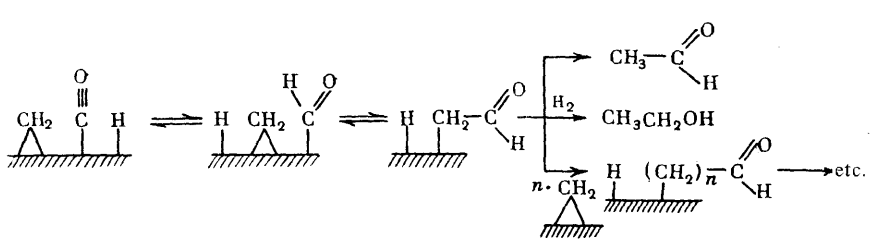
$$CH_4 \overset{2H_2}{\leftarrow} [C] + H_2O \rightleftarrows [CHOH],$$
$$2[CHOH] + H_2 \rightleftarrows [C_2H_4OH] + H_2O,$$
$$[C_2H_4OH] + [CHOH] + H_2 \rightleftarrows [C_3H_6OH] + H_2O.$$

The study of the characteristic features of the model stoichiometric reaction



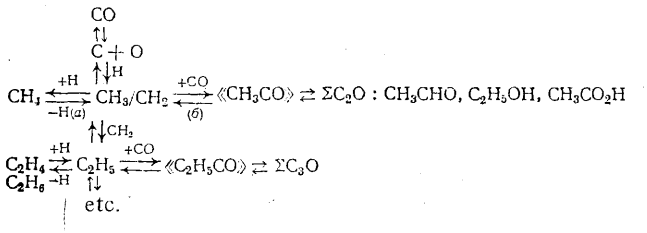
enabled Hackenbruch et al.[111] to postulate a novel hybrid mechanism, which has received definite confirmation in experiments on the synthesis from CO and H_2 in the presence of the Co/SiO_2 heterogeneous catalysis using methanol as the third component (nucleophile) and also in experiments with labelled reactants. The results agree with the postulated Scheme 3:

Scheme 3



Chain initiation takes place as a result of nucleophilic attack by the hydride on the CO molecule coordinated to the active centre with formation of a formyl intermediate. The interaction of the formyl group or its homologues (acyl groups) with the surface methylene intermediates leads to chain propagation, while chain termination is a consequence of the oxidative addition of hydrogen to M–C bond or the β-elimination of hydrogen.

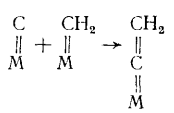
A mechanism has been proposed[113,114] for the formation of hydrocarbons and oxygen-containing products in the presence of promoted deposited rhodium catalysts on the basis of data obtained using ^{13}C-labelled reactants[112] and IR spectroscopy *in situ* under high pressure:[91]



The chain propagation in the formation reactions of hydrocarbons and oxygen-containing compounds includes the same stages and takes place on centres for the dissociative adsorption of CO, while chain termination probably occurs on different centres [stages (*a*) and (*b*)]. The C_n ($n \geqslant 2$) oxygen-containing compounds have a common precursor; for the C_2 compound, this is the "CH_3CO" acyl group formed when CO is inserted in a CH_3 or CH_2 surface hydrocarbon intermediate.

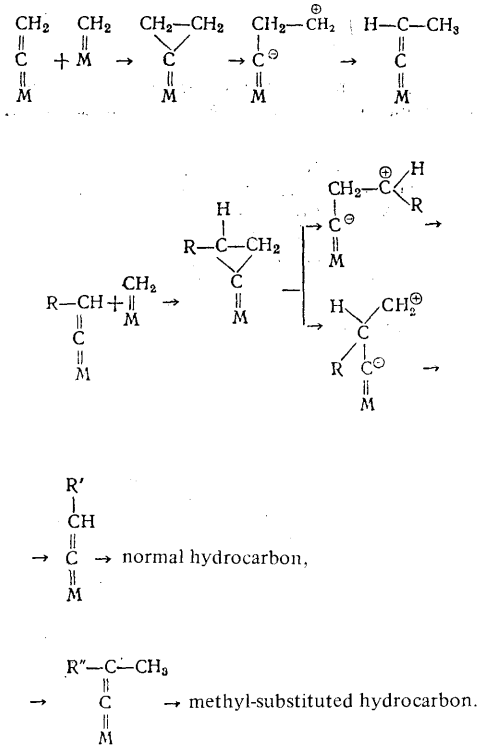
Analogous reaction mechanisms according to which oxygen-containing products and hydrocarbons are formed on different catalytic centres[90,115,116] or via different pathways,[117] had also been proposed previously. This was based on the difference between the coefficient α (the chain propagation parameter) in the Schulz–Flory equation for oxygen-containing products and hydrocarbons. However, according to data[118] for alcohols and hydrocarbons obtained in the presence of iron catalysts, the coefficients α are similar, which enabled Kagan et al.[37] and Berke et al.[119] to put forward the hypothesis that in the presence of iron catalysts, oxygen-containing compounds and hydrocarbons have a common precursor—a surface alkyl intermediate. The formation of methyl-substituted compounds as the principal isomeric products of the FT synthesis and the absence of a quaternary carbon atom in them was the reason why a modified version of the carbide mechanism was put forward.[120]

It is suggested that in this case the chain initiation stage involves the interaction of a surface carbon atom with a methylene intermediate to form the primary vinylidene complex:



Chain propagation takes place as a result of the interaction of the surface methylene groups with this complex to form a cyclopropylidene intermediate, which then readily rearranges to the normal or methyl-substituted homologues of the initial vinylidene complex:

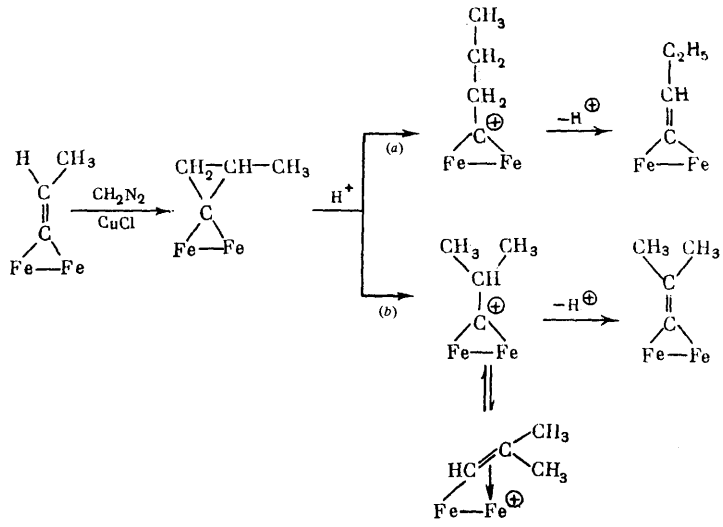
Scheme 4



Analysis of the stability of the carbonium ions formed made it possible to explain why the methyl-substituted products predominated and to put forward a mechanism for the formation of trace amounts of ethyl-substituted compounds.[120] In contrast to the insertion mechanisms described previously, here it is suggested that, in the growing vinylidene complex, the α-carbon atom in relation to the metal remains constantly bound to the metal and that the methylene intermediate is inserted in the double bond between the α- and β-carbon atoms in the surface compound.

However, the results of a study of the model homogeneous reaction of a cyclopropylidene complex of this kind permit the claim[121] that the methylene-vinylidene mechanism postulated[120] conflicts with experiment, because in the model reaction (Scheme 5) the pathway (*a*) does not occur (if the FT synthesis took place via the methylene-vinylidene mechanism, branched isomers should have predominated among its products, which has not been observed experimentally):

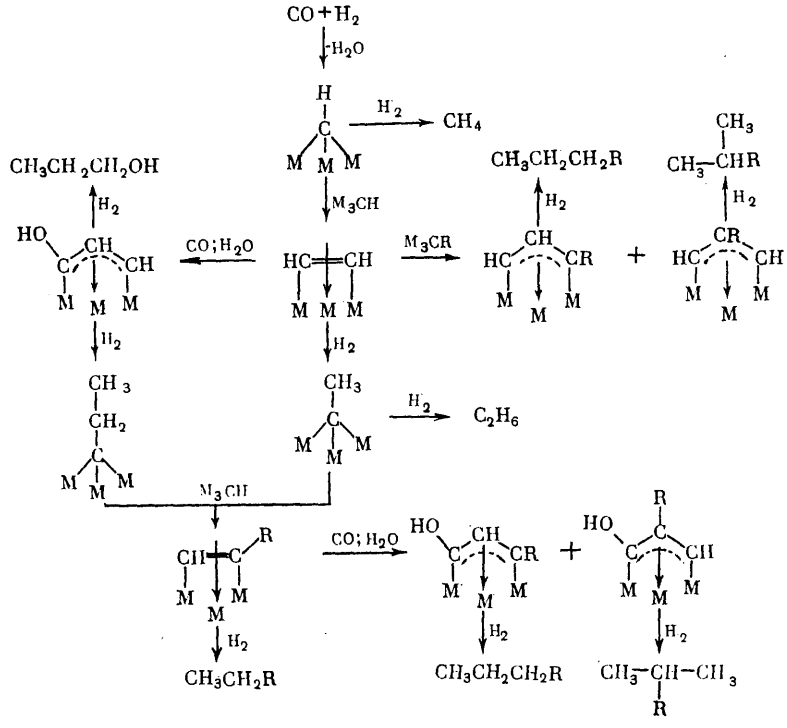
Scheme 5



On the basis of a model reaction carried out on ruthenium clusters, a mechanism has been proposed[122] for chain propagation, whose key stage is the addition of an alkyne to an alkylidyne (CR) with formation of a 1,3-dimetalloallyl, which is then hydrogenated and converted into an alkylidyne (CCH_2R) containing one CH_2 group more than the initial alkylidyne:

In the interaction of CO with H_2 on the surface, water and a surface methylene or methylidyne group are formed. The interaction of two methylidyne groups leads to the formation of an acetylene complex bound to the surface, whose reduction leads to the appearance of ethylidyne. The products of the hydrogenation of any alkylidyne is the corresponding alkane and the β-elimination of

Scheme 6



hydrogen from the intermediate containing more than two carbon atoms can lead to the formation of an α-alkene. The reaction of an alkyne with methylidyne or CO + H_2O leads to intermediates which serve as sources of the formation of branched hydrocarbons and oxygen-containing compounds. Analysis of the products of a model reaction carried out on a ruthenium cluster[122] permits the claim that the main products of the FT synthesis in this case should be unbranched compounds and that 2-methyl derivatives should predominate among the isomeric structures. According to Scheme 6, the principal oxygen-containing compounds are terminal functional compounds.

An interesting pathway leading to the formation of a C–C bond in the catalytic hydrogenation of CO has been proposed.[123] The authors[123] believe that the C–O bond is dissociated as a consequence of the deoxygenation of a formyl surface complex with its subsequent conversion into an alkyl surface compound. The only products of the deoxygenation of formaldehyde in its interaction with a titanium complex (I) were μ-oxotitanium complexes (II) and ethylene:

$$\underset{\text{(I)}}{2[CpTiCl_2(THF)_{1.5}]} + CH_2O \rightarrow \underset{\text{(II)}}{[CpTiCl_2]_2O} + CH_2{=}CH_2.$$

The data obtained suggested two mechanisms of the formation of ethylene (Scheme 7):

Thus one can postulate the possibility of the formation of surface CH_2 groups via the successive reactions

$$CO + H_2 \rightarrow (CH_2O) \xrightarrow{\text{deoxygenation}} (CH_2).$$

This pathway is an alternative to the mechanisms according to which the reaction of the CH_2O intermediate is accompanied by dehydration.[37,74,76]

An unusual example of the formation of a C–C bond has been described.[124] The carbonyl complex Tâ(CO)$_2$(dmpe)$_2$Cl [dmpe = 1,2-bis(dimethylphosphino)ethane] was reduced to Ta($Me_3SiOC{\equiv}COSiMe_3$)(dmpe)$_2$($SeiMe_3$), which contains an acetylenic diether ligand incorporating the C≡C multiple bond. A similar method of formation of a C–C bond in the reduction of the carbonyl ligand using metallic sodium had been described earlier.[125]

VI. The mechanism of the Fischer–Tropsch synthesis from the standpoint of organometallic synthesis

The vigorous investigation of reactions involving the homogeneous hydrogenation of carbon monoxide during the last few years[126] made it possible to obtain interesting information about the mechanisms of the individual stages of this reaction and about the structures and reactivities of the postulated intermediates in the FT synthesis.

In a number of studies,[28,127–135] it has been postulated that CO is hydrogenated via the pathway

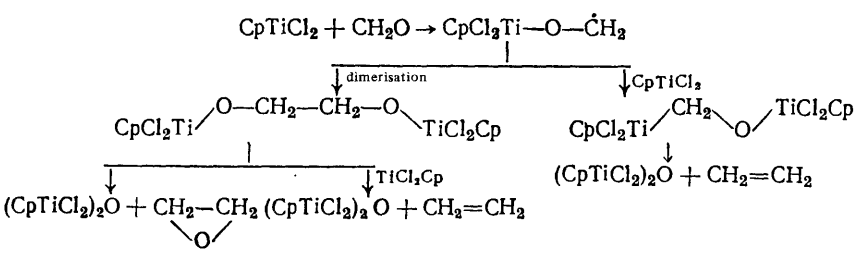
$$M{-}CO \rightarrow M{-}CHO \rightarrow M{-}CH_2OH \rightarrow M{-}CH_3,$$

in which the key intermediates are formyl and hydroxymethylene complexes.

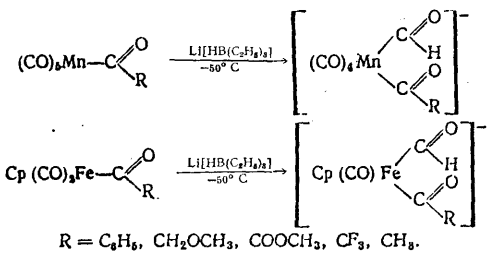
The first formylmetal complex has been obtained in a reaction with participation of the mixed anhydride of formic and acetic acids.[136] Subsequently the possibility of the hydride attack on the carbonyl coordinated in the metal complex was demonstrated convincingly in a series of model systems. Initially a large set of anionic formylmetal complexes was obtained by treating various metal carbonyls with strong hydride donors such as the trialkoxyboron hydrides $Na^+HB(OCH_3)_3^-$ and $K^+HB[C_3H_7\text{-iso}]_3^-$.[137] The structures of the mononuclear formylmetal complex $(C_2H_5)_2\overset{+}{N}$.[3,5-$(CH_3)_2C_6H_3O)_3P$]$(CO)_3FeCHO^-$ and the dinuclear complex $(C_2H_5)_4\overset{+}{N}(CO)_9Re_2CHO^-$ have been most fully characterised.[138,139]

The formation of a series of unstable formylmetal complexes of many metals has been demonstrated with the aid of physicochemical analytical methods (IR spectroscopy, ^{13}C NMR, and especially ^1H NMR, because the proton in the $-C\overset{O}{\diagdown\!\!\diagup H}$ group gives rise to the characteristic chemical shift δ = 14–16 p.p.m.).[140] It is of interest that, on treating the anionic ion complex $(CO)_4FeCHO^-$ with hydrogen chloride, the formation of formaldehyde was observed. Treatment of osmium and iridium carbonyl clusters with hydride donors of the type of $Li[HB(C_2H_5)_3]$ leads to the reduction of one of the carbonyl ligands to the formyl ligand and the formation of the cluster anions $[Os_3(CO)_{11}CHO^-]$ and $[Ir_4(CO)_{11}CHO^-]$.[141,142] Carbonyl complexes containing acyl ligand as well as the formyl

Scheme 7



ligand synthesised:[143]

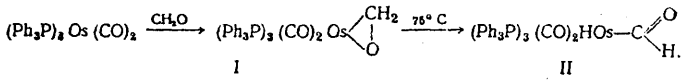


$R = C_6H_5$, CH_2OCH_3, $COOCH_3$, CF_3, CH_3.

The study of the properties of the fairly stable anionic iron carbonyl complex $[(C_6H_5O)_3P](CO)_3Fe-CHO$ showed that the formyl complexes can function also as hydride donors in relation to ketones, alkyl halides, and metal carbonyls (in the last case a new formylmetal complex is formed) and as "the target" of further hydride attack.[137,138]

Quantum-chemical calculations[144] indicate the instability of the formyl complex $[(CO)_4FeCHO]^-$, but analogous calculated data of the same workers[145] show that the alkali metal ion (Li^+), coordinated to the carbonyl ligand of the $[HFe(CO)_4]^-$ anion, promotes the insertion of CO in the Fe–H bond (the migration of the hydride group to the carbonyl ligand), affording a stable formyl complex in which the alkali metal ion is coordinated to the formyl oxygen.

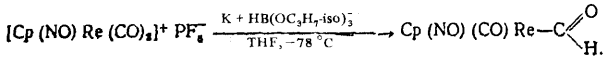
The neutral formylmetal complex (II) and not the anionic complex is probably a closer analogue of the surface intermediates formed in the FT synthesis. It was first detected when formaldehyde was added to an osmium carbonyl complex with subsequent rearrangement:[146]



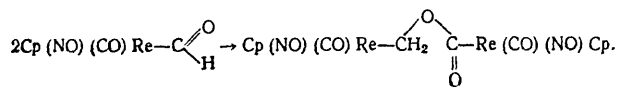
I II

The complex (I) contains coordinated formaldehyde, which can be regarded as a tautomer of the hydroxymethylene ligand $-C\begin{matrix}H\\OH\end{matrix}$.

The reduction of the carbonyl ligand to the formyl ligand via external transfer of hydride hydrogen was first achieved by means of the reaction [147]

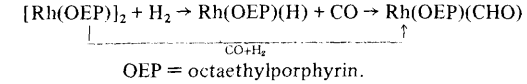


The complex Cp(NO)(CO)ReCHO has also been synthesised, isolated, and identified in other studies.[148,149] It has been shown that the formyl complex can behave as a hydride donor in relation to the formyl group:[150]



According to numerous data obtained in the study of the reactions leading to the formyl complexes of rhenium,[147–149] titanium,[151] and niobium and iron,[152] an obligatory condition for the formation of such compounds is probably only the outer-sphere transfer of hydride hydrogen as a result of the nucleophilic attack by strong hydride on the coordinated carbonyl.

However, there have been a number of reports[153–156] about the inner-sphere hydride transfer in carbonyl hydride complexes. Thus the complex $[CpFe(CO)_2H]$ in solution in an alcohol R–OH forms the intermediate [CpFe(CO)(CHO)(ROH)], in which the formate HCOOR is produced as a result of the interaction between the ligands CHO and R–OH.[153] The synthesis of a formyl complex by the direct insertion of CO in the M–H bond has also been reported:[157–158] the authors of these studies achieved the following reactions:

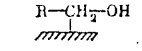


OEP = octaethylporphyrin.

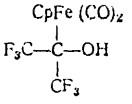
The formyl complex proved to be stable in the solid state and in solution in benzene.

Thus the possibility of the existence of the structures $M-C\begin{matrix}O\\H\end{matrix}$ as intermediates in the FT synthesis has been established for a large group of metals.

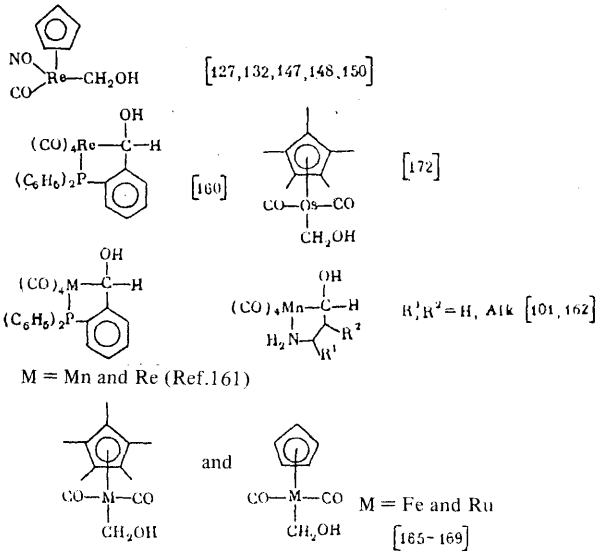
It was noted above that the involvement of the α-hydroxymethylene complex



as the most important intermediate has also been postulated in the mechanisms of the FT synthesis based on the insertion of CO. A structure close to the hydroxymethylene structure was first identified by Blackmore et al.:[159]



Subsequently it was possible to obtain similar complexes for rhenium,[101,127,132,147,148,150,160–162] osmium,[163,164] iron,[119,165–169] ruthenium,[165–169] manganese,[101,161,162] and rhodium.[170,171] Some of them are presented below [the numerals in square brackets denote references (Translator)]:



M = Mn and Re (Ref. 161)

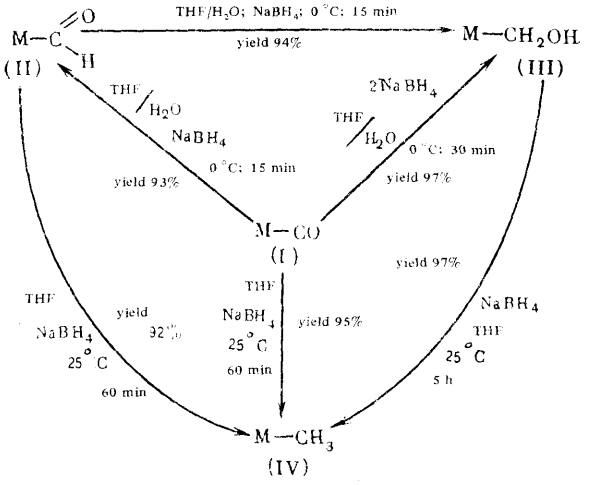
and

All the intermediate forms in the CO hydrogenation reaction in the presence of model systems have been isolated and identified.[148–150] The reduction of CO in the mononuclear rhenium

carbonyl complex has been achieved using $NaBH_4$ as the reductant.[148] The existence of the postulated stages and intermediates in the FT synthesis, namely M–CO, M–CHO, $M-CH_2OH$, and $M-CH_3$, has been demonstrated.

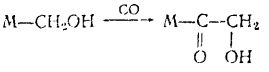
The authors were able to obtain, isolate, and identify the following compounds: $CpRe(CO)(NO)CHO$ (II), $CpRe(CO)(NO)CH_2OH$ (III), and $CpRe(CO)(NO)CH_3$ (IV). It was established that the reduction reaction pathways are in accordance with the parallel-consecutive Scheme 8:

Scheme 8

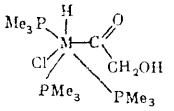


Similar results have been obtained in other studies.[149,150]

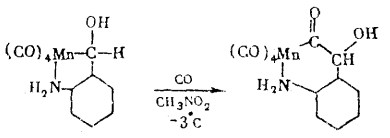
Although the possibility of the migration insertion of CO in the M–C bond has been demonstrated,[85–87] the attempts to achieve the formation of an α-hydroxyacyl complex in the presence of the hydroxylated complexes indicated via the reaction



were unsuccessful.[132] Such a hydroxyacyl complex is assumed to be an intermediate in certain mechanisms of the FT synthesis. A complex of this kind has, however, been obtained recently by the oxidative addition of 2,5-dihydroxy-1,4-dioxan to $(C_8H_{14})M(PMe_3)_3Cl$, where M = Ir or Rh:[102]

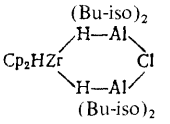


A hydroxyacyl complex is also formed in the carbonylation of an α-hydroxyalkyl complex:[101]

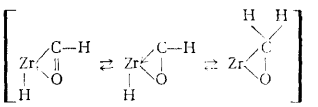


The possibility of the formation of diacyl complexes of the type $PhCH_2-C(=O)-C(=O)-M(CO)_4$ as a result of the double insertion of CO has been demonstrated.[173,174]

Cases are known where the hydrogenation of carbonyl ligands leads to the formation of not only the oxygen-containing products, typical for catalytic reactions based on CO and H_2. Thus it has been shown[175] that the following complex is formed in a solution of diisobutylaluminium hydride (DIBAH) in the presence of Cp_2ZrCl_2:

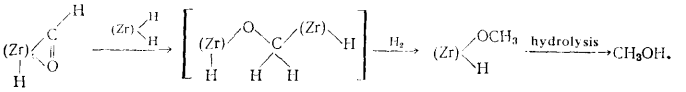


Its treatment with carbon monoxide at a pressure of 1–4 atm and room temperature leads to the precipitation of $CpZrCl_2$ and the formation of a mixture of aluminium alkyls, the hydrolysis of the latter resulting in the formation of aliphatic C_1-C_5 n-alcohols. The proposed reaction mechanism includes the dissociation of the complex with elimination of DIBAH and the liberation of a coordination site at the Zr atom. Intramolecular migration of the Zr–H hydride or external attack on the Al–H hydride is tentatively the first stage in the reduction of CO. There are data indicating the stoichiometric reduction of CO to methanol using pentadienylzirconium complexes.[127,153] On the basis of a series of indirect data, it has been postulated that a formylzirconium hydride complex is a key intermediate:



Such binding of the formyl ligand ensures, according to the authors, its stabilisation. The methoxy-ligand is formed in accordance with Scheme 9:

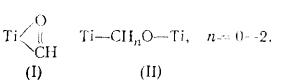
Scheme 9



A similar scheme has been described by Fachinetti et al.[176]

C_1-C_4 hydrocarbons have been obtained by treating $(CO)_5MnCH_3$ or $CpFe(CO)_2CH_3$ with carbon monoxide and B_2H_6.[177]

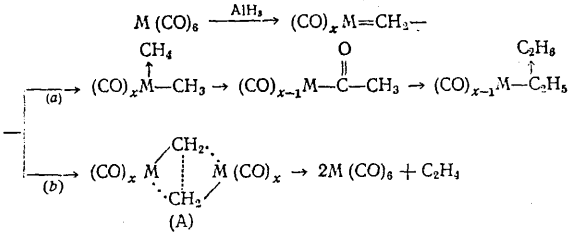
The homogeneous hydrogenation of CO to methane has been achieved[129] using $Cp_2Ti(CO)_2$. After the reaction, the active titanium complex is converted into the inactive octanuclear cluster $Cp_6Ti_8O_8$, whose formation is attributed to the liberation of water in the methane formation process. The π-formyl (or η^2-formyl) complex (I) or the μ_2-complex (II) is an intermediate in this case:



The stoichiometric reduction of CO in the interaction of $CpNbH_3$ with the metal carbonyls $M(CO)_6$, where M = Mo, W, or Cr, at 45 °C and a pressure of 1 atm in the presence of hydrogen leads to the formation of a mixture of C_1-C_3 hydrocarbons (the main product is C_2H_6).[178]

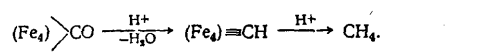
The stoichiometric model reaction involving the multistage reduction of CO to valeric acid has been achieved recently. After treatment with strong hydrogenating agents ($LiAlH_4$ or $NaBH_4$), the complex $[CpFe(CO)_2(PMe_3)]^+PF_6^-$ was converted into $Cp(PMe_3)(CO)FeMe$. Treatment of this complex with carbon monoxide at atmospheric pressure in the presence of $AgBF_4$ in tetrahydrofuran (THF) or CH_2Cl_2 led to the acyl complex $Cp(PMe_3)(CO)FeC(O)Me$, the reduction of which with tetrahydroborates afforded the alkyl complex $Cp(PMe_3)(CO)FeEt$. Numerous repetition of the CO insertion reaction and of the reduction of the resulting acyls made it possible to obtain the compound $Cp(PMe_3)$. .$(CO)FeC(O)Bu$. Finally treatment of this acyl complex with bromine water led to valeric acid $CH_3(CH_2)_3COOH$.[179]

The conversion of CO and H_2 into ethylene with a selectivity of 95% (the remainder being ethane and traces of methane and propane) in the $M(CO)_6$ (M = Cr, Mo, or W) system in the presence of a fourfold excess of AlH_3 in THF at 22 °C has been reported.[180] Experiments with deuterium have shown that AlH_3 is the only source of hydrogen. In order to account for the "anomalous" selectivity with respect to ethylene, the authors suggested the existence of carbene intermediates (A):

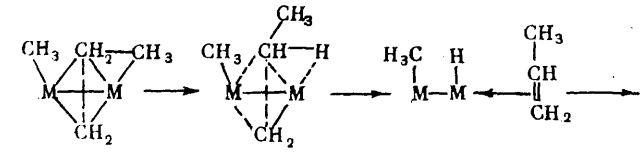


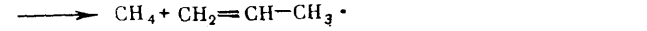
The pathway (*a*) includes the CO insertion stage leading to the formation of C_2 and C_3 hydrocarbons, while the pathway (*b*) leads to the dimerisation of the carbene intermediates, which gives rise to ethylene. The pathway (*b*) is probably preferred. Similar conclusions have been reached in other investigations.[181,182]

An interesting method of reducing CO by protonating polynuclear clusters with strong acids has been applied.[183] Treatment of the anionic cluster $[Fe_4(CO)_{13}]^{2-}$ with the strong protonating agent HSO_3CF_3 at room temperature led to the formation of methane, its yield depending greatly on the acidity of the medium. Isotope data showed that methane is formed from the carbonyl ligand as a result of the direct attack by an acid proton; after the elimination of water, a carbide is formed whose hydrogenation leads to methane:

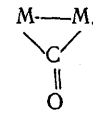


Interesting data supporting the carbide mechanism of the FT synthesis have been obtained in a study of the interaction of $[(RhC_5Me_5)_2Cl_4]$ with $LiCH_3$, which resulted in the formation of *cis*- and *trans*-$[(RhC_5Me_5)_2(\mu\text{-}CH_2)_2Me_2]$.[184] Propene, methane, and traces of ethylene are formed on pyrolysis of the *trans*-isomer, which confirms the possibility of the polymerisation of methylene species on the metal surface, initiated by a metal hydride, as the key stage in the carbide mechanism:

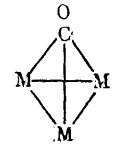




Much work has been devoted in recent years to the creation of homogeneous catalysts of the FT synthesis. It was shown in 1977[185] that the carbonyl clusters $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ in toluene at 140 °C, a synthesis mass ratio ($CO:H_2$ = 1:4), and a pressure of 2 atm convert the CO + H_2 mixture into methane at an insignificant rate (the degree of conversion of CO is 1% after 3–5 days). The addition of PPh_3 or PMe_3 increases slightly the activity of the catalysts and leads to the appearance of traces of ethane and propane. The authors note that the reduction of CO requires specifically polynuclear clusters in order to achieve the many-centre CO–metal interaction. Such activation of CO reduces greatly the C–O bond order.[19,186] It has been suggested[19,187] that cluster systems make it possible to model more effectively the characteristics of heterogeneous catalysis than mononuclear homogeneous systems. When CO is coordinated to two or more transition metal atoms, the bond order is greatly reduced. Thus whereas terminal carbonyl ligands are usually characterised by $\nu(CO) = 2000-2100\ cm^{-1}$, for bridged carbonyl complexes $\nu(CO) = 1700-1850\ cm^{-1}$ is characteristic of CO ligands bound to two metal atoms:



The bridged carbonyls linked to three metal atoms,



are characterised by an even greater decrease in the bond order involved in the binding of CO, because $\nu(CO) \simeq 1600\ cm^{-1}$ for μ^3-CO.[21]

The significant role of Lewis acids as effective cocatalysts in the homogeneous CO hydrogenation reaction has been confirmed in a study[188] that was a continuation of investigations initiated by Thomas et al.[185] Thus the clusters $Ir_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Rh_4(CO)_{12}$, and $Ru_3(CO)_{12}$ exhibited a high activity in the homogeneous CO-hydrogenation reaction in $AlCl_3$, $AlBr_3$, or BBr_3 melts at 180 °C and 1 atm, the activity of, for example, $Ir_4(CO)_{12}$, being approximately 100 times greater under these conditions than in the absence of the Lewis acid.[188] The reaction products were C_1-C_4 hydrocarbons and their ratios depended greatly on the reaction conditions—temperature, pressure, and the catalytic system used.

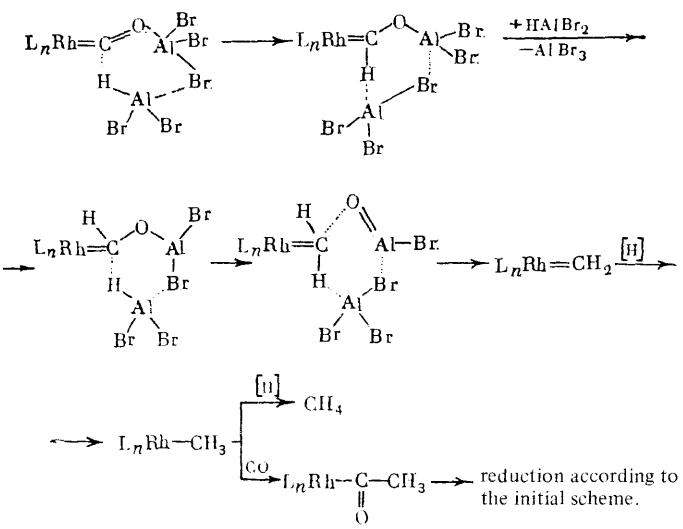
The carbonyl cluster $Os_3(CO)_{12}$ (the precursor of the catalyst) and BBr_3 (solvent and cocatalyst) proved to be active in the hydrogenation of CO to C_1-C_5 hydrocarbons.[189] It was shown that the osmium cluster $Os_2(CO)_6Br_4$, acting as the catalyst, is formed during the reaction.

Comparison of the data of Demitras and Muetterties[188] and Choi and Muetterties[189] with those of Thomas et al.[185] permits the conclusion that the presence of the Lewis acid does indeed stimulate the formation of the C–C bond in the hyrogenation of CO. It has been suggested[189] that BBr_3 facilitates the insertion of CO in the Os–C bond with formation of intermediates of the type $Os-CR-OBBr_3$.

Similar results have been obtained in the presence of the complex $Ir_4(CO)_{12}$ in a flow reactor, where the productivity of 0.2 mol of CO per mole of $Ir_4(CO)_{12}$ per minute was achieved with respect to C_1-C_6 hydrocarbons.[190]

When the $M_n(CO)_m-AlBr_3-Al$ homogeneous catalytic system was used, a mixture of C_1-C_4 hydrocarbons was formed from CO and H_2.[191,192] The metals tested fell within the following series in terms of their activities: Rh > Ir > Ru > Os > Ni. Under the catalytic conditions, an aprotic system possessing strong reducing and acid properties is formed in this case. The binding of the water evolved in the reduction process prevents the decomposition of the catalytic process. Apart from aluminium, magnesium or $LiAlH_4$ may be used as the reductant. The following mechanism has been proposed on the basis of the experimental data:[192]

Scheme 10

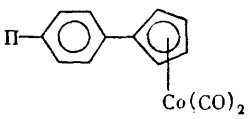


A whole series of processes involving the reduction of CO by hydrogen in the presence of soluble Rh clusters at high temperatures and very high pressures have been patented.[193] The reaction products are methanol, ethylene glycol, and propylene glycol. The true catalyst is the polynuclear anionic cluster $[Rh_{12}(CO)_{34}]^{2-}$ formed under the reaction conditions from various precursors.

It has been suggested that the rhodium bis-sulphide cluster $[Rh_{17}(CO)_{32}(S)_2]^{8-}$ be used for the conversion of the CO + H_2 mixture into aliphatic alcohols.[194]

As already mentioned above, it is best to use polynuclear metallic active centres in the hydrogenation of CO. However, some workers believe that the active centre for the hydrogenation of CO has the structure of a mononuclear complex.[133] The homogeneous hydrogenation of CO by hydrogen to ethanol (main product), ethanol, propanol, and the formates of these three alcohols using as the catalyst the mononuclear carbonyl hydride $HCo(CO)_4$, formed under the reaction conditions from the $Co_2(CO)_8$ cluster, has been reported.[195] The conversion of the CO + H_2 mixture into methanol and methyl formate has been observed using the ruthenium clusters, unstable under reaction conditions (225–275 °C, 1300 atm) as the catalyst precursors.[196] It was then established that the true reaction catalyst is mononuclear ruthenium pentacarbonyl $Ru(CO)_5$.

Mention should be made of a study[197] in which the homogeneous hydrogenation of CO to a mixture of C_1-C_{20} normal alkanes (170–200 °C, 30 atm, CO : H_2 = 1 : 3, solvent—n-octane) was achieved in the presence of an immobilised cobalt catalyst:



grafted to a polymer П. Control experiments established that activity in this reaction is shown in fact by the immobilised mononuclear cobalt centre and not by soluble cobalt compounds or metallic cobalt.

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In conclusion one should note that the enormous amount of experimental data concerning the mechanism of the FT synthesis accumulated at the present time makes it possible to assume confidently that the reaction proceeds via a multiplicity of pathways. The preference for a particular pathway is determined by the composition of the catalyst, the conditions of the synthesis, and a number of factors, the type of catalyst being decisive.

References

1. P Sabatier, J B Senderens *Compt. Rend.*, 1902, **134** 514
2. F Fischer, H Tropsch *Brennstoff. Chem.*, 1923, **4** 276
3. F Fischer, H Tropsch *Brennstoff. Chem.*, 1924, **5** 201
4. H Liebgott, W Herbert, G Baron *Erdöl, Kohle, Erdgas, Petrochem. Brennstoff. Chem.*, 1972, **25** 75
5. D Ballivet-Tkatchenko, N D Chau, H Mozzaneda, et al. *Amer. Chem. Soc. Symp. Ser.*, 1981, **152** 187
6. H Pichler, F Bellstedt *Erdöl, Kohle, Erdgas, Petrochem. Brennstoff. Chem.*, 1973, **26** 560
7. Y T Shan, A J Perrotta *Ind. Eng. Chem. Prod. Res. Dev.*, 1976, **15**(2) 123
8. H Pichler, H Schulz, D Kühne *Brennstoff. Chem.*, 1968, **49** 344
9. A N Bashkirov, Yu B Kagan, L I Zvezdkina *Dokl. Akad. Nauk SSSR*, 1956, **109** 525
10. D W Nooner, R J Oro *Adv. Chem. Ser.*, 1979, **178** 159
11. J F Knifton *J. Catal.*, 1985, **96** 439
12. R L Pruett *Ann. New York Acad. Sci.*, 1977, **295** 239
13. G A Mills, F W Steffgen *Catal. Rev. Sci. Eng.*, 1973, **8** 159
14. R Sheldon *Chemicals from Synthesis Gas Catalytic Reactions of CO and H_2*, D Reidel Publ. Co., Dordrecht, 1983, 217 pp
15. M A Vannice *Catal. Rev. Sci. Eng.*, 1978, **14** 153
16. S Uchiyama, Y Obayashi, M Shibata, et al. *J. Chem. Soc., Chem. Comm.*, 1985, 1071

17. W Keim *Catalysis in C-Chemistry* (Translated into Russian), Izd. Khimiya, Leningrad, 1987, 295 pp
18. G Henrici-Olive, S Olive *Coordination and Catalysis* (Translated into Russian), Izd. Mir, Moscow, 1980, 421 pp
19. E L Muetterties, J Stein *Chem. Rev.*, 1979, **79** 479
20. I Tkatchenko *Fundamental Research in Homogeneous Catalysis*, Plenum Press, New York, 1979, **3** 119
21. A L Lapidus, M M Savel'ev, *Uspekhi Khim.*, 1984, **53**(6) 925 [Russ. Chem. Rev., 1984(6)]
22. C K Rofer-DePoorter *Chem. Rev.*, 1981, **81** 447
23. C Masters *Adv. Organometal. Chem.*, 1979, **17** 61
24. R Ugo *Catal. Rev. Sci. Eng.*, 1975, **11** 225
25. A T Bell *Catal. Rev. Sci. Eng.*, 1981, **23** 203
26. W A Herrmann *Angew. Chem. Int. Ed.*, 1982, **21** 117
27. L C Costa *Catal. Rev. Sci. Eng.*, 1983, **25** 325
28. J A Gladysz *Adv. Organometal. Chem.*, 1982, **20** 1
29. P Biloen, W M H Sachtler *Adv. Catal.*, 1981, **30** 163
30. P Biloen *Rec. Trav. Chim. Pays-Bas*, 1980, **99**(2) 33
31. J Falbe *Chemical Feedstocks from Coal* (Translated into Russian), Izd. Khimiya, Moscow, 1980, 614 pp
32. Ya T Eidus *Uspekhi Khim.*, 1967, **36** 824 [*Russ. Chem. Rev.*, 1967(5)]
33. S M Loktev *J. Mol. Caytal.*, 1982, **17** 225
34. S M Loktev *Khim. Prom.*, 1983(5) 270
35. A L Lapidus, Kh M Minachev *Zhur. Vses. Khim. Obshch. im. Mendeleeva*, 1984, **29** 407
36. O A Tyukova *Khimicheskaya Promyshlennost' za Rubezhom* (Chemical Industry Abroad), Izd. NIITEKhIM, Moscow, 1984, Vol. 10, p. 21
37. Yu B Kagan, A Ya Rozovskii, S M Loktev, A N Bashkirov *Dokl. Akad. Nauk SSSR*, 1980, **250** 1151
38. F Fischer, H Tropsch *Ber.*, 1926(59) 830
39. S R Craxford *Trans. J. Faraday Soc.*, 1946, **42** 576
40. S R Craxford, E K Rideal *J. Chem. Soc.*, 1939, 1604
41. P R Wentercek, B J Wood, H Wise *J. Catal.*, 1976, **43** 363
42. M Araki, V Ponec *J. Catal.*, 1976, **44** 439
43. D W Goodman, J T Yates *J. Catal.*, 1983, **82** 255
44. M P Kaminsky, N Winograd, G L Geoffroy *J. Amer. Chem. Soc.*, 1986, **108** 1315
45. P Biloen, J N Nelle, W M H Sachtler *J. Catal.*, 1979, **58** 95
46. R W Joyner *Surface Sci.*, 1977, **63** 291
47. J G McCarty, H Wise *Chem. Phys. Lett.*, 1979, **61** 323
48. T N Rhodin, C F Brucker *Solid State Comm.*, 1977, **23** 275
49. B C Broden, T N Rhodin, C Brucker, Z Hurych *Surface Sci.*, 1976, **59** 593
50. J A Rabo, A P Risch, M L Poutsma *J. Catal.*, 1978, **53** 295
51. G Low, A T Bell *J. Catal.*, 1979, **57** 397
52. R Bouwman, I L C Freriks *Appl. Surface Sci.*, 1980, **4** 21
53. W M H Sachtler *Proceedings of 8th International Congress on Catalysis, West Berlin, 1984*, Verlag Chem., West Berlin, 1984, Vol. 1, p. 151
54. R C Brady, R Pettit *J. Amer. Chem. Soc.*, 1981, **103** 1287
55. R C Brady, R Pettit *J. Amer. Chem. Soc.*, 1980, **102** 6181
56. W A A van Barneveld, V Ponec *J. Catal.*, 1984, **88** 382
57. J C McCarty, H Wise *J. Catal.*, 1979, **57** 406
58. L M Tav, S Borcar, D Bianchi, C O Bennett *J. Catal.*, 1984, **87** 26
59. P P Vaishnava, P I Ktorides, P A Montano, et al. *J. Catal.*, 1985, **96** 301
60. Zhang Hong-bin, G L Schrader *J. Catal.*, 1985, **95** 325
61. J G Ekerdt, A T Bell *J. Catal.*, 1980, **62** 19
62. C J Wang, J G Ekerdt *J. Catal.*, 1983, **80** 172
63. C J Wang, J G Ekerdt *J. Catal.*, 1984, **86** 239
64. M Pijolat, V Perrichon *Appl. Catal.*, 1985, **13** 321
65. H Storch, N Golumbic, R Anderson *The Fischer-Tropsch and Related Syntheses* (Translated into Russian), Inostr. Lit., Moscow, 1954, 416 pp
66. H Kölbel, G Patschke, H Hammer *Brennstoff. Chem.*, 1966, **47** 4
67. H Kölbel, G Patschke, H Hammer *Z. Phys. Chem.*, Frankfurt, 1966, **48** 3
68. M V C Sastri, R Balaji, B Gupta, B Viswanatham *J. Catal.*, 1974, **32** 325
69. H Kölbel, D Hanus *Chem. Ind. Techn.*, 1974, **46** 1042
70. M J Heal, E C Leisegang, R G Torrington *J. Catal.*, 1978, **51** 314
71. H Kölbel, K D Tillmetz *J. Catal.*, 1974, **34** 307
72. A Ya Rozovskii *Kinetika i Kataliz*, 1964, **5** 609
73. A Ya Rozovskii *Kinetika i Kataliz*, 1967, **8** 1143
74. H Pichler, H Schulz *Chem. Ind. Techn.*, 1970, **42** 1102
75. H Schulz, A Z el Deen *Fuel Process. Technol.*, 1977, **1** 31
76. G Henrici-Olive, S Olive *Angew. Chem. Int. Ed.*, 1976, **15** 136
77. G Henrici-Olive, S Olive *J. Mol. Catal.*, 1982, **16** 187
78. G Henrici-Olive, S Olive *Angew. Chem. Int. Ed.*, 1979, **18** 77
79. G Henrici-Olive, S Olive *J. Mol. Catal.*, 1984, **24** 7
80. G Henrici-Olive, S Olive *J. Catal.*, 1979, **60** 481
81. G Henrici-Olive, S Olive *J. Mol. Catal.*, 1982, **16** 111
82. G Henrici-Olive, S Olive *J. Mol. Catal.*, 1983, **19** 397
83. G Henrici-Olive, S Olive *J. Mol. Catal.*, 1983, **18** 367
84. L S Benner, Y H Lai, K P C Vollhardt *J. Amer. Chem. Soc.*, 1981, **103** 3609
85. G Henrici-Olive, S Olive *Coordination Catalysis* (Translated into Russian), Izd. Mir, Moscow, 1980, 421 pp
86. K Noak, F Calderazzo *J. Organometal. Chem.*, 1967, **10** 101
87. F Calderazzo *Angew. Chem. Int. Ed.*, 1977, **16** 299
88. Yu B Kagan, E V Slivinskii, Yu P Voitsekhovskii, et al. *Neftekhimiya*, 1986, **26** 532
89. Yu B Kagan, E V Slivinskii, Yu P Voitsekhovskii, et al. *Kinetika i Kataliz*, 1985, **26** 1018
90. K G Anderson, J G Ekerdt *J. Catal.*, 1985, **95** 602
91. T Fukushima, H Arakawa, M Ichikawa *J. Chem. Soc. Chem. Comm.*, 1985, 729
92. S M Loktev, A N Bashkirov, Yu B Kagan, et al. *Dokl. Akad. Nauk SSSR*, 1973, **211** 1126
93. Yu B Kagan, S M Loktev, V A Zhilin, et al. *USSR P. 806669;* Byul. Izobret., 1981(8) 36
94. Yu B Kagan, E V Slivinskii, Yu P Voitsekhovskii, et al. *USSR P. 1198053;* Byul. Izobret., 1985(46) 97
95. S M Loktev, Yu B Kagan, E V Slivinskii, et al. *USSR P. 1097594;* Byul. Izobret., 1985(22) 47
96. E S Kline, R Kafafi, R H Hauge, J L Margrave *J. Amer. Chem. Soc.*, 1985, **107** 7559
97. Yu B Kagan, G V Isagulyants, V A Zhilin, et al. *Kinetika i Kataliz*, 1974, **15** 1518
98. E V Slivinskii, V Yu Rumyantsev, Yu B Kagan, S M Loktev *Neftekhimiya*, 1986, **26** 642
99. Yu B Kagan, E V Slivinskii, Yu P Voitsekhovskii, et al. *5 Mezhdunarodnyi Simpozium po Svyazi Mezhdu Gomogennym i Geterogennym Katalizom: Tezisy Dokladov* (The 5th International Symposium on the Relation between Homogeneous and Heterogeneous Catalysis. Abstracts of Reports), Izd. Nauka, Novosibirsk, 1986 p. 112

100. J A Connor *Top. Cur. Chem.*, 1977, **71** 71
101. G D Vaughn, J A Gladysz *J. Amer. Chem. Soc.*, 1986, **108** 1473
102. D Milststein, W C Fultz, J C Calabrese *J. Amer. Chem. Soc.*, 1986, **108** 1336
103. L S Glebov, A I Mikaya, A E Jatsenko, et al. *Tetrahedron Lett.*, 1985, **26** 3373
104. Yu B Kagan, E V Slivinskii, V Yu Rumyantsev, et al. *Kinetika i Kataliz*, 1986, **27** 1017
105. E V Slivinskii, Yu P Voitsekhovskii, V Yu Rumyantsev, et al. *Kinetika i Kataliz*, 1986, **27** 1511
106. E V Slivinskii, Yu P Voitsekhovskii, L I Zvezdkina, et al. *Kinetika i Kataliz*, 1987, **28** 502
107. W A A van Barneveld, V Ponec *J. Catal.*, 1978, **51** 426
108. Yu B Kryukov, Abstract of Doctoral Thesis in Chemical Sciences, Institute of Petrochemical Synthesis, USSR Academy of Sciences, Moscow, 1969
109. H Matsumoto, C O Benett *J. Catal.*, 1978, **53** 331
110. H H Nijs, P A Jacobs *J. Catal.*, 1980, **66** 401
111. J Hackenbruch, W Keim, M Röper, H Strutz *J. Mol. Catal.*, 1984, **26** 129
112. M Ichikawa, T Fukushima *J. Chem. Soc., Chem. Comm.*, 1985, **321**
113. T Fukushima, M Ichikawa, S Matsushita, et al. *J. Chem. Soc. Chem. Comm.*, 1985 1209
114. M Ichikawa, A J Lang, D F Shriver, W M H Sachtler *J. Amer. Chem. Soc.*, 1985, **107** 7216
115. A Razzaghi, J P Hinderman, A Kiennermann *Appl. Catal.*, 1984, **13** 193
116. M Inone, T Miyake, Y Takegami, T Inui *Appl. Catal.*, 1984, **11** 103
117. J A Sibilia, J M Dominguez, R G Herman, K Klier *Prepr. Div. Fuel Chem. Amer. Chem. Soc.*, 1984, **29** 261
118. G A J Huff, C N Satterfield *J. Catal.*, 1984, **85** 370
119. H Berke, G Hutter, G Weiler, L Zsolnai *J. Organometal. Chem.*, 1981, **219** 353
120. L E McCandlish *J. Catal.*, 1983, **83** 362
121. E L Hool *Organometallics*, 1986, **5** 587
122. L R Beanan, J B Keister *Organometallics*, 1985, **4** 1713
123. S Gambarotta, C Floriani, A Chiesi-Villa, C Guastini *Organometallics*, 1986, **5** 2425
124. P A Bianconi, I D Williams, M P Engeler, S J Lippard *J. Amer. Chem. Soc.*, 1986, **108** 311
125. H Behrens, R Weber *Z. anorg. Chem., B*, 1957, **291** 122
126. J R Blackborow, R J Daroda, G Wilkinson *Coord. Chem. Rev.*, 1982 **43** 17
127. J R Sweet, W A G Grahman *J. Amer. Chem. Soc.*, 1982, **104** 2811
128. J M Manriquez, D R McAlister, R D Sanner, J E Bercaw *J. Amer. Chem. Soc.*, 1976, **98** 6733
129. J C Huffman, J G Stone, W C Krusell, K G Caulton *J. Amer. Chem. Soc.*, 1977, **99** 5829
130. J A Labinger, K S Wong, W R Scheidt *J. Amer. Chem. Soc.*, 1978, **100** 3254
131. W Taw, G Y Lin, W K Wang, et al. *J. Amer. Chem. Soc.*, 1982, **104** 141
132. C P Casey, M A Andrews, D R McAlister, et al. *J. Mol. Catal.*, 1981, **13** 43
133. K G Caulton *J. Mol. Catal.*, 1981, **13** 71
134. W Keim, M Berger, A Eisenbeis, et al. *J. Mol. Catal.*, 1981, **13** 95
135. R C Schoening, J L Vidal, R A Fiato *J. Mol. Catal.*, 1981, **13** 83
136. J P Collman, S R Winter *J. Amer. Chem. Soc.*, 1973, **95** 4089
137. C P Casey, S M Neumann *J. Amer. Chem. Soc.*, 1978, **100** 2544
138. C P Casey, S M Neumann, M A Andrews, D R McAlister *Pure Appl. Chem.*, 1980, **52** 625
139. J A Gladysz, W Tam *J. Amer. Chem. Soc.*, 1978, **100** 2545
140. C P Casey, S M Neumann *J. Amer. Chem. Soc.*, 1976, **98** 5395
141. R L Pruett, R C Schoening, J L Videl, R A Fiato *J. Organometal. Chem.*, 1979, **182** C57
142. G R Steinmet, G L Geoffrey *J. Amer. Chem. Soc.*, 1981, **103** 1278
143. J A Gladysz, W Tam *Tetrahedron Lett.*, 1978, 319
144. G Blyholder, K M Zhao, M Lawless *Organometallics*, 1985, **4** 1371
145. G Blyholder, K M Zhao, M Lawless *Organometallics*, 1985, **4** 2170
146. K L Brown, G R Clark, C E L Headford, et al. *J. Amer. Chem. Soc.*, 1979, **101** 503
147. C P Casey, M A Andrews, J E Rinz *J. Amer. Chem. Soc.*, 1979, **101** 741
148. W A G Graham, J R Sweet *J. Organometal. Chem.*, 1979, **173** C9
149. W Tam, W K Wong, J A Gladysz *J. Amer. Chem. Soc.*, 1979, **101** 1589
150. C P Casey, M A Andrews, D R McAlister, J E Rinz *J. Amer. Chem. Soc.*, 1980, **102** 1927
151. L J Guggenberger, F N Teble *J. Amer Chem. Soc.*, 1976, **98** 4137
152. J A Labinger, K S Wang, W R Scheidt *J. Amer. Chem. Soc.*, 1978, **100** 3254
153. J M Manriquez, D R McAlister, R D Sanner, J E Bercaw *J. Amer. Chem. Soc.*, 1978, **100** 2716
154. R S Threlkel, J E Bercaw *J. Amer. Chem. Soc.*, 1981, **103** 2650
155. A Cameron, V H Smith, M C Balrd *Organometallics*, 1983, **2** 466
156. P Belmonte, R R Schrock, M R Churchill *J. Amer. Chem. Soc.*, 1980, **102** 2858
157. B B Wayland, B A Woods *J. Chem. Soc. Chem. Comm.*, 1981, 700
158. B B Wayland, B A Woods, R Pierce *J. Amer. Chem. Soc.*, 1982, **104** 302
159. T Blackmore, M I Bruce, P J Davidson, et al. *J. Chem. Soc. A*, 1970, 3153
160. G D Vaughn, C E Strause, J A Gladysz *J. Amer. Chem. Soc.*, 1986, **108** 1462
161. G D Vaughn, J A Gladysz *J. Amer. Chem. Soc.*, 1981, **103** 5608
162. G D Vaughn, J A Gladysz *Organometallics*, 1984, **3** 1596
163. C E L Headford, W R Roper *J. Organometal. Chem.*, 1980, **198** C7
164. G R Clark, C E L Headford, K Marsden, W R Roper *J. Organometal. Chem.*, 1982, **231** 335
165. G O Nelson *Organometallics*, 1983, **2** 1474
166. C Lapinte, D Astruc *J. Organometal. Chem.*, 1984, **260** C13
167. Y C Lin, D Milstein, S S Wreford *Organometallics*, 1983, **2** 1461
168. C Lapinte, D Astruc *J. Chem. Soc., Chem. Comm.*, 1983, 430
169. T Bodnar, E Coman, K Menard, A Cutler *Inorg. Chem.*, 1982, 1275

170. B B Wayland, B A Woods, V M Minda *J. Chem. Soc. Chem. Comm.*, 1982, 634
171. S L van Voorhees, B B Wayland *Organometallics*, 1985, **4** 1887
172. C J May, W A G Graham *J. Organometal. Chem.*, 1982, **234** C49
173. H Alper, H Abbayes *J. Organometal. Chem.*, 1977, **134** C11
174. J N Cawse, R A Fiato, R L Pruett *J. Organometal. Chem.*, 1979, **172** 405
175. L I Shoer, J Schwartz *J. Amer. Chem. Soc.*, 1977, **99** 5831
176. G Fachinetti, C Floriani, F Morchetti, S Merlino *Chem. Comm.*, 1976, 552
177. R E Stimson, D F Shriver *Organometallics*, 1982, **1** 787
178. K S Wong, J A Labinger *J. Amer. Chem. Soc.*, 1980, **102** 3652
179. S L Brown, S G Davies *J. Chem. Soc. Chem. Comm.*, 1986, 84
180. C Masters, C Woude, J A Doorn *J. Amer. Chem. Soc.*, 1979, **101** 1633
181. P T Wolczanski, R S Threlkel, J E Bercow *J. Amer. Chem. Soc.*, 1979, **101** 218
182. J A Marsella, K Folting, J C Huffman, K G Caulton *J. Amer. Chem. Soc.*, 1981, **103** 5596
183. K Whitmire, D E Shriver *J. Amer. Chem. Soc.*, 1980, **102** 1456
184. K Isobe, D G Andrews, B E Mank, P M Maittlis *J. Chem. Soc. Chem. Comm.*, 1981, 805
185. M G Thomas, B F Beier, E L Muetterties *J. Amer. Chem. Soc.*, 1976, **98** 1296
186. E L Muetterties *Bull. Soc. Chim. Belg.*, 1976, **85** 451
187. E L Muetterties, T N Rhodin, E Band, et al. *Chem. Rev.*, 1979, **79** 91
188. G C Demitras, E L Muetterties *J. Amer. Chem. Soc.*, 1977, **99** 2796
189. H W Choi, E Muetterties *Inorg. Chem.*, 1981, **20** 2664
190. H K Wang, H W Choi, E L Muetterties *Inorg. Chem.*, 1981 **20** 2661
191. A L Lapidus, M M Savel'ev *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 335
192. A L Lapidus, M M Savel'ev, L T Kondrat'ev, E V Yastrebova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1564
193. A K Smith, J M Basset *J. Mol. Catal.*, 1977, **3** 229
194. J L Vidal, W E Walker, R L Pruett, et al. *Fundamental Research in Homogeneous Catalysis*, Plenum Press, New York, 1979, Vol. 3, p. 499
195. J W Rathke, H M Feder *J. Amer. Chem. Soc.*, 1978, **100** 3625
196. J S Bradley *J. Amer. Chem. Soc.*, 1979, **101** 7419
197. P Perkins, K P C Volhardt *J. Amer. Chem. Soc.*, 1979, **101** 3985

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The synthesis of ethylene glycol from formaldehyde

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ABSTRACT. The literature and patent data on the hydroformylation of formaldehyde to glycolaldehyde—an intermediate in the synthesis of ethylene glycol—are surveyed. The principal types of catalytic systems based on rhodium and cobalt carbonyl complexes and the characteristic features of the reaction are examined and compared with the hydroformylation of olefins. The reaction mechanism is discussed in the light of the reactions of the formaldehyde complexes of transition metals.
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I. Introduction

The wide-scale employment of ethylene glycol in various fields has led to an increasing requirement for this compound. The world output of ethylene glycol in 1983 was 4.5 million tonnes.[1] It is obtained industrially from ethylene as the raw material, the cost of which has been continuously growing.

The search for new methods of synthesising ethylene glycol, especially without involving ethylene, is of practical interest. Methods based on the use of the synthesis gas (Table 1) are recognised as being the most promising.

According to technical-economic forecasts,[1] processes involving the carbonylation of formaldehyde are especially attractive. Information about them is available in recently published monographs[3–6] and reviews.[2,7–15]

Apart from the procedures listed in Table 1, the following methods of synthesis of ethylene glycol are known.

(1) Condensation of formaldehyde:

$$2\,CH_2O \rightarrow HOCH_2CHO \xrightarrow{H_2} CH_2OH{-}CH_2OH.$$

The process is carried out[16] in the presence of alkaline catalysts, deposited on zeolites, at 90–100 °C using aqueous formaldehyde solutions. The yield of glycolaldehyde is about 12% and the rate of its formation is 2.5–4.5 mol litre^{-1} h^{-1}.

(2) Redox reaction (radical coupling, radical condensation):[8,17–20]

$$CH_3OH + CH_3OH \rightarrow CH_2OH{-}CH_2OH + (H_2),$$
$$CH_3OH + CH_2O \rightarrow CH_2OH{-}CH_2OH.$$

The reaction is carried out either in the liquid phase or in the gas phase at a pressure of 5–14 MPa at 225–350 °C using radical generators. The yield of ethylene glycol is 200 kg m^{-3} h^{-1}.

(3) The coupling of methyl formate with formaldehyde:[5,21]

$$HCOOCH_3 + CH_2O \rightarrow HOCH_2COOCH_3.$$

Table 1. The synthesis of ethylene glycol and its derivatives.[1]

Starting materials	Catalyst	Temperature, °C	Pressure MPa	Products	Selectivity, %	Turnover number, 10^3 s^{-1}
$CO + H_2$	$Cs_3Rh_{17}(CO)S_2$	200	100	ethylene glycol methanol	69 21	18.1
$CH_3OH + CO + O_2$	PdI_2—$CuSO_4$	120	2	dimethyl oxalate dimethyl carbonate	78 22	37.0
	Pd/γ-Al_2O_3—NO	120	2	dimethyl oxalate dimethyl carbonate	80 20	21.7
$HCHO + CO + H_2O$	HF	50	2	glycolic acid	94	0.07
$CH_2OCH_2OCH_2O + CO + H_2O$	$RhCl_3$—HI	150	7	glycolic acid acetic and formic acids	39 61	6.4
Paraformaldehyde + H_2 + CO	$Co_2(CO)_8$	120	10	glycolaldehyde methanol	77 23	11.6
	$RhCl(CO)(PPh_3)_2$—NEt_3—PPh_3			glycolaldehyde methanol and carbohydrates	76 24	148.0
Paraformaldehyde + BuOH + H_2 + CO	$Co(OAc)_2(C_5Me_5)$	160	19	monobutyl ether of ethylene glycol dibutyl ether of ethylene glycol methanol	62 6 4	18.8
$H_2C(OMe)_2 + CO + H_2$	$Co_2(CO)_8$	180	20	methyl ether of ethylene glycol dimethyl ether of ethylene glycol methanol and others	46 9 45	3.1

The reaction is performed at atmospheric pressure and a temperature of about 90 °C in the presence of strong acids—HF, H_2SO_4, etc. (selectivity up to 90%). The replacement of methyl formate by formic acid leads to the formation of glycolic acid.

This review considers the method of synthesis of glycolaldehyde (the intermediate in the synthesis of ethylene glycol) by the hydroformylation of formaldehyde:

$$HCHO + CO + H_2 \rightarrow HOCH_2CHO \xrightarrow{H_2} CH_2OH{-}CH_2OH.$$

II. The state of research into formaldehyde hydroformylation processes

Hitherto this reaction has been usually carried out as a homogeneous-catalytic process in solutions of cobalt and rhodium complexes. The subsequent reduction of glycolaldehyde to ethylene glycol was carried out in the same reactor using ruthenium catalysts.[22]

A process involving the hydroformylation of formaldehyde on heterogeneous rhodium catalysts modified by tertiary phosphines immobilised on solid carriers has been patented:[23] at 25 MPa and 120–160 °C, the degree of conversion of formaldehyde into glycolaldehyde in the liquid-phase process is 60–80%. Paraformaldehyde, trioxan, or an aqueous formaldehyde solution can serve as the starting material. In the last case, the selectivity with respect to the target product is low because of the acceleration of the side reaction involving the hydrogenation of glycolaldehyde to methanol. The use of trioxan makes it necessary to carry out the reaction at high temperatures (~300 °C) in order to form monomeric formaldehyde; for the depolymerisation of paraformaldehyde it is sufficient to carry out the reaction at temperatures in the range 90–130 °C,[24] which makes formaldehyde the most suitable reagent.

The high reactivity of formaldehyde and glycolaldehyde leads to many side and secondary reactions, which lower the selectivity of the hydroformylation. Among them, the main reactions are the Cannizzaro–Tishchenko reaction, hydrogenation to methanol and its conversion into higher homologues, and the aldol condensation of formaldehyde to carbohydrates. The last three reactions are catalysed by the components of the catalytic system and the condensation involves the target product (glycolaldehyde) in undesirable reactions. Undesirable side and secondary reactions are accelerated particularly strongly by cobalt catalysts. Thus in the hydroformylation of formaldehyde in the presence of $Co_2(CO)_8$ in dioxan at 120 °C, the maximum selectivity does not exceed 40%; under the same conditions, $RhCl(CO)(PPh_3)_2$ affords glycolaldehyde in 85% yield.[25]

The severe hydroformylation conditions (pressure 15.0–25.0 MPa, temperature 150–170 °C), the low selectivity, and the low rate of reaction in the presence of cobalt catalysts (turnover number 11.6 s^{-1} [26] compared with 148.0 s^{-1} for the rhodium system[27]) made it necessary to give preference to rhodium catalysts. The patent and scientific publications in recent years have been concerned predominantly with processes occurring in solutions of rhodium complexes.

Satisfactory parameters (selectivity up to 95%, degree of conversion of formaldehyde more than 95%, catalyst turnover number about 150 × 10^3 s^{-1}) are attained when promoting agents are introduced into the phosphine–rhodium catalytic system: acids of organic[28] and inorganic[29] origin, organometallic compounds or metal salts,[30–35] and bases.[36,37]

The technological formulation of the synthesis of ethylene glycol by the hydroformylation of formaldehyde is at present in the research and development stage; in the versions proposed, either a single-stage process, combining the hydroformylation of formaldehyde and the hydrogenation of glycolaldehyde in a single reactor,[38] or a two-stage process,[39] in which the catalyst of the first stage is a rhodium complex (in solution, in the form of a suspension, or deposited on a solid carrier), are used. It has been proposed that the process be carried out with a low degree of conversion of formaldehyde[40] in order to reduce the amount of condensation products.

Rhodium catalysts modified with PAr_3 are most often used; they are deactivated, as in the hydroformylation of olefins,[41,42] by the transformation of the phosphine ligand resulting from the *ortho*-metallation of the aromatic substituent.[43] There is no information about the regeneration of such catalysts.

The catalyst can be returned to the cycle when a phosphine amide ligand is used. The following solvent system is employed for this purpose: a low-boiling solvent (acetonitrile), a non-polar high-boiling solvent (*m*-xylene), and a small amount of a second low-boiling solvent (diethyl ether) to decompose the acetonitrile–methanol azeotrope. The most complete regeneration is attained when the ligand is 3-(diphenylphosphino)-*N*-methyl-*N*-oxadecylpropionamide $PPh_2(CH_2)_2C(O)N(CH_3)(C_{18}H_{37})$. A selectivity with respect to glycolaldehyde up to 93–99% is then ensured; the degree of conversion of formaldehyde after the first cycle is reduced by 13% and the residual rhodium content in glycolaldehyde is 26 p.p.m.[44,45]

Glycolaldehyde may be hydrogenated to ethylene glycol in the presence of heterogeneous hydrogenation catalysts: Raney nickel (100% conversion of formaldehyde for 49% selectivity with respect to ethylene glycol is achieved at 110 °C and 7.0 MPa), palladium on charcoal (70 °C, 70 MPa, 100% conversion, 73% selectivity), etc.[46,47] Methods for the hydrogenation of glycolaldehyde to ethylene glycol in quantitative yields have been patented.[48,49]

There exists an example of the selective homogeneous hydrogenation of glycolaldehyde in a static system in solution of $Rh(acac)CO_2$ in *m*-xylene, tetraglyme, or dioxan containing PPh_3: the yield of ethylene glycol is 90.2 mole % at 80 °C, a pressure of 10 MPa, and a $CO:H_2$ ratio of 1:1.[50]

The catalytic method for the hydroformylation of formaldehyde which have been described can be arbitrarily divided into two groups: (a) with participation of carboxylic acid *NN*-dialkylamides in the coordination sphere of rhodium; (b) based on the activation of the catalytic system with the aid of solvents or promoting agents which exhibit a very pronounced basicity ensuring the ionisation of the catalytic complex.

III. Hydroformylation of formaldehyde in solution in amides

The study of the characteristic features of the catalytic hydroformylation of formaldehyde has shown[51] that, in contrast to the reaction with olefins, high rates of formation of glycolaldehyde in the presence of rhodium complexes are attained only when carboxylic acid *NN*-dialkylamides are used as solvents. Only methanol is formed in other solvents (Table 2).

Best results have been obtained in dimethylacetamide using chlorine-containing triphenylphosphine rhodium complexes, especially $RhCl(CO)(PPh_3)_2$, as precursors of the catalyst. The inhibition of the reaction by glycolaldehyde has been noted.[51]

Among other features distinguishing this reaction from the hydroformylation of olefins, the presence of chlorine in the coordination sphere of the active rhodium species and the independence of the rate and selectivity of the reaction of the basicity of the ligand are important. The exclusion of the ligand PR_3 from the catalytic system renders it inactive, which is also uncharacteristic of the hydroformylation of olefins.

The kinetic study of the reaction in the presence of $RhCl(CO)(PPh_3)_2$—the catalyst precursor—in dimethylformamide (DMF) showed that [25,52] the introduction of $Et_3N.HCl$ or Et_3N

into the reaction mixture does not alter the initial rate of hydroformylation. Since the hydroformylation of olefins in the presence of $HRh(CO)(PPh_3)_3$ proceeds at higher rates than in the presence of $RhCl(CO)(PPh_3)_2$ and the catalytic activity of the latter is attributed to the reaction[53,54]

$$RhCl(CO)(PPh_3)_2 + Et_3N + H_2 \rightleftarrows HRh(CO)(PPh_3)_2 + Et_3N \cdot HCl,$$
$$RhCl(CO)(PPh_3)_2 + H_2 \rightleftarrows HRh(CO)(PPh_3)_2 + HCl,$$

the addition of $Et_3N.HCl$ should reduce the rate of reaction, while the addition of Et_3N or the use of $HRh(CO)(PPh_3)_3$ from the very beginning should increase it. The absence of these effects as well as the absence of an induction period when $RhCl(CO)(PPh_3)_2$ is used and also the detection of this complex among the hydroformylation products permitted the conclusion that chlorine enters into the composition of the catalytically active complex.

Table 2. Hydroformylation of formaldehyde in the presence of various catalyst precursors and solvents.[51]

Catalyst precursor	Solvent	Yield, %	
		of glycolaldehyde	of methanol
$HRh(CO)(PPh_3)_3$	acetic acid	0.0	18.6
	acetone	0.0	42.0
	acetonitrile	2.8	43.0
	benzene	0.0	19.7
	1,4-dioxan	0.0	31.7
	pyridine	2.8	4.4
	dimethylacetamide	5.6	4.1
	dimethylformamide	12.3	4.7
$RhCl(CO)(PPh_3)_2$*	"	39.8	2.3
	formamide	0.0	0.0
	methylformamide	0.0	0.0
	methylphenylformamide	0.0	0.0
	dimethylacetamide	49.7	1.2
$Rh_4(CO)_{12}$	dimethylformamide	0.0	0.0
$RhCl(CO)_2(PPh_3)$	"	19.6	0.4
$Rh(C_8H_{12})(PPh_3)_2 \cdot BPh_4$	"	3.8	26.7

Note. Reaction conditions: [Rh] = 5×10^{-3} M, [HCHO] = 2 M, $CO:H_2$ = 1:1, temperature 110 °C, pressure 8 MPa, reaction time 3 h, 100 ml of solvent.
*[HCHO] = 1 M, pressure 13 MPa.

Taking the above into account, the mechanism of the hydroformylation of formaldehyde must provide for the presence of Cl in the intermediates; overall, it resembles the familiar mechanism of the hydroformylation of olefins:[25]

$$RhCl(CO)(PPh_3)_2 \overset{k_1}{\rightleftarrows} RhCl(CO)(PPh_3) + PPh_3,$$
$$RhCl(CO)(PPh_3) + H_2 \overset{k_2}{\rightleftarrows} RhH_2Cl(CO)(Ph_3P),$$
$$RhH_2Cl(CO)(PPh_3) + HCHO \overset{k_3}{\rightleftarrows} RhHCl(CO)(PPh_3)(CH_2OH),$$
$$RhHCl(CO)(PPh_3)(CH_2OH) + CO \overset{k_4}{\rightleftarrows} \underset{(I)}{RhHCl(CO)(PPh_3)(COCH_2OH)},$$
$$(I) \overset{k_5}{\rightleftarrows} RhCl(CO)(PPh_3) + HOCH_2CHO.$$

On the assumption that the initial rate of reaction is $v_0 = k_5[I]$ when $RhCl(CO)(PPh_3)_2$ with an excess of PPh_3 in solution in a dimethylamide is used, the rate constants for the individual stages (k_1, k_2, k_3, and k_4) were determined and it was shown that the equation derived, namely

$$v_0 = {}^1/_2 k_1 k_2 k_3 k_4 k_5 P_{H_2} P_{CO} [HCHO]_0 \left\{ \left(1 + \frac{4[Rh]_0}{k_1 (1+X)} \right)^{1/2} - 1 \right\}, \quad (1)$$

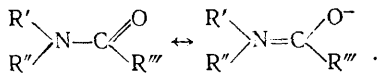
where

$$X = k_2 P_{H_2} + k_2 k_3 P_{H_2} [HCHO]_0 + k_2 k_3 P_{H_2} P_{CO} [HCHO]_0,$$

describes satisfactorily the experimental kinetics.[52] The activation energy for the reaction is 18.3 kcal mol^{-1}.

It is noteworthy that the proposed mechanism does not provide for the participation in the reaction of the chlororhodium dicarbonyl complex with PPh_3, namely $RhCl(CO)_2(PPh_3)$, since such species were incapable of activating H_2 in the oxidative addition reaction in the first stage. At the same time, it is known that the strength of the Rh–CO bond in chlororhodium monocarbonyl complexes of this kind is high and the mobility of the CO group is therefore low.[54] The hydroformylation conditions favour the stabilisation of the dicarbonyl derivative,[55] which may be formed in the reaction with CO or as a result of the decarbonylation of the amide or formaldehyde.[55,56] Such a derivative is characterised by the lability of the carbonyl ligand.[54,55]

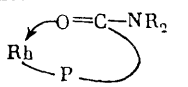
The inhibition of the hydroformylation of formaldehyde by an excess of the phosphine ligand[46,51] confirms a dissociative mechanism analogous to that of the hydroformylation of olefins. Here *NN*-dialkylamides are regarded as electron-donating ligands. A specific feature of such molecules is the presence of resonance structures:



There are numerous data supporting the coordination interaction of the amide with the transition metal. In the vast majority of cases, the coordination is to the oxygen atom of the carbonyl group of the amide[57,58] but there are data also for other types of coordination.[56,59] The possibility of rotation about the C–N bond makes it possible to explain the absence of the activating influence of asymmetrically substituted amides (for example *N*-methyl-*N*-phenylformamide—see Table 2) on the hydroformylation of formaldehyde by the steric hindrance to the coordination.[51]

The coordination interaction of the amide with rhodium has been confirmed as a result of a study[45] in which the hydroformylation of formaldehyde was investigated (130 °C, pressure of 1:1 CO + H_2 mixture 12.9 MPa) in the presence of two different rhodium catalysts: $RhCl(CO)(PPh_3)_2$ (Spencer's catalyst) and $RhCl(CO)[PPh_2(CH_2)_2.(CO)N(CH_3)_2]_2$. When acetonitrile is used as the solvent, the degree of conversion of formaldehyde after 3 h in the presence of a rhodium catalyst with the *NN*-dimethyl-3-(diphenylphosphino)-propionamide ligand was 62% for a selectivity with respect to glycolaldehyde of 75% (the yield of methanol was 2%), i.e. higher parameters were attained than in the presence of $RhCl(CO)(PPh_3)_2$.

On the other hand, when an *NN*-dialkylamide was used as the solvent, no differences were observed between the catalytic activities of Spencer's catalyst and the catalyst with the *NN*-dimethyl-3-(diphenylphosphino)propionamide ligand, which indicates the similarity of the catalytic systems. It has been suggested[51,60] that the phosphineamiderhodium catalyst contains the Rh–amide coordinate bond:



The chelate effect in this complex apparently decreases the concentration of the amide groups in the reaction medium.

The hydroformylation of formaldehyde under mild conditions (80 °C, 5.0 MPa) with a conversion close to 100% and a selectivity up to 64% proved to be possible when the dimeric rhodium thiolate complex $Rh_2(\mu\text{-}S\text{-t-Bu})_2(PPh_3)_2$ (A) was used as the precursor of the catalyst with an excess of PPh_3 in solution in *NN*-dialkylamides.[61] After the reaction had been carried out, the complex was isolated unchanged. The complex $Rh_2(\mu\text{-}S\text{-t-Bu})_2(CO)_4$ (B), which has no phosphine ligands, was inactive, as in the hydroformylation of olefins.[62] An excess of the ligand hinders the transformation (A) → (B) and thereby prevents the deactivation of the catalyst. The replacement of the PPh_3 ligands by the more electron-donating PMe_3 ligands promotes the formation of methanol.

In the presence of $RhCl(CO)(PPh_3)_2$, the selectivity with respect to glycolaldehyde can be increased by carrying out the hydroformylation of formaldehyde in pyridine (selectivity 98%, conversion 83.7%, pressure 9.0 MPa, H_2:CO = 2:1),[48] while in the presence of the complex (A) the use of this solvent did not allow the attainment of such high parameters.[61] The employment of the catalyst precursor (A) produces best results in *NN*-dialkylamides and the reaction then proceeds under milder conditions and at higher rates than in the case when Spencer's catalyst is used. Parameters of the hydroformylation of formaldehyde analogous to those obtained using Spencer's catalyst in DMF [51] are attained in the given instance at a pressure of 1.5 MPa, while the use of hexamethylphosphoramide makes it possible to avoid hydrogenation to methanol. Since the observed selectivity and activity are not the same as those obtained in the presence of $RhCl(CO)(PPh_3)_2$ and are attained under milder conditions, while the dinuclear rhodium thiolate complex remains unchanged after the reaction, it has been suggested that the catalysis is affected by another active species of unknown nature.

It has been established that, in the hydroformylation of olefins in the presence of the rhodium complex (A), the dinuclear carbonyl phosphine rhodium thiolate species is active.[62]

The selective hydroformylation of formaldehyde in solution in DMF using $Rh_4(CO)_{12}$ modified with PPh_3 and promoted with HI as the catalyst precursor has been reported.[63]

IV. Hydroformylation in the presence of basic promoting agents or solvents

Another group of catalytic systems used in formaldehyde hydroformylation reactions includes a basic promoting agent, for example, amines or highly basic solvents, which makes it possible to eliminate amides from the composition of the catalytic solution. Table 3 presents data indicating the influence of the nature of the solvent on the yield of the formaldehyde hydroformylation products.[43] The use of pyridine and its derivatives increases significantly the activity and selectivity of the process.

In the hydroformylation in the presence of rhodium complexes promoted by organic bases or alkalis,[27,37,64] the active catalytic system is formed from neutral or cationic rhodium complexes both containing and not containing chlorine, while the employment of amide or highly basic solvents is not obligatory in this instance (Table 4). Thus the addition of a small amount of triethylamine to the $RhCl(CO)(PPh_3)_2$ system in tetraglyme (Table 4) made it possible to increase the degree of conversion of formaldehyde in the hydroformylation reaction almost from zero to 90% for a selectivity with respect to glycolaldehyde of 76%.

Table 3. The influence of the nature of the solvent on the hydroformylation of formaldehyde.[43]

Solvent	Yield, %		
	glycol-aldehyde	ethylene glycol	methanol
γ-Picoline	49.4	0.3	0.4
β-Picoline	43.0	0.3	0.2
Pyridine	42.9	0.4	0.2
4-Pentylpyridine	39.7	0.4	0.4
3,5-Diethylpyridine	35.1	0.1	0.1
Triethylamine	9.4	0.0	0.4
Dimethylformamide	4.3	0.0	0.1
Dioxan	0.8	0.0	0.1
Dimethyl sulphoxide	7.4	0.0	0.2
Acetone	~0	~0	0.1

Note. $[CH_2O]$ = 19.1 mM, $[RhCl(CO)(PPh_3)_2]$ = 0.05 mM, temperature 70 °C, pressure of 1:1 CO + H_2 mixture 5 MPa, reaction time 3 h.

Table 4. Promotion of the rhodium catalysts $RhCl(CO)(PPh_3)_2$ + $n PPh_3$ by bases.[27]

n	Solvent	Base	Concentration of base, M	Reaction time, min	Conversion of CH_2O, %	Selectivity, %		
						glycol-aldehyde	methanol	condensation products
0	tetraglyme	—		30	traces			
0	»	NEt_3	$1\cdot10^{-2}$	30	84	71	6	
0	»	NEt_3	$2\cdot10^{-2}$	30	90	76	6	
8	»	NaOAc	$1.8\cdot10^{-2}$	15	94	14	11	
30	*NN*-dubutyl-formamide	KOH	$5\cdot10^{-3}$	60	75	56	20	
30	»	KOH *	$2.5\cdot10^{-2}$	30	62	2	10	
30**	*NN*-dimethyl-acetamide	NEt_3	$0.84\cdot10^{-2}$	30	43	86	5	9
30**	»	NEt_3	$1.8\cdot10^{-2}$	30	95	71	2	27
30**	»	NEt_3	$45\cdot10^{-2}$	15	95	17	6	77

Note. Reaction conditions: $[Rh] = 5 \times 10^{-3}$ M, $[CH_2O]$ = 2 M, $CO:H_2$ = 1:1, 17.5 MPa, 110 °C.
*The reaction is carried out in the presence of the 18-crown-6 ether to improve the dissolution of KOH.
**Pressure 21.0 MPa.

When the formaldehyde hydroformylation reaction was carried out in the presence of $HRh(CO)_2(PPh_3)_2$, it was established that the catalytic system includes, together with $HRh(CO)_2(PPh_3)_2$, also the anionic species $[Rh(CO)_4]^-$ and $[Rh(CO)_2(PPh_3)_2]^-$.[27] It was suggested that the amine additive serves as a bifunctional promoting agent for the catalytic system. By deprotonating the rhodium carbonyl hydride, it gives rise to an anionic species, to which catalytic activity is attributed:

$$HRh(CO)_2(PPh_3)_2 \rightleftarrows [Rh(CO)_2(PPh_3)_2]^- .$$

Furthermore, the amine serves as a source of protons, which are essential for the formation of the hydroxymethyl complex:

$$[R_3NH]^+ + CH_2O + [Rh(CO)_3(PPh_3)]^- \rightarrow HOCH_2Rh(CO)_3(PPh_3) + R_3N.$$

Being strong bases, the anionic rhodium complexes afford hydrides on interaction with weak acids (H_2, ROH).[65] The formation of the anionic rhodium complexes also in the absence of amine promoting agents can apparently be explained by the reversibility of this reaction:

$$[Rh(CO)_x(PPh_3)_{4-x}]^- + MeOH \rightleftarrows HRh(CO)_x(PPh_3)_{4-x} + [MeO]^-.$$

The activity of $[Rh(CO)_2(PPh_3)_2]^-$ and the inertness of $[Rh(CO)_4]^-$ have been demonstrated by special experiments.[27] However, it is still not understood at which stage the activity of PPh_3 is manifested.

According to the existing ideas, the anionic precursors of the catalyst react with formaldehyde to form a hydroxymethyl complex which catalyses in its turn the hydrogenation, via the elimination of methanol, after interaction with H_2 or H^+:

Scheme 1

$$CH_2O + [Rh(CO)_2(PPh_3)_2]^- + H^+ \rightarrow HOCH_2Rh(CO)_2(PPh_3)_2$$

$$\downarrow -CO \qquad\qquad \downarrow H^+$$

$$HOCH_2Rh(CO)(PPh_3)_2 \qquad CH_3OH + [Rh(CO)_2(PPh_3)_2]^+$$

$$\downarrow H_2 \qquad\qquad \downarrow H_2$$

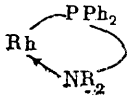
$$CH_3OH + HRh(CO)_2(PPh_3)_3 \qquad H^+ + HRh(CO)_2(PPh_3)_2 .$$

Experiment shows that both pathways can be followed, since the yield of methanol increases in the presence of an excess of the proton-donating reagent or with increase in the H_2:CO ratio.[27]

The effect of the amide in the presence of Spencer's catalyst is analogous to the effect of amines. The mechanism of its action is determined by its weak electron-donating properties.[27]

In the presence of both organic and inorganic basic promoting agents, the rate of hydroformylation of formaldehyde increases, but its condensation is at the same time accelerated sharply, which impairs the process selectivity (Table 4). Apart from methanol, trioses, tetroses, pentoses, and hexoses, have been identified among the side products, the rate of their formation increasing with increase in temperature and in the basicity of the medium. In addition, glyceraldehyde, 1,3-dihydroxypropanone, erythrose, 1,3-dihydroxybutanone, etc. have been detected in systems of this kind.[66]

In contrast to the above, the use of phosphineaminerhodium complexes with ligands of the type $PPh_2(CH_2)_2N(CH_3)_2$ [45] in acetone lowers the content of side products to 9%, which can be explained by the close proximity of the amino-group to the metal complex-forming atom and the chelate effect:



There is no information about the contribution of the condensation reaction of formaldehyde in its hydroformylation to glycolaldehyde. The only mention is in a communication[67] where the hydroformylation of $[^{13}C]$-CH_2O using a polynuclear rhodium complex in amide solvents in the presence of dimethylimidazole or *N*-methylpyrrolidinone is described. The results of the analysis of the positions of the labels in the products permitted the conclusion that under these conditions the dimerisation of formaldehyde to glycolaldehyde does not occur.

It has also been postulated that the catalytically active mononuclear species participating in the hydrogenation of CO to ethylene glycol are anionic in character. In tetraglyme, in the presence of the $Rh(acac)(CO)_2$ catalyst precursor promoted with *N*-methylimidazole (*N*-MI) (the latter is taken in a large excess),[68] whereupon the reaction is believed to proceed via the intermediate formation of formaldehyde and its hydroformylation, the catalyst is the mononuclear anionic rhodium complex formed when rhodium hydride is acted upon by a base:

$$HRh(CO)_3(N\text{-}MI) \rightarrow HRh(CO)_4 \rightarrow [N\text{-}MI]^+[Rh(CO)_4]^-.$$

The fact that the hydrogenation of CO to ethylene glycol, proceeding via the hydroformylation of formaldehyde, is catalysed by polynuclear complexes has been confirmed.[69] The anionic nature of such clusters is also determined, according to the authors, by the action of basic additives or solvents.

On the basis of the idea that the species active in the catalysis of the hydroformylation of formaldehyde are anionic in character and, as the function of the basic promoting agents and polar solvents consists in reducing the oxidised rhodium precursors to low-valence catalytically active anions, Marchionna and Longoni[70] used anionic rhodium carbonyl complexes as direct catalyst precursors. Because of this, they were able to exclude completely basic promoting agents and solvents from the composition of the catalytic system, ensuring nevertheless a high degree of conversion of formaldehyde and a high selectivity of the formation of glycolaldehyde. The $[Rh_5(CO)_{15}]^- - [Rh(CO)_2Cl_2]^- - PPh_3$ catalytic system (with a composition of 1:5:10) at 110 °C, 12 MPa, and with the ratio $CO:H_2 = 1:1$ makes it possible to obtain glycolaldehyde in 87.9% yield in acetone, while the yield of methanol is 9.4%.

It had been shown earlier[63] that selective hydroformylation is possible when one uses the $Rh_4(CO)_{12} - PPh_3 - HI$ catalytic system in which the postulated catalytically active species $[Rh_5(CO)_{15-x}(PPh_3)_x]^-$ with $x = 1,2$ and $[Rh(CO)_2Cl_2]^-$ were identified by IR spectroscopy. In the presence of PPh_3, the complex $[Rh_5(CO)_{15}]^-$ produces $[Rh_5(CO)_{15-x}(PPh_3)_x]^-$.[70] Its combination with $[Rh(CO)_2Cl_2]^-$ leads to the formation of a system analogous to that generated from $Rh_4(CO)_{12} - PPh_3 - HI$.

It has been suggested that each of the two anionic species $[Rh_5(CO)_{15-x}(PPh_3)_x]^-$ and $[Rh(CO)_2Cl_2]^-$ participates in the catalytic cycle, accelerating different hydroformylation stages.

The increased activity of the first of these complexes in the hydroformylation of formaldehyde to methanol provided grounds for the hypothesis that it has an activating effect on H_2 and CH_2O. According to the authors,[70] the anion $[Rh(CO_2)Cl_2]^-$, to which an enhanced activity is attributed in the migration insertion of carbon monoxide with formation of a hydroxyacyl intermediate,[71] is responsible for the high selectivity of the formation of glycolaldehyde. The combination of such or similar species in optimum proportions can ensure a fairly high rate of hydroformylation of formaldehyde with a satisfactory selectivity with respect to glycolaldehyde.

A two-component Co–Rh catalytic heterometallic anionic system has been described.[72] Using mixtures of $Rh_4(CO)_{12}$ and $CoCl_2.6H_2O$ or the mixed cluster $Co_2Rh_2(CO)_{12}$ as the catalyst precursors in DMF, it was possible to achieve a selectivity with respect to glycolaldehyde up to 65%. At the same time, the formation of ethylene glycol was observed. The experiments were performed at 110 °C and a pressure of 10–12 MPa. It was established that at least two types of catalytically active species are generated in the system: species of one type catalyse the formation of glycolaldehyde, while others catalyse its hydrogenation as well as the hydrogenation of CH_2O to ethylene glycol and methanol respectively. The identified structure of the carbonyl complexes before and after the

reaction indicates the reduction of the cobalt and rhodium carbonyls to $[Co(CO)_4]^-$ and $[Rh(CO)_4]^-$ respectively:

$$5Co_2Rh_2(CO)_{12} \rightarrow 2[Rh_5(CO)_{15}]^- + 4Co^{2+} + 6[Co(CO)_4]^- + 6CO,$$
$$5Rh_4(CO)_{12} + 2H_2O + 4DMF + 2CO \rightarrow 4[Rh_5(CO)_{15}]^- + 4DMFH^+ + 2CO_2,$$
$$[Rh_5(CO)_{15}]^- + Cl^- \rightleftarrows [Rh_5(CO)_{14}Cl]^{2-} + CO,$$
$$[Rh_5(CO)_{15}]^- + 10Cl^- + 2Co^{2+} + 3CO \rightarrow 5[Rh(CO)_2Cl_2]^- + 2[Co(CO)_4]^-.$$

The nature of the species active in hydroformylation was not established, but it has been suggested that the monometallic rhodium anion $[Rh(CO)_4]^-$ plays this role.

One should apparently not rule out also the possible activity of mixed Co–Rh carbonyls. The formation of an equilibrium mixture of the Co–Rh clusters $Co_2Rh_2(CO)_{12}$ and $Co_3Rh(CO)_{12}$ and the complexes $CoRh(CO)_8$ and $CoRh(CO)_7$ from $Co_2(CO)_8$ and $Rh_4(CO)_{12}$ under CO pressure at 80–90 °C in solutions in dioxan has been reported.[73]

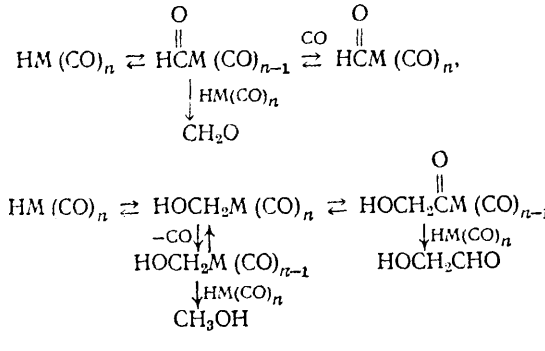
A gradual deactivation of the Co–Rh catalytic system is attributed to the reduction of $[Co(CO)_4]^-$ and $[Rh(CO)_4]^-$. The highest selectivity is observed in the system containing cobalt(II) compounds, which is attributed to their ability to oxidise rhodium complexes to anionic carbonyls and to serve as the buffer for the stabilisation of the active rhodium, the formal oxidation state of which is between +1 and −0.2.

An alternative explanation consists in the cooperative action of the cobalt and rhodium complexes in different oxidation states, analogous to the situation arising in the catalytic hydrogenation of CO to ethylene glycol in the presence of ruthenium carbonyls.[74,75]

V. The chemistry of coordinated formaldehyde and the hydroformylation mechanism

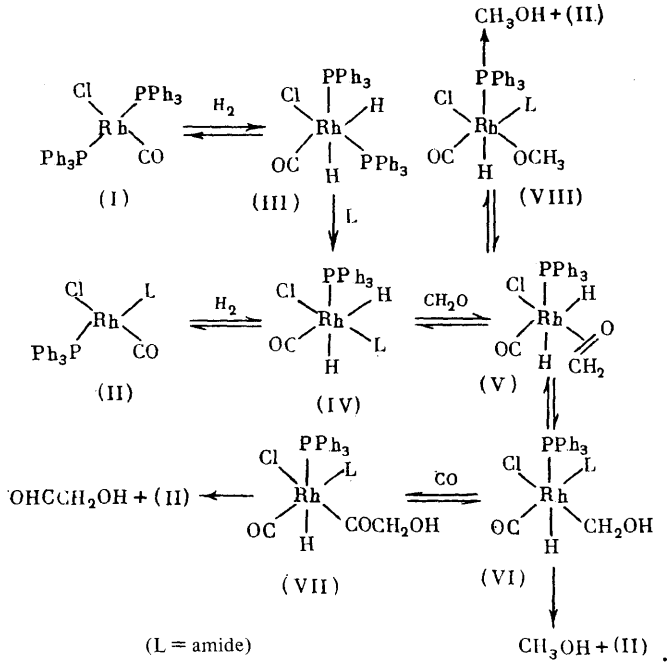
It is believed that the mechanism of the hydroformylation of formaldehyde is on the whole analogous to the known mechanism of the hydroformylation of olefins. In particular, the reaction is determined by the polar character of formaldehyde. It has been suggested that the formation of formaldehyde is an intermediate stage in the homogeneous-catalytic hydrogenation of CO to methanol, methyl formate, ethylene glycol, and other polyhydric alcohols in the presence of transition metal complexes (Scheme 2); the hydroformylation of CH_2O determines the content of ethylene glycol in the products:[4,76]

Scheme 2



Spencer[51] proposed a mechanism for the hydroformylation of formaldehyde in which provision is made for catalysis by a chlororhodium complex in the presence of an *NN*-dialkylamide:

Scheme 3



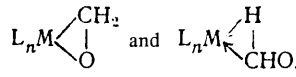
According to this Scheme, the dialkylamide should influence the stages involving the formation of the products (IV)–(VII). The absence of a directing effect of the amide is explained by its displacement by formaldehyde [the reaction (IV) ⇄ (V)]. Evidently this stage represents the interaction of formaldehyde with a solution of the metal complex. Such reactions are known for many neutral or cationic transition metal complexes.[77,78] The reactions of anionic complexes with CH_2O have not been described, which must be borne in mind in connection with the postulated mechanism of their catalytic action.[22,70]

Metal complexes are also capable of interacting with a suspension of paraformaldehyde,[77] gaseous formaldehyde,[52] or an aqueous formalin solution;[53] when trioxan is used, higher temperatures are required for its degradation.[24] In most cases, the complex with the η^2-CH_2O ligand (a π-complex) or a metal carbonyl are formed under very mild conditions.[79,80] It has been established that the complex with the η^2-CH_2O ligand is the most probable precursor in all subsequent reactions of the coordinated formaldehyde,[77] its formation being promoted by the presence of the PR_3 ligands, which are readily substituted in the interaction with CH_2O. As a result of the ligand exchange with CH_2O, stable complexes of this type have been obtained. The first such complex $(CO)_2(PPh_3)_2Os(CH_2O)$ was described in 1979.[81] The complexes $(CO)_2FeL_2(CH_2O)$,[80] $Cp_2V(CH_2O)$,[82] $CpRe(CO)_2(CH_2O)$,[83] $Cp_2Mn(CH_2O)$,[84] and the cationic complex $CpRe(NO)(PPh_3)(CH_2O)^+$ [85] have also been obtained. There are data concerning the bridge type coordination of the μ-CH_2O ligand, which are of interest in connection with the hypothesis that polynuclear and tetrametallic complexes of the type

$$(\eta^5\text{-}C_5H_5)_2Zr(Cl)(\mu\text{-}CH_2O)(Cl)Zr(\eta^5\text{-}C_5H_5)_2$$

are active.[76,86]

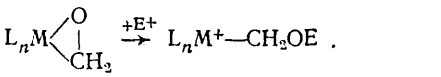
The interaction of formaldehyde with ML_n can lead to the bidentate binding of CH_2O of two types:[81,83,87,88]



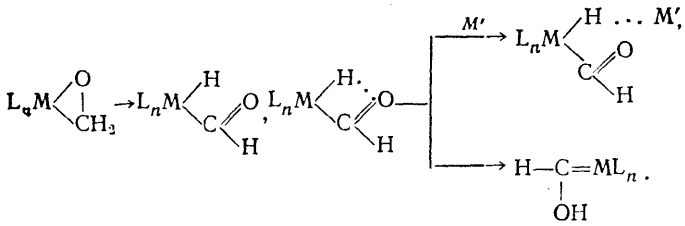
A characteristic feature is the weakening of the C=O bond in such compounds compared with the bond in the non-coordinated formaldehyde, which is manifested by the ν(CO) stretching vibration frequency.

The reactions of the coordinated formaldehyde η^2-CH_2O in the transition metal complex are summarised below:[77,89]

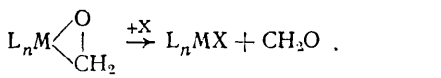
(1) attack on the oxygen atom of the coordinated formaldehyde:[80,82]



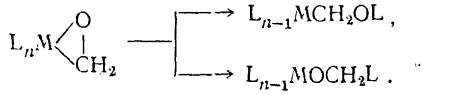
(2) Oxidative addition with formation of a formyl derivative:[81]



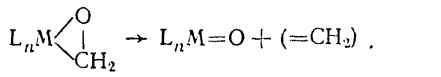
(3) Displacement of formaldehyde from the coordination sphere:[82]



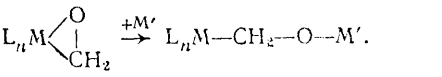
(4) Insertion of formaldehyde in an M–H [82] or M–C [90] bond:



(5) Dissociation of the C=O bond of formaldehyde with its deoxygenation:[89]



(6) Ditto with formation of the bridging μ-CH_2O form:[86,89]



The mode of reaction and its rate are determined by the nature of the metal, the ligand environment, and the reaction conditions.

Certain other, perhaps unexpected, reactions have also been described. Thus the interaction of the cation $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3).(\eta^2\text{-}CH_2O)]^+$ with PR_3 (R = Rh or Me) at 25 °C led to the formation of the adduct[91]

$$[(\eta^5\text{-}C_5H_5)\,Re\,(NO)\,(PPh_3)\,(OCH_2PR_3)]^+.$$

instead of the expected substitution of the coordinated CH_2O by PR_3.

Reactions (1)–(4) should apparently be assigned to the hydroformylation mechanism proper.

A metal characterised by appropriate oxophilic properties can combine with formaldehyde oxidatively with participation of the C=O or C–H bonds.

The last reaction, leading to the formation of the formyl complex, is of interest in connection with the mechanism, postulated by Keim et al.,[92] of the formation of ethylene glycol in the presence of solutions of cobalt carbonyls in the hydrogenation of CO:

$$(CO)_n\,Co{-}CHO \xrightarrow{HCo(CO)_n} (CO)_n\,Co{-}CH_2O{-}Co\,(CO)_n \xrightarrow{CO}$$
$$\rightarrow (CO)_n\,Co{-}CO{-}CH_2O{-}Co\,(CO)_n \xrightarrow{H_2} CH_2OH{-}CH_2OH.$$

The key stage is that of the interaction of the formyl complex, formed from CO and H_2, with the carbonyl hydride. In addition, it may prove to be the key stage in the formation of active carbonyl derivatives of the metal in the carbonylation of metal complexes by formaldehyde.

The decarbonylation of formaldehyde by metal complexes proceeds via an oxidative addition stage with formation of a formyl complex.[77,93] The equilibrium

$$H_yM\,(Co)_x \rightleftarrows H_{y-1}M\,(Co)_{x-1}\,(CHO)$$

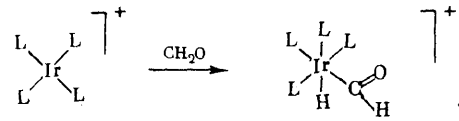
explains the relative instability of the formyl intermediates.[93]

It has recently been reported that nickel complexes are capable of rapidly decarbonylating formaldehyde via the stoichiometric reaction[89]

$$Ni\,(PR_3)_4 + CH_2O \rightarrow Ni\,(PR_3)_3\,(CO) + H_2.$$

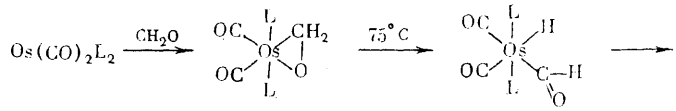
The presence of the rigid bulky np_3 ligand {np_3 = tris[2-diphenylphosphino)ethylamine]} in the coordination sphere makes it possible to alter the formaldehyde reaction pathway and the decarbonylation reaction may become catalytic.[79]

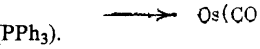
Relatively stable formyl complexes are obtained by the oxidative addition of formaldehyde to cationic or neutral square planar iridium(I) complexes:[80]



Many mono- and poly-nuclear, cationic, neutral, and anionic formyl complexes have been described.[77,78,94] It has been shown for some of them that the M–CHO fragment is an effective hydride donor[91,95] and that it can be stabilised by an electrophile.[96]

The rearrangement $(\eta^2\text{-}CH_2O)M \rightarrow HM{-}CHO \rightarrow MCO$ has been observed for the osmium carbonyl complex:[81]





The main reaction of the coordinated formaldehyde in the hydroformylation process is reaction (4) (L = H) with formation of a hydroxymethyl derivative, which is a precursor of glycolaldehyde: the methoxy-intermediate controls the formation of methyl formate, both affording methanol after reductive elimination.

The insertion of formaldehyde in the M–H bond in the hydroformylation process with formation of the M–O and M–C bonds should determine the ratio of the methyl formate and

glycolaldehyde formed. However, there also exists the view that the presence of a compound with the M–O bond is not an obligatory condition for the formation of formate, since it can be obtained via the reaction[97]

$$HO-CH_2M(CO)_n + RCH_2OH \rightarrow RCH_2\overset{O}{\overset{\|}{O}}CH + HM(CO)_n.$$

Examples of the methoxy-complexes described in the literature are fairly rare, one of them being $Cp_2W(CH_3)(OCH_3)$.[98]

The formation of the methoxy-derivative from the zirconium carbonyl complex has been observed in its reaction with hydrogen, which proceeds tentatively via the intermediate hydroformyl derivative $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH)_3$.[99] The hydride donating capacity of the formyl derivative of Re^+ made it possible to obtain a 52% yield of the methoxy-complex from the $\eta^2\text{-}CH_2O$ cation:[91]

$$[CpRe(NO)(PPh_3)(\eta^2\text{-}CH_2O)]^+ + CpRe(NO)(PPh_3)(CHO) \rightarrow$$
$$\rightarrow CpRe(NO)(PPh_3)(OCH_3) + [CpRe(NO)(PPh_3)(CO)]^+.$$

The interaction of this methoxy-complex with $[Ph_3C]^+[PF_6]^-$ in CH_2Cl_2 results in the reformation of the initial complex.

The insertion of formaldehyde in the M–H bond in octaethylporphyrinrhodium hydride led to the formation of a hydroxymethyl derivative:[100] $Rh-H + CH_2O \rightarrow Rh-CH_2-OH$.

There exist numerous examples of similar complexes with different metals.[77,78]

Apparently both types of insertion, with formation of both M–C and M–O bonds, are possible under the conditions of the catalytic reactions of the carbonyl group in solutions of metal complexes.

The stoichiometric hydroformylation of formaldehyde has been carried out using $HCo(CO)_4$ as the source of hydrogen under the conditions of an excess of CO (the reaction was carried out at 0 °C and a pressure of 1 atm in CH_2Cl_2):[101]

$$2\,HCo(CO)_4 + CH_2O \xrightarrow{CO} HOCH_2CHO + Co_2(CO)_8.$$

The yield with respect to the $HCo(CO)_4$ which reacted amounted to 60–90%. There was no methyl formate among the reaction products, which indicates the addition of formaldehyde to the carbonyl hydride complex with formation of a Co–C bond.

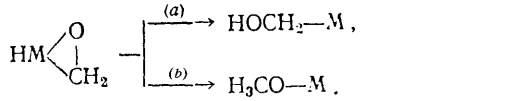
The possibility of the direct interaction of aldehydes with $HCo(CO)_4$ involving coordination via the oxygen atom of the carbonyl group has been noted;[97] the conversion of aldehydes into alcohols takes place in this way. The catalytic hydroformylation of epoxides presupposes the formation of the Co–C bond; both Co–C and Co–O bonds can participate in the reduction of CO.

The formation of methyl formates (Co–O) (yield up to 40%) in the complete absence of hydroxyaldehydes (Co–C) has been observed in the catalytic hydroformylation of aldehydes in the presence of cobalt carbonyls modified with PR_3.[102] Hydroxyaldehydes are also not formed under the conditions of the hydroformylation of olefins in the presence of cobalt or rhodium catalysts. The principal products of the secondary reactions of aldehydes in oxo synthesis are alkyl formates.[6,103]

In this connection one should note that, in contrast to other aliphatic aldehydes, formaldehyde is capable of undergoing π-type coordination ($\eta^2\text{-}CH_2O$). Coordination via the oxygen atom is characteristic of other aldehydes and π-type coordination is not observed.[104]

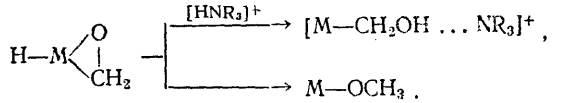
Methyl formate is formed in trace amounts in the catalytic hydroformylation of formaldehyde, the selectivity with respect to the target product (in the absence of condensation) being determined by the glycolaldehyde/methanol ratio and not by the glycolaldehyde/methyl formate ratio. The appreciable yield of methyl formate observed in the study of Marchionna and Longoni[72] can be explained by the interaction of formaldehyde with CO and the Cannizzaro–Tishchenko reaction.

It is apparently so far impossible to identify the precursor of methanol (the hydroxymethyl or methoxy-intermediate), but the majority of investigators incline to the view that the formation of methanol via a methoxy-derivative is unlikely, i.e. that pathway (*b*) does not play a significant role under the reaction conditions:



This can be accounted for by several causes. In particular, by thermodynamic control for certain metals. Thus it has been shown that the Ir–O bond in iridium complexes is weaker than the Ir–C bond.[105]

In addition it has been suggested[27] that the suppression of pathway (*b*) is due to the use of basic promoting agents and polar media which promote the hydroxymethyl hydrogen transfer:



and also to the nucleophilic character of the attack on the active anionic metal carbonyl species in their interaction with CH_2O:[27]

$$[Rh(CO)_2(PPh_3)_2]^- \overset{CH_2O,H^+}{\rightleftharpoons} HOCH_2Rh(CO)_2(PPh_3)_2.$$

The promotion of rhodium catalysts by acids also drives the reaction towards the formation of the M–C bond:[3,63]

$$CH_2O + HI \rightarrow ICH_2OH,$$
$$ICH_2OH + M \rightarrow HOCH_2MI.$$

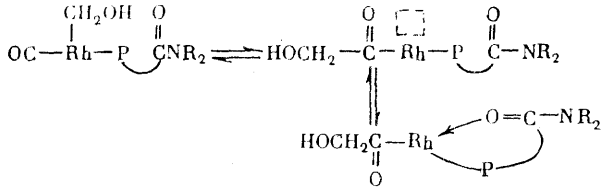
In most cases, it is impossible to state unambiguously how formaldehyde is converted into the hydroxymethyl intermediate: via insertion in the M–H bond, as a result of oxidative addition, or via a bimolecular mechanism.

The migration insertion of CO in hydroxymethylcarbonyl complexes leads to the formation of a hydroxyacyl intermediate (see Scheme 3). This reaction has been achieved recently for the octaethylporphyrin (OEP) complex of rhodium:[106]

$$(OEP)Rh(CH_2OH) \xrightarrow{CO} (OEP)RhCOCH_2OH.$$

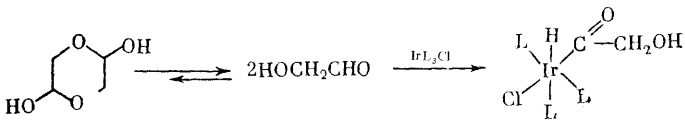
In contrast to alkylmetal carbonyl complexes, the carbonylation of the hydroxyalkyl derivatives proceeds with difficulty.[107,108] It has been suggested that this reaction is accelerated in the presence of electron-donating solvents, in particular amides, and in the presence of basic ligands. This hypothesis is based on the analogy with the migration insertion of CO in alkylmetal complexes with formation of acyl derivatives, which is promoted by alkali metal cations, amide solvents, basic promoting agents, and basic ligands.[4,76,109] For example, in the reaction involving the formation of acylmanganese complexes from the alkyl complexes, a significant increase in the rate was observed after the replacement of the solvent (mesitylene) by DMF.[76] The $HOCH_2CH_2OH$:CH_3OH ratio in the products must be determined by the ratio of the rates of insertion of CO and of the

reductive elimination of CH_3OH from the common intermediate for these compounds. It is believed that the rate of the migration insertion with formation of a hydroxyacyl complex can greatly exceed the rate of the irreversible stage involving the reductive elimination of ethanol only in highly electron-donating solvents;[76] the participation of an electron-donating ligand in the reactions of compounds (IV)–(VII) (see Scheme 3) has therefore been postulated. A characteristic feature of the phosphine amide ligand is, according to Jacobson,[45] the acceleration of the reaction (VI) → (VII) as a consequence of the nucleophilic attack on the coordinatively-unsaturated organometallic centre:



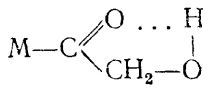
Whereas hydromethyl complexes are relatively well known, the hydroxyacyl complexes have been studied to a much smaller extent.

Apart from the octaethylporphyrinrhodium complex,[106] the hydroxyacyliron complex $Fe(COCH_2OH)[P(OMe)_3]_2$ has been described.[110] Data are available concerning the stabilisation of the hydroxyacyl complexes by chelating ligands.[111] The hydroxyacyl-iridium and hydroxyacylrhodium hydride complexes have been recently characterised. They were obtained by the oxidative addition of glycolaldehyde to square-planar iridium(I) and rhodium(I) complexes:[105]



The hydroxyacylrhodium complex is formed in 92% yield from the glycolaldehyde dimer (2,5-dihydroxy-1,4-dioxan) at 25 °C; it is stable in the solid state, decomposing slowly in solution.

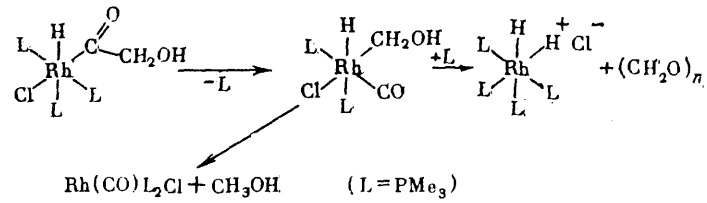
An important structural feature of such complexes proved to be the presence of an intramolecular hydrogen bond C=O...H–O, which leads to the formation of a five-membered ring:[105]



This was demonstrated by IR spectroscopy, showing a lack of dependence of ν_{OH} on the concentration of the complex in C_6D_6.

Since the $M-CH_2OH$ complexes show a greater tendency towards the migration insertion of CO than their analogues $M-CH_2OR$, it has been suggested that the presence of the intramolecular hydrogen bond is a general phenomenon for the α-hydroxyacyl complexes.

The reactions observed in the study of the thermal decomposition of the hydroxyacylrhodium complex[105] may serve as models of the reactions (V) → (IV), (VI) → CH_3OH + (II), and (VII) → (VI) (see Scheme 3). It has been established that the hydroxyacylrhodium complex undergoes on heating a reaction which is the reverse of the migration insertion of CO with formation of $Rh(CO)L_2Cl$ and CH_3OH from the hydroxymethyl intermediate. β-Elimination results in the formation of formaldehyde and a hydride, the reaction being the dominant one:

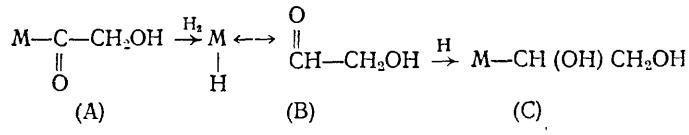


In addition, the elimination of glycolaldehyde was observed.

The fact that the introduction of the electron-donating ligand (PMe_3) inhibits the decomposition of the hydroxyacyl complex can apparently be associated with its activating effect in hydroformylation. The reversible formation of the hydroxyacyl complex via the oxidative addition of glycolaldehyde is consistent with Spencer's hypothesis of the reaction equilibrium (VII) ⇄ (II) (not shown in the Scheme), by means of which he explains the inhibition of the hydroformylation by the excess glycolaldehyde. A probable cause of this phenomenon may be the blocking of the coordination centres by the bidentate ligand $HOCH_2CHO$.[4] The reversibility of this stage distinguishes the mechanism considered from the mechanism of the hydroformylation of olefins, in which the reversible reductive elimination of the aldehyde has been demonstrated.

An alternative mechanism of the elimination of glycolaldehyde from the hydroxyacyl complex may involve intermolecular reductive elimination with participation of carbonyl hydride complexes. An analogous mechanism is known for the hydroformylation of olefins.[4,112,113]

The reactions



are of key importance in the formation of ethylene glycol.[114] The intermediate (C) may serve as a source of ethylene glycol or can enter into the chain propagation reaction under the influence of CO. The reduction of compound (B) can lead to the formation of ethylene glycol via the intermediate (C) or via the *O*-bonded alkoxy-complex. The latter does not participate in the chain propagation reaction.

The (A) → (B) → (C) chain of reactions has been investigated for the methoxyacetyliron complex $Cp(CO)_2Fe-C(O)-CH_2OCH_3$.[114]

As stated above, the selective hydrogenation of glycolaldehyde to ethylene glycol under the conditions of a homogeneous-catalytic reaction has been demonstrated in a solution of $Rh(acac)(CO)_2$.[50]

The intermediate transition metal complexes, which are believed to be formed in a hydroformylation of formaldehyde, can be distinguished by means of their spectral characteristics (Table 5).

VI. Conclusion

The formaldehyde hydroformylation reaction is of interest not only as a method of synthesis of glycolaldehyde and ethylene glycol but also as the postulated intermediate stage in the homogeneous-catalytic hydrogenation of CO to methyl formate, ethylene glycol, and other polyhydric alcohols. The formation of ethylene glycol from CO to H_2 requires severe conditions, probably because of the thermodynamic difficulties in the formaldehyde formation stage.

The absence of this energetically difficult stage in the synthesis of ethylene glycol by the hydroformylation of formaldehyde makes it possible to carry out the reaction under mild conditions: 8–10 MPa using mononuclear precursors of the rhodium catalyst and 1.5 MPa in the presence of the dinuclear rhodium complex.

Table 5. The stretching vibration frequencies in the spectra of the formaldehyde complexes of transition metals.

Complex	ν, cm^{-1}	Refs.
	ν_{CO} (η^2-CH_2O)	
CH_2O	1746	[24]
$Os(PPh_3)_2(CO)_2(\eta^2\text{-}CH_2O)$	1017	[81]
$Cp_2V(\eta^2\text{-}CH_2O)$	1160	[89]
$[(CH_3O)_3P]_3(CO)_2Fe(\eta^2\text{-}CH_2O)$	1220	[80]
$[CpZrCl]_2(\eta^2\text{-}CH_2O)$	1015	[86]
	ν_{CO} (CHO)	
$(np_3)Ni(CHO)$	1615	[79]
$OsH(CO)_3(PPh_3)(CHO)$	1601	[81]
$[Rh_{17}(CO)_{32-n}S_2(CHO)]^{(3+n)-}$	1585—1600	[94]
$(CO)_3Fe(\mu\text{-}PPh_2)_2Os(CO)_2(CHO)$	1545	[115]
$Co_2Fe_2(CO)_{10}(PPh_3)_2(CHO)$	1570	[116]
	ν_{OH} (CH_2OH)	
$OsCl(CO)_2(PPh_3)_2(CH_2OH)$	3540	[81]
	ν_{CO} ν_{OH}($COCH_2OH$)	
$HRhCl(PMe_3)_3(COCH_2OH)$	1630 3395	[105]
$Rh(OEP)(COCH_2OH)$	1697 3424	[106]

The hydroformylation of formaldehyde differs from the analogous hydroformylation of olefins by a multiplicity of features due to the characteristics of the structure of the substrate molecule and the ability of formaldehyde to be coordinated in different ways to the transition metal complex. The formaldehyde hydroformylation mechanism postulated by analogy with the hydroformylation of olefins does not take into account all the experimentally observed features of this reaction and requires certain modifications.

References

1. P Chaumette, F Hugues *Rev. Inst. Franç. Petrole*, 1985, **40**(1) 91
2. A Aquilo, J S Alder, D N Freeman, R J H Voorhoeve *Neft', Gaz, Neftekhimiya za Rubezhom*, 1983, (3) 68
3. R A Sheldon *Catalysis by Metal Complexes*, Vol. 3, *Chemicals from Synthesis Gas* (Translated into Russian), Izd. Khimiya, Moscow, 1987, 248 pp
4. G Henrici-Olive, S Olive *The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide* (Translated into Russian), Izd. Mir, Moscow, 1987, 245 pp
5. W Keim *Catalysis in C-Chemistry* (Translated into Russian), Izd. Khimiya, Leningrad, 1987, 296 pp
6. Y Falbe *New Synthesis with Carbon Monoxide* Springer Verlag, New York, 1980, 465 pp
7. M G Katsnel'son, V A Rybakov, M V Khokhlova *Okis' Ugleroda i Vodorod Vmesto Etilena v Neftekhimicheskikh Sintezakh* (The Replacement of Ethylene by Carbon Monoxide and Hydrogen in Petrochemical Syntheses), Izd. TsNIIteneftekhim, Moscow, 1986, 48 pp
8. J Kollar *Chem. Technol.*, 1984, 504
9. E V Anderson *Chem. Eng. News*, 1984, **62**(29) 9
10. H Izawa *Chem. Econ. Eng. Rev.*, 1980, **12**(3) 17
11. E M Ermolaeva, G L Avrekh, A E Ioffe *Khim. Prom.*, 1982, (7) 432
12. I I Moiseev *Zhur. Vses. Khim. Obshch. im Mendeleeva*, 1982, **27** 309
13. I I Moiseev *Khim. Prom.*, 1985, (4) 230
14. I Tkatchencho *Inf. Chim.*, 1984, **249** 115
15. J Gautier-Lafaye, R Perron *Methanol et Carbonylation* Rhone-Poulenc, Paris, 1986, 248 pp
16. A Weiss, S Trigerman, G Dunnells, et al. *Ind. Eng. Chem. Proc. Des. Develop.*, 1979, **18** 552
17. H Arakawa *Shokubai (Catalyst)* 1983, **25** 392
18. Japanese P. 57-81 422; *Chem. Abs.*, 1983, **97** 38 492
19. Japanese P. 58-81 423; *Chem. Abs.*, 1983, **97** 38 493
20. Japanese P. 53-73 506; *Chem. Abs.*, 1980, **88** 190 077
21. BRD P. 2 625 072; *Chem. Abs.*, 1981, **88** 89 114
22. Japanese P.57-118 527; *Chem. Abs.*, 1982, **97** 215 530
23. US P. 4 405 821; *Chem. Abs.*, 1983, **99** 194 433
24. S K Ogorodnikov *Formal'degid* (Formaldehyde), Izd. Khimiya, Leningrad, 1984, 279 pp
25. F Suzuki *Nippon Kagaku Kaishi*, 1982, (8) 1357
26. US P. 3 920 753; *Chem. Abs.*, 1975, **82** 124 761
27. A S C Chan, W E Carrol, D E Willis *J. Mol. Catal.*, 1983, **19** 377
28. Europ. P. 0 096 905; *Chem. Abs.*, 1987, **100** 191 374
29. Europ. P. 0 061 791; *Chem. Abs.*, 1983, **98** 34 242
30. Japanese P. 57-130 940; *Chem. Abs.*, 1982, **97** 215 527
31. K Wada, F Onoda *J. Synth. Org. Chem.*, 1983, **41** 515
32. US P. 4 358 411; *Chem. Abs.*, 1982, **94** 120 902
33. Japanese P. 57-165 337; *Chem. Abs.*, 1983, **98** 34 242
34. Japanese P. 58-88 333; *Chem. Abs.*, 1983, **98** 429
35. Europ. P. 0 072 051; *Chem. Abs.*, 1983, **99** 5209
36. US P. 4 405 821; *Chem. Abs.*, 1983, **99** 194 433
37. US P. 4 405 814; *Chem. Abs.*, 1985, **100** 5855
38. Japanese P. 76-128 903; *Chem. Abs.*, 1980, **92** 65 481
39. US P. 4 200 765; *Chem. Abs.*, 1981, **88** 190 089
40. L.Nawata, H Migazeki *J. Synth. Org. Chem.*, 1983, **41** 545
41. P E Garrow *Chem. Techn.*, 1985, **15** 123
42. T Sakakura, T A Kobayashi, T Hayashi, et al. *J. Organomet. Chem.*, 1984, **427** 171
43. W R Moser, C J Papile, S J Weininger *J. Mol. Catal.*, 1987, **41** 293
44. US P. 4 496 781; *Chem. Abs.*, 1987, **102** 203 599
45. S E Jacobson *J. Mol. Catal.*, 1987, **41** 163
46. Europ. P. 0 002 908; *Chem. Abs.*, 1982, **92** 6064
47. B. P. 2 085 426; *Chem. Abs.*, 1982, **94** 120 867
48. T Okano, M Marino, H Konishi *Chem. Lett.*, 1985, (12) 1793
49. French P. 2 363 538; *Chem. Abs.*, 1981, **93** 113 951
50. E Watanabe, J Hara, K Wada, et al. *Chem. Lett.*, 1986, (2) 285
51. A J Spencer *J. Organomet. Chem.*, 1980, **194** 113
52. F Suzuki *Bull. Chem. Soc. Jap.*, 1982, **55**(2) 169
53. D Evans, J A Osborn, G J Wilkinson *J. Chem. Soc.A*, 1968, 3133
54. A B Sanger *Can. J. Chem.*, 1985, **63** 571
55. Yu S Varshavskii, T G Cherkasova, N V Kiseleva, et al. *Zhur. Neorg. Khim.*, [*Russ. J. Inorg. Chem.*], 1986, **30** 152
56. Yu S Vashavskii *Kompleksy Metallov Platinovoi Gruppy v Sinteze i Katalize* (Platinum Group Metal Complexes in Synthesis and Catalysis), Chernogolovka, 1983, p. 52

57. R Y Mawby, F Bassolo, R G Pearson *J. Amer. Chem. Soc.*, 1966, **44** 1881
58. O S Roshchupkina, A V Bulatov, Ya Kh Samovarov, et al. *Koord. Khim.*, 1987, **13** 321
59. J E Parmeter, U Schwalke, W H Weinberg *J. Amer. Chem. Soc.*, 1987, **109** 5083
60. P Abley, F J McQuillin *J. Chem. Soc. Chem. Comm.*, 1969, 477
61. C Claver, J Fis, P Kalck *C1 Mol. Chem.*, 1987, **2** 25
62. A Dedieu, P Escaffre, J M France, et al. *Nouv. J. Chim.*, 1986, **10** 631
63. M Marchionna, G Longoni *Gazzetta*, 1986, **116** 453
64. US P. 4 477 685; *Chem. Abs.*, 1982, **96** 134 553
65. A S C Chan, H S Shieh, J P Hill *J. Organomet. Chem.*, 1985, **279** 171
66. US P. 4 238 418; *Chem. Abs.*, 1982, **94** 120 867
67. Y Ohgomori, S Mori, S Y Yoshida, Y Watanaba *J. Mol. Catal.*, 1987, **40** 223
68. Y Kiso, M Tanaka, T Hayashi, et al. *J. Organomet. Chem.*, 1987, **322** C32
69. G A Olah, L.Ohannesian, M Arvanghi *Chem. Rev.*, 1987, **87** 671
70. M Marchionna, G Longoni *Organometallics*, 1987, **6** 606
71. G D Vaughn, J A Gladysz *J. Amer. Chem. Soc.*, 1986, **108** 1473
72. M Machionna, G Longoni *J Mol. Catal.*, 1986, **35** 107
73. J Ojima *J. Mol. Catal.*, 1986, **37** 25
74. B D Dombeck *Adv. Catal.*, 1983, **32** 325
75. B D Dombeck *Organometallics*, 1985, **4** 1707
76. L C Costa *Catal. Rev.*, 1983, **25** 325
77. D L Thorn *J. Mol. Catal.*, 1982, **17** 279
78. J A Gladysz *Adv. Organomet. Chem.*, 1982, **20**(1) 1
79. C Bianchini, A Meli *Organometallics*, 1985, **4** 1537
80. H Berke, W Bankhardt, G Huttner, et al. *Chem. Ber.*, 1981, **114** 2754
81. K L Brown, G R Clark, C E L Headford, et al. *J. Amer. Chem. Soc.*, 1979, **101** 503
82. S Gambarotta, C Floriani, A Chiesi-Villa, et al. *J. Amer. Chem. Soc.*, 1982, **104** 2019
83. H Berke, R Birk, G Huttner, et al. *Z. Naturforsch. B: Anorg. Chem. Org. Chem.*, 1984, **39B** 1380
84. S Gambarotta, C Floriani, A Chiesi-Villa, et al. *J. Amer. Chem. Soc.*, 1985, **107** 2985
85. W E Buhro, S Georgiou, J Fernandez, et al. *Organometallics*, 1986, **5** 956
86. S Gambarotta, C Floriani, A Chiesi-Villa, et al. *Organometallics*, 1983, **105** 1690
87. P T Barger, J E Bercaw *Organometallics*, 1984, **3** 278
88. D L Thorn *Organometallics*, 1982, **1** 197
89. S Gambarotta, C Floriani, A Chiesi-Villa, et al. *Organometallics*, 1986, **5** 2425
90. P Leoni, M Pasquali *J. Organomet. Chem.*, 1983, **255** C1
91. W E Buhro, S Georgiou, J M Fernandez, et al. *Organometallics*, 1986, **5** 956
92. W Keim, M Berger, A Eisenbeis, et al. *J. Mol. Catal.*, 1981, **13** 19
93. Yu N Kukushkin *Koord. Khim.*, 1986, **12** 147
94. R C Schoening, J L Vidal, R A Fiato *J. Mol. Catal.*, 1981, **13** 83
95. W Tam , G I Lin, W K Wong, et al. *J. Amer. Chem. Soc.*, 1982, **104** 14
96. I L C Freriks, P C de Jong-Versloot, A G T Kortbeek, et al. *J. Chem. Soc. Chem. Comm.*, 1986, 253
97. B R James *Homogeneous Hydrogenation* (Translated into Russian), Izd. Mir, Moscow, 1976, 570 pp
98. L Farrugia, M L H Green *J. Chem. Soc. Chem. Comm.*, 1975, 416
99. P T Wolczanski, J E Bercaw *Acc. Chem. Res.*, 1980, **13** 121
100. B B Wayland, B A Woods, V M Minda *J. Chem. Soc. Chem. Comm.*, 1982, 634
101. J A Roth, M Orchin *J. Organomet. Chem.*, 1979, **172** C27
102. C D Wood, P E Garrow *Organometallics*, 1984, **3** 170
103. V Yu Gankin, G S Gurevich *Tekhnologiya Oksosinteza* (The Technology of the Oxo Synthesis), Izd. Khimiya, Leningrad, 1981, 262 pp
104. I B Kim, C S Chin *Polyhedron*, 1984, **3** 1151
105. D Milstein, W C Fultz, J C Calabrese *J. Amer. Chem. Soc.*, 1986, **108** 1336
106. S L Van Voorheese, B B Wayland *Organometallics*, 1985, **4** 1887
107. G O Nelson *Organometallics*, 1983, **2** 1474
108. Y C Lin, D Milstein, S S Wreford *Organometallics*, 1983, **2** 1461
109. R J Mawby, F Bassolo, R G Pearson *J. Amer. Chem. Soc.*, 1964, **86** 3994
110. H Berke, G Huttner *J. Organomet. Chem.*, 1981, **219** 353
111. G D Vaughn, J A Gladysz *Organometallics*, 1984, **3** 1596
112. H Henrici-Olive, S Olive *Coordination and Catalysis* (Translated into Russian), Izd. Mir, Moscow, 1980, 421 pp
113. M E Mirbach *J. Organomet. Chem.*, 1984, **265** 205
114. E J Crauford, T W Bodnar, A R Cutler *J. Amer. Chem. Soc.*, 1986, **108** 6202
115. S Rosenberg, S P Lockledge, G L Geoffroy *Organometallics*, 1986, **5** 2517
116. M G Richmond, J K Kochi *J. Organomet. Chem.*, 1987, **323** 219

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The synthesis of organochlorine compounds from one-carbon molecules

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ABSTRACT. Studies on the synthesis of organochlorine compounds from one-carbon molecules are surveyed. The thermodynamics, kinetics, and mechanisms of the direct and oxidative chlorination of methane, the esterification of methanol by hydrogen chloride, the hydrochlorination of acetylene, the hydrodechlorination of carbon tetrachloride, and the carbonylation of chloromethanes, the catalysts employed, and the practical applications of these reactions are examined.
The bibliography includes 143 references.

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I. Introduction

The great importance of organochlorine compounds in modern chemistry and technology is determined by their extensive and rapidly growing applications. By virtue of a wide variety of physical and chemical properties, they are used in virtually all branches of industry, agriculture, and domestic technology.[1]

Poly(vinyl chloride) is "plastic number two" (after polyethylene) and chloromethanes serve as the raw materials in the manufacture of organosilicon products, fluorinated plastics, and Freons. Chloromethanes have also found extensive applications as highly effective solvents, for example, in the manufacture of cine-film and of synthetic fibre. The use of carboxylic acid chlorides for the modification of polymers is extremely promising.

Methods have now been developed for the synthesis of these organochlorine compounds from one-carbon molecules. A cheap and readily available raw material is especially necessary bearing in mind the large-scale requirements for these compounds.

We shall examine the following one-carbon substances used for the synthesis of organochlorine compounds: natural gas, methanol synthesised from carbon monoxide and hydrogen, which are in their turn obtained from natural gas, acetylene, which is a methane pyrolysis product or is obtained from calcium carbide, and carbon monoxide obtained from natural gas or coal. In fact the main starting material in all cases is natural gas or coal.

II. Direct chlorination of methane and its chloro-derivatives

The chlorination of methane and its chloro-derivatives by molecular chlorine is one of the most thoroughly investigated reactions, which has in addition found extensive practical applications.[2–4]

The chlorination of methane yields as a rule the entire range of chloromethanes:

$$CH_4 \xrightarrow[-HCl]{Cl_2} CH_3Cl \xrightarrow[-HCl]{Cl_2} CH_2Cl_2 \xrightarrow[-HCl]{Cl_2} CHCl_3 \xrightarrow[-HCl]{Cl_2} CCl_4.$$

Over a wide temperature range, the formation reactions of all chloromethanes are virtually irreversible, the heat of each successive substitution of a hydrogen atom by a chlorine atom in methane amounting to 100–102 kJ mol^{-1}.[2,3] The main advances achieved in the study of this process have been described in reviews.[2,3,5–7] Problems associated with the variation of the ratio of the products obtained towards the preferential formation of one of them, the removal of a large amount of heat of reaction at a high rate of the process, the formation of chlorohydrocarbons of the ethane–ethylene series on chlorination of methane, and the utilisation of the hydrogen chloride evolved in a large amount during the reaction are examined below.

Table 1. The ratios of the rate constants for the chlorination of methane and chloromethanes.

Catalyst	*T*, K	Relative chlorination rate constants				Refs.
		CH_4	CH_3Cl	CH_2Cl_2	$CHCl_3$	
Without catalyst	573	1	1.67	1.22	0.42	[10]
»	673	1	0.40	0.24	0.07	[10]
	673	1	3.32	1.48	1.10	[8]
Sand	573	1	2.8	1.58	0.41	[9]
»	623	1	2.60	1.50	0.50	[9]
»	673	1	2.45	1.43	0.60	[9]
»	673	1	2.00	1.00	0.50	[11]
»	623	1	1.40	0.80	0.50	[12]
Kaolin	573	1	1.83	1.23	0.35	[9]
»	673	1	1.44	0.95	0.43	[9]
Activated charcoal	573	1	5.0	10.5	9.1	[9]
ditto	648	1	5.0	7.3	6.6	[9]
»	673	1	5.0	6.6	6.0	[9]
»	648	1	0.63	1.50	2.36	[13]
$CuCl_2$.KCl on diatomite	573	1	1.92	1.27	0.66	[14]
ditto	673	1	2.17	1.47	0.50	[14]

Figs.1–3 illustrate the molar proportions of the products of the chlorination of methane as a function of the chlorine : methane ratio, obtained experimentally in the gas-phase chlorination in a hollow container[8] and in a fluidised catalyst bed.[9] Table 1 presents the ratios of the rate constants for the chlorination of methane and chloromethanes obtained by different investigators by chlorination in a hollow container and on a catalyst.

Figs. 1–3 and Table 1 show that the composition of the chloromethanes obtained can change on chlorination of methane in a fluidised bed of a solid material. Whereas the presence of quartz sand has little influence on the reactivity of methane and chloromethanes,[9,11,12] in the presence of activated charcoal the composition of chloromethanes shifts sharply towards the preferential formation of tetrachloromethane.[9,13]

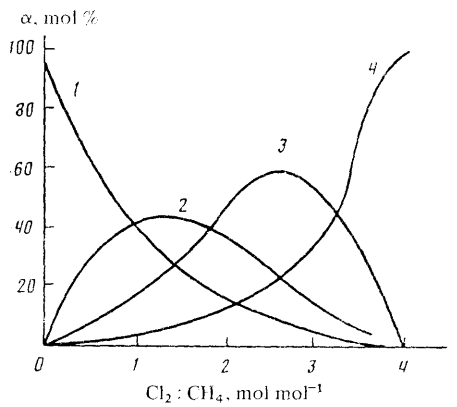


Figure 1. Free volume chlorination of methane:[8] *1*) CH_3Cl; *2*) CH_2Cl_2; *3*) $CHCl_3$; *4*) CCl_4; α—composition of reaction products.

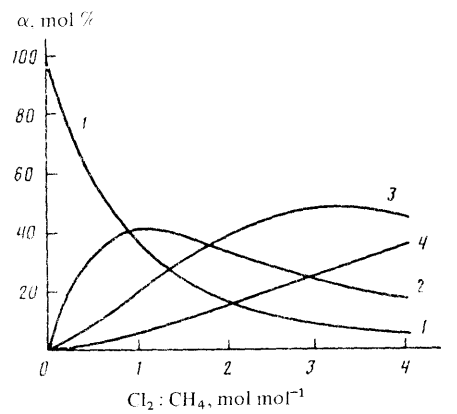


Figure 2. Chlorination of methane on quartz sand.[9]

In terms of absolute magnitude, the rate constants for the chlorination of methane and chloromethane in a fluidised quartz sand bed at 573 K are higher only by a factor of 1.5–2.6 than in a hollow container, while in the presence of activated charcoal the chlorination takes place at a much higher rate (Table 2).

Table 2. The ratios of the rate constants for chlorination in space[10] and on a catalyst[9] (the rate constants in bulk are quoted after Treger[1]).

Catalyst	*T*, K	Relative chlorination rate constants			
		CH_4	CH_3Cl	CH_2Cl_2	$CHCl_3$
Sand	573	1.5	2.6	2.0	1.5
»	673	0.6	3.4	3.4	5.0
Kaolin	573	6.3	7.2	6.8	5.5
»	573	1.7	6.5	7.2	11.6
Activated charcoal	573	6.3	18.1	55.7	142
ditto	673	0.95	11.9	26.0	83.7

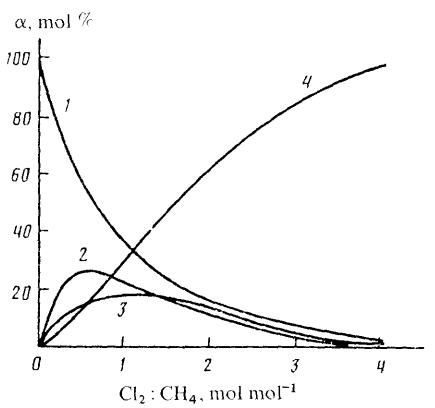


Figure 3. Chlorination of methane on activated charcoal.[9]

The heats and energies of activation for the adsorption of methane and its chloro-derivatives obtained by Belenko[15] enabled the author to put forward a mechanism for the catalytic participation of activated charcoal, kaolin, and sand in the chlorination process involving weak chemisorption of methane and chloromethanes on the surfaces of these catalysts. For activated charcoal, the activity series of methane and chloromethanes agree fully with the series based on their heats of adsorption (10.0 kJ mol^{-1} for CH_4, 29.5 kJ mol^{-1} for CH_3Cl, 43.5 kJ mol^{-1} for CH_2Cl_2, and 38.5 kJ mol^{-1} for $CHCl_3$).

It has been shown that the interaction of methane with a chlorinated carbon surface entails the substitution of chlorine atoms by CH_3 groups:[16]

$$\equiv C{-}Cl + CH_4 \rightarrow \equiv C{-}CH_3 + HCl.$$

The reaction takes place at temperatures above 470 K and at 770 K the chlorine atoms are adsorbed on the surface of technical carbon and are fully substituted, while those on the surface of activated charcoal are 78% substituted. It may be that the adsorbed CH_3 groups are rapidly chlorinated to CCl_3, which in fact explains the increased yield of tetrachloromethane when methane is chlorinated on activated charcoal.

On the other hand, one must note the fairly considerable scatter of the relative rate constants obtained by different investigators under the same chlorination conditions in a hollow container or in a fluidised catalyst bed (Table 1). The possible causes of this may be experimental difficulties [the necessity to maintain an isothermal regime under the conditions of an appreciable heat evolution and a high rate of reaction, failure to take into account the initiation of the reaction by light, different surface to volume ratios (S/V) for the reactor, and the deposition of carbon on the reactor walls or on the catalyst employed as a result of the decomposition of the chloromethanes]. It has been shown that the deposition of carbon on the catalyst increases the yield of tetrachloromethane.[17] Hence it is necessary to "condition" (coat with carbon) the walls in order to obtain reproducible results.[7]

The composition of the chloromethanes obtained on chlorination of methane can vary markedly depending on the gas flow regime in the reactor employed. Calculations have shown that on passing from the ideal displacement to the ideal mixing regime, the yield of the more chlorinated products increases.[18] Comparison of the results of the chlorination of methane in an isothermal ideal displacement reactor and in an industrial reactor showed that in the latter the yield of trichloromethane and tetrachloromethane is higher as a result of the reverse mixing.[19]

In the chlorination of methane in a hollow container,[10] the activation energy and the pre-exponential factor in the Arrhenius equation for the substitution of each successive hydrogen atom decrease steadily, since an increase in the number of chlorine atoms results in a decrease of the C–H bond energy in the chloromethane molecule but at the same time the attack by a chlorine atom on the hydrogen atom becomes more difficult. This behaviour is not observed in chlorination on catalysts.[9,14]

It is notable that the rate of chlorination both in a hollow container[10] and on a fluidised catalyst bed[9,11,12] depends on the concentrations of the initial reactants with an exponent of unity, which corresponds to the identical character of the chain termination reactions.

Different kinetics of the chlorination of methane in the presence of porous fillers of different nature have been obtained on a flow-circulation apparatus.[20] For the gas-phase reaction in the absence of fillers, the reaction orders with respect to the reactants were found to be unity and the activation energy was 121.3 ± 8.4 kJ mol^{-1}. The rate of reaction proved to be twice as high as in the study of Arai et al.[10] On the other hand, as will be seen in the discussion of the mechanism of the chlorination of methane, the first order reactions with respect to the reactants indicate chain termination on the wall, which should be more characteristic of the reaction in the presence of fillers.

The gas-phase chlorination of methane is initiated as a result of the effect of temperature, the catalytic effect of various solid materials or vessel walls, the effect of radiation and light, and various homogeneous catalysts. Because of its simplicity, the thermal chlorination of methane is used in virtually all industrial manufacturing processes.

The initiating influence of the surface consists in reducing the activation energy for the dissociation of the chlorine molecule by the heat of adsorption of the chlorine atom:[21]

$$\begin{array}{l} Cl_2 + 2S = 2SCl, \quad E_1 = \Delta H - 2q_{ClS}, \\ SCl = S + Cl^{\cdot}, \qquad E_2 = q_{ClS}, \end{array} \tag{1}$$

$$Cl_2 + S = SCl + Cl^{\cdot}, E_3 = \Delta H - q_{ClS}. \tag{2}$$

The activation energy for the formation of a chlorine atom in the gas phase, based on the activation energy for the gas-phase decomposition of a chlorine molecule into atoms of 238.5 kJ mol^{-1} and the heat of adsorption of a chlorine atom on glass amounting to 67 kJ mol^{-1}, is $238.5-67 \simeq 172$ kJ mol^{-1}. Gorokhovatskii[22] proposed relations for reactions (1) and (2) linking the heat of dissociation of the adsorbed chlorine molecules ($Q_{Cl_2\,ads}$) to the heat of dissociation of chlorine in space (Q_{Cl_2}) and to the heats of adsorption of molecular (q_{Cl_2}) and atomic (q_{Cl}) chlorine, from which it is seen that Q_{Cl_2ads} must be less than Q_{Cl_2}, because q_{Cl} is always greater than q_{Cl_2}:

$$Q_{Cl_2\,ads} = Q_{Cl_2} + q_{Cl_2} - 2q_{Cl},$$
$$Q_{Cl_2\,ads} = Q_{Cl_2} + q_{Cl_2} - q_{Cl}.$$

It has been shown[23] that the heterogeneous two-stage dissociation of chlorine in the above scheme is kinetically more favourable than the heterogeneous one-stage or gas-phase dissociation for $E_3 < 170$ kJ mol^{-1} and its rate is a maximum for $E_3 \simeq 70$ kJ mol^{-1} and $E_2 \simeq 170$ kJ mol^{-1}. The rate of dissociation via the two-stage scheme is then higher by 10–11 orders of magnitude than the rate of the gas-phase dissociation. This indicates the enormous role of the wall and of the ratio of the surface area of the reactor to its volume in the study of gas-phase radical-chain reactions. In an industrial reactor, it is essential to take into account this factor for the successful performance of the process.

The experimental Arrhenius parameters for the elementary stages of the chain propagation in the chlorination of methane are available.[7,24,25] Calculated and experimental data have been published by Bell et al.[25] The energy parameters of the chain termination stages are given in Kondrat'ev's handbook;[24] the activation energies for these reactions are zero. The process kinetics vary as a function of the dominant type of chain termination.[26]

Theoretically, it is to be expected that, on chlorination, for example, in an industrial reactor, the dominant type of chain termination varies as chlorine is consumed and there is a corresponding change in the chlorine : methane ratio, from quadratic termination by chlorine atoms, through cross-termination between alkyl radicals and chlorine atoms, to quadratic termination by alkyl (or halogenoalkyl) radicals. The process kinetics should vary accordingly.

Variable reaction orders with respect to the reactants have been established experimentally, for example, in the study of the kinetics and mechanism of the vapour-phase chlorination of trichloromethane.[27,28] For the ratio of trichloromethane and chlorine concentrations $[CHCl_3]:[Cl_2] = 10:1$ and temperatures in the range 643–696 K, the rate of chlorination of trichloromethane is described by the equation

$$w = k[Cl_2] \cdot [CHCl_3]^{0.5}.$$

When trichloromethane is chlorinated in an excess of chlorine with $[CHCl_3]:[Cl_2] = 1:7$, the dependence of the rate of reaction on the reactant concentrations is described by a different equation:

$$w = \frac{k}{B^{0.5}}[Cl_2]^{0.5}\,[CHCl_3],$$

where B is the adsorption coefficient.

In studies[20,29] of the chlorination of methane in the presence of adsorbents (including adsorbents impregnated with LiCl or $K_2S_2O_4-K_2S_2O_7$), different reaction orders were also obtained depending on the ratio of the amounts of chlorine and methane in the reaction mixture. Thus, for $p_{Cl_2}/p_{CH_4} < 1$, the order with respect to chlorine was unity and that with respect to methane was 0.5, which corresponds to cross termination of the chain. For $p_{Cl_2}/p_{CH_4} > 3$, the reaction orders with respect to chlorine and methane were respectively 0.5 and 1, which indicates quadratic termination by chlorine atoms. In the transitional range of the above ratios, the reaction orders with respect to chlorine and methane had intermediate values, for example, 0.8 and 0.6 respectively.

In the chlorination of methane in a fluidised catalyst bed, the chain initiation and termination take place preferentially on the wall and a direct dependence of the reaction rates on the chlorine and methane concentration was therefore obtained.[7,10,24] Many investigators believe that the solid materials used for the chlorination of methane, other than activated charcoal, are not catalysts but constitute an "expanded wall", functioning simultaneously as a heat exchanger. Rozlovskii and Treger[30] question the catalytic function of the catalyst (with the exception of activated charcoal) in a fluidised bed reactor on the grounds that, under the conditions of the high-temperature chlorination, equilibrium in the dissociation of chlorine is always attained. It has been concluded[31] that the rates of chlorination of methane attained in a hollow container[8,10] are close to those found in a fluidised catalyst bed.[9,10] The rate proved to be higher by an order of magnitude only on activated charcoal. All these features indicate a weak non-specific catalytic effect of the majority of catalysts used for chlorination. This effect is manifested in the chain initiation and subsequent chlorination stages as a result of the stronger adsorption of chloromethanes compared with methane.

There is no unanimous view concerning the mechanism of the catalytic action of salts; the acceleration of the chlorination of methane by systems based on transition metal chlorides is sometimes attributed to their ability to generate atomic chlorine as a result of their decomposition at a lower temperature than that required for the dissociation of chlorine molecules. A mechanism including a stage in which copper chloride undergoes thermal dissociation has been adopted for the chlorination of methane by a melt of copper and zinc chlorides.[32]

Another version of the catalytic action consists in the polarisation of the adsorbed chlorine molecule and subsequent ionic chlorination. This mechanism has been considered in greater detail by Shatalov.[33] The heterogeneous mechanism is supported by the absence of an inhibiting effect by oxygen. In gas-phase chlorination, oxygen is known to inhibit the reaction as a result of the formation of the relatively inactive $\dot{R}O_2$ radicals. Depending on the thermal stability of the peroxy-radicals, inhibition is shown up to a specific temperature.

It has been established[14,29] that the presence of transition metal chlorides in the salt composition is obligatory for catalytic chlorination. On the other hand, according to the estimate by Aglulin,[14] the rate of chlorination in the presence of metal chlorides on a carrier (at temperatures below 673 K and for $p_{O_2} \to 0$) is approximately 5 times lower than on a clean carrier. Thus metal chlorides proved in this instance to be less active than the carrier, apparently as a result of the greater affinity of metal chlorides for atomic chlorine.

In contrast to lithium chloride and potassium pyrosulphate (see above), in the presence of which variable reactions orders with respect to chlorine and methane have been observed, for other salt systems ($CuCl_2-KCl$, $CuCl_2-KCl-LaCl_3$, $FeCl_3-KCl$, CsCl, LiF, and $LiCl-KCl$), the order of the methane chlorination reaction is unity with respect to methane and is close to 1/2 with respect to chlorine over the entire range of conditions investigated up to extremely low partial pressures of chlorine ($\sim 10^{-3}$ kPa),[29] which indicates the attainment of equilibrium in the chlorine dissociation stage even under these conditions. The authors[29] also concluded that the reactivities of chlorine atoms on the surface and in space are similar.

On comparing the experimental data and the results of calculations based on the known rate constants for the elementary stages in the chlorination of methyl chloride, Lebedev et al.[35] concluded that the photochemical and radiation-chemical chlorination of methane has no significant advantages as regards selectivity (with respect to individual chloromethanes) over the thermal chlorination. The use of catalysts also does not change the ratios of the chloromethanes obtained. The latter claim is insufficiently well founded especially in relation to activated charcoal as the catalyst.

The ratios of the rate constants for the consecutive-parallel reactions in the photochemical chlorination of chloromethane and dichloromethane have been determined in a bubbler apparatus at temperatures in the range 263–308 K.[36] It was shown that the selectivity of the chlorination is described satisfactorily on the assumption that the reaction is of first order with respect to the compounds chlorinated. The relative constants are almost independent of temperature, the presence of inhibitors, and the intensity of irradiation, but are influenced by the composition of the reaction medium. The last finding is interpreted by the authors as due to the influence of the polarity of the medium on the rate of the rate-limiting stage in chain propagation. In the liquid-phase initiated chlorination of trichloromethane, the order of the reaction was found to be zero with respect to trichloromethane, unity with respect to chlorine, and 0.5 with respect to the initiator (azobisisobutyronitrile). The activation energy was 157 $\pm$ 12 kJ mol^{-1}. The difference between the orders of the chlorination reaction with respect to trichloromethane when different methods are used is apparently associated with the change in the character of chain termination.

In the study of the kinetics of the liquid-phase chlorination of methane in the temperature range 150–293 K in dichlorodifluoromethane, the following kientic equations were obtained for 293 K:[37]

$$w_{Cl_2} = k_1 \cdot In^{0.6\pm0.1}[Cl_2] \quad \text{when } [CH_4]:[Cl_2] > 300,$$
$$w_{Cl_2} = k_2 \cdot In^{0.6\pm0.1} \cdot [CH_4] \quad \text{when } [CH_4]:[Cl_2] < 10,$$

where *In* is the intensity of the adsorbed light.

Estimation of the rate constants for the elementary stages under the conditions for the first equation showed that the rate constant for the interaction of methyl radicals with chlorine molecules is six times smaller than the value calculated from literature data, while the rate constant for the reaction of atomic chlorine with methane is smaller by two orders of magnitude compared with the literature data. Such appreciable differences are associated mainly with the decrease in the pre-exponential factor, since the activation energy obtained for this stage (12.5 $\pm$ 2.5 kJ mol^{-1}) is almost identical with the value known for the gas phase.

In our view, examination of the chemical engineering problems arising in the direct chlorination of methane and chloromethanes requires the differentiation of the following factors.

In the first place there is the problem of the removal of a large amount of heat of reaction which in the existing methane chlorination processes in hollow adiabatic reactors is solved by the recirculation of a large amount of methane. At the same time, the excess methane is used to overcome the upper limit to the susceptibility to explosion of chlorine–methane mixtures.

The above problem can be solved effectively by using a fluidised catalyst bed or by carrying out the process in the liquid phase. The presence of a liquid and a solid simultaneously prevent explosion and make it possible thereby to work with concentrated mixtures of chlorine and methane or chloromethane.

Another task is to increase the process selectivity with respect to the individual intermediates in the chlorination reaction, in the first place with respect to trichloromethane. This problem is especially acute at the present time in connection with the signing in September 1987 in Montreal of the Protocol on chlorofluorocarbons, according to which it is necessary to reduce and then stop the manufacture of Freons which decompose the ozone layer, especially Freons 11 and 12 obtained from tetrachloromethane. One of the most realistic ways of converting the Freon 11 and 12 industries is to switch them to the manufacture of Freon 22 from trichloromethane.

The increase in the yield of trichloromethane and the decrease in the yield of tetrachloromethane in chloromethane manufacturing processes is therefore at present of extremely great current interest. In the industrial manufacture of chloromethanes by the chlorination of methane at a temperature of about 773 K, with a chlorine content in the initial mixture of 20–25%, and for the recycling of the entire chloromethane formed, the trichloromethane : tetrachloromethane weight ratio in the reaction products is about 5. In the chlorination of methane on a fluidised coke bed,[17] the ratio was 3, the reaction temperature was 648 K, and the chlorine : methane molar ratio was 1.3.

A high selectivity with respect to trichloromethane $CHCl_3 : CCl_4 = 5–7:1$) was obtained in the liquid-phase chlorination of chloromethane;[38] the reaction temperature was 333–343 K, the $CH_3Cl : Cl_2$ ratio was approximately unity, and the initiator employed was azobisisobutyronitrile.

The selectivity with respect to trichloromethane increases with decrease in the degree of conversion of chloromethane or dichloromethane during a pass, which necessitates the corresponding increase in the extent to which they are recycled. In this case, it is economical to carry out the process by combining the chlorination reaction with fractionation. Yet another problem to which little attention has been devoted in the literature but which is of interest from both theoretical and practical points of view is that of the formation of admixtures of chlorohydrocarbons of the ethane–ethylene series in the chlorination of methane. Some of these admixtures have a boiling point close to that of one of the chloromethanes (for example, 1,1-dichloroethane, *cis*-1,2-dichloroethylene, and trichloromethane), while others form an azeotrope with a boiling point close to that of the main substance (1,2-dichloroethane and tetrachloromethane). Periodic processes leading to the loss of the product, additional consumption of materials and other resources, and the formation of a large amount of waste are usually employed to remove these impurities from chloromethanes. Thus, it has been suggested that dichloromethane be purified by treatment with potassium permanganate solution; trichloromethane is nowadays purified by treatment with oleum and is then neutralised with a solution of caustic soda and dried. In view of the impossibility of separating 1,2-dichloroethane, tetrachloromethane is not isolated at all as a commercial product in the industrial manufacture of chloromethanes by the chlorination of methane. It is noteworthy that the requirements specified by the USSR state standards (GOS) as regards the contents of individual impurities are fairly stringent: the amount of 1,1-dichloroethane in trichloromethane and of 1,2-dichloroethane in tetrachloromethane must be not more than 0.002%. The concentration of the impurities formed in the industrial manufacture of chloromethanes by the chlorination of methane in a hollow reactor has been quoted by Nikitenko et al.[39]

Evidently the C_2 chloro-derivatives are formed as a result of the recombination of radicals since the initial methane is freed from homologues, including ethane. The ways which should be employed to rule out the formation of impurities are also indicated: firstly, one can attempt to prevent the quadratic termination by hydrocarbon radicals and secondly it is desirable to increase the chain length.

The influence of temperature and of the dilution of the initial mixture by an inert gas on the formation of C_2 chlorohydrocarbons in the volume chlorination of methane has been investigated.[40] A decrease in temperature alters the composition and amount of the impurities formed, one of the causes of which is apparently an increase in chain length and a decrease in the degree of decomposition of the chloromethanes. However, a significant decrease in the amount of impurities to the required level could not be achieved.

As already stated, in the chlorination of methane in a fluidised catalyst bed chain termination takes place on the surface of the solid material ("wall"). As a result, the chloromethanes obtained in this way contain virtually no impurities.[41] However, despite the evident advantages of the fluidised bed such as high productivity, the possibility of working with virtually any chlorine : methane ratio, and the excellent quality of the chloromethanes obtained, the chlorination of methane in a fluidised catalyst bed has not so far actually found application in industrial practice. Two small industrial plants of the Japanese company Asahi Glass[42] and the Indian Company Standard Alkali[43] are known.

The use of a fluidised bed is desirable for exhaustive chlorination but for the preferential yield of chlorination intermediates it has not so far been possible to use this method in industrial practice. The point is that chloromethanes decompose during the chlorination of methane and carbon is deposited on the catalyst. According to Shatalov's data,[17] under these conditions the yield of tetrachloromethane on the carbon-coated silica gel or on coke with a specific surface of 1–3 $m^2 g^{-1}$ increases to the same level as on activated charcoal with a specific surface of 1000–2000 $m^2 g^{-1}$.

The use of an inert solid (quartz sand) made it possible to increase the duration of the operation of the apparatus to 1500 h,[44] while pumice became blocked with the decomposition and charring products after 20 h. Even the use of an inert solid does not fully guarantee the absence of carbon deposition, since adiabatic heating of an equimolar mixture of chlorine and methane results in a temperature rise of more than 1000 °C and any breakdowns in the structure of the fluidised bed in the form of bubbles or thickened regions[45] can lead to local overheating and decomposition of chloromethanes. On the Asahi Glass apparatus[42] provision is made for the supply of oxygen to burn off the carbonaceous deposits. Yet another disadvantage of the fluidised bed is that, with increase in diameter on passing to industrial apparatus, an increase in the yield of tetrachloromethane is also to be expected as a result of the approach of the operating regime of the reactor to the ideal mixing model.

III. Decomposition of chloromethanes

In connection with the great influence of the decomposition of chloromethanes on the stable course of the chlorination process in a fluidised catalyst bed and also in a hollow reactor, where abrupt process terminations with an abundant release of carbon also occur, it is useful to examine the kinetics and mechanisms of these reactions. Studies by Shilov and Sabirova[46-48] have made a great contribution to the investigation of the chloromethane decomposition reactions. According to data obtained in a vacuum flow apparatus for short contact times, chloromethane decomposes at 1116 and 1147 K to hydrogen chloride, methane, acetylene, and a small amount of hydrogen, the amount of methane being three times smaller than that of HCl.[47] The activation energy for the decomposition (358 kJ mol^{-1}) is close to the bond energy. The authors suggest the following mechanism of the decomposition process:

$$CH_3Cl \rightarrow \dot{C}H_3 + Cl^{\cdot},$$
$$\dot{C}H_3 + CH_3Cl \rightarrow CH_4 + \dot{C}H_2Cl,$$
$$Cl^{\cdot} + CH_3Cl \rightarrow HCl + \dot{C}H_2Cl,$$
$$\dot{C}H_2Cl + \dot{C}H_2Cl \rightarrow CH_2Cl{-}CH_2Cl \rightarrow HCl + CH_2{=}CHCl,$$
$$CH_2{=}CHCl \rightarrow HCl + CH{\equiv}CH.$$

The thermal decomposition of tetrachloromethane[47] (827–874 K) results in the formation of chlorine, hexachloroethane, and tetrachloroethylene. The activation energy for the decomposition is 230 kJ mol^{-1}. The proposed mechanism is based on experimental data showing that hexachloroethane is an intermediate:

$$CCl_4 \rightarrow \dot{C}Cl_3 + Cl^{\cdot},$$
$$Cl^{\cdot} + CCl_4 \rightarrow Cl_2 + \dot{C}Cl_3,$$
$$\dot{C}Cl_3 + \dot{C}Cl_3 \rightarrow C_2Cl_6,$$
$$C_2Cl_6 \rightarrow C_2Cl_4 + Cl_2.$$

The thermal decomposition of tetrachloromethane to tetrachloroethylene, i.e. $2CCl_4 \rightleftarrows C_2Cl_4 + 2Cl_2$, is used in the industrial manufacture of perchlorocarbons by the exhaustive destructive chlorination of C_1–C_3 hydrocarbons and their chloroderivatives in order to obtain tetrachloroethylene and tetrachloromethane in variable proportions. The process is carried out in a hollow reactor at temperatures in the range 833–873 K or in a fluidised sand bed at 773–823 K.

Despite the fact that the C–Cl bond energy in trichloromethane is higher than in tetrachloromethane, the rate of decomposition of the latter at 832 K is 15 times smaller than that of trichloromethane.[44] This is explained[44] by the biradical decomposition of trichloromethane ($CHCl_3 \rightarrow HCl + :CCl_2$), after which the following reactions can occur:

$$:CCl_2 + CHCl_3 \rightarrow HCl + C_2Cl_4 \text{ or}$$
$$:CCl_2 + CHCl_3 \rightarrow CHCl_2CCl_3 \rightarrow HCl + C_2Cl_4,$$
$$:CCl_2 + CHCl_3 \rightarrow \dot{C}Cl_3 + \dot{C}HCl_2,$$
$$2\dot{C}Cl_3 \rightarrow C_2Cl_6.$$

The temperature dependence of the rate constant is described by the equation $k = 2.61 \times 10^{11} \exp(-197\,000/RT)$ s^{-1}.

Another expression has been quoted[49] for the trichloromethane decomposition rate constant: $k = 6.3 \times 10^8 \exp(-157\,000/RT)$ s^{-1}, but the values of the constant at temperatures in the range 750–850 K differ little from those of Shilov and Sabirova.[48] A radical mechanism has been proposed for the decomposition process: $CHCl_3 \rightarrow \dot{C}HCl_2 + Cl^{\cdot}$. The main decomposition products are HCl and C_2Cl_4, as well as C_2Cl_6, C_2HCl_5, etc.

The study of the thermal decomposition of trichloromethane with the aid of shock waves[50] has confirmed the formation of the $:CCl_2$ biradicals and hydrogen chloride.

In the thermal decomposition of dichloromethane (806 K), CH_3Cl, $CHCl{=}CCl_2$, C_2Cl_4, $CHCl_3$, CCl_4, and *cis*- and *trans*-$CHCl{=}CHCl$ were detected.[51] The activation energy for the decomposition is 184 kJ mol^{-1}. The authors[51] propose a degenerate-branched mechanism involving the formation of an intermediate (dichloroethylene), chain propagation with the aid of $Cl^{\cdot}$ atoms and the radicals $\dot{C}H_2Cl$, and the chain branching reaction $CHCl{=}CHCl \rightarrow \dot{C}_2H_2Cl + Cl^{\cdot}$.

It must be recognised that the biradical decomposition of dichloromethane is nevertheless more probable. The formation of biradicals (or carbenes) in the decomposition of dichloromethane and trichloromethane was demonstrated in an early study by Semenov.[26]

The decomposition of dichloromethane was not observed in the temperature range 673–753 K in a gradient-free quartz reactor with a stirrer which had been coated with carbon beforehand.[52]

The heterogeneous thermal decomposition of tetrachloromethane[53] as well as trichloromethane and dichloromethane[54] has been studied at temperatures in the range 773–873 K on a quartz fibre (S_{sp} = 0.26 m^2 g^{-1}) and on carbon black (S_{sp} = 100 m^2 g^{-1}) both of which had been coated beforehand with a layer of pyrolytic carbon obtained as a result of the decomposition of toluene.

The ratios of the rate constants (in g cm^{-2} s^{-1} Pa^{-1}) for the pyrolysis of tetrachloromethane, trichloromethane, and dichloromethane at 773 K are 1:80.6:15.7. The rate of formation of pyrolytic carbon on quartz in the decomposition of dichloromethane is given by the equation $w = 7.7 \times 10^{-4} p \exp(-163\,000/RT)$, while in the decomposition of trichloromethane the equation is $w = 2.1 \times 10^{-3} p \exp(-159\,000/RT)$.

The decomposition of chloromethanes on the surface of pyrolytic carbon at a low pressure in the temperature range 850–1280 K has been investigated.[55] While CH_3Cl is stable under the conditions investigated, the decomposition of CH_2Cl_2 and CCl_4 over clean silicon dioxide surface takes place initially with appreciable self-acceleration as a result of the formation of soot on the reactor walls and then the rate of the decomposition reaction remains constant but twice as high as the rate of the homogeneous pyrolysis under the same conditions.

An analogous increase in the rate of reaction during the initial period in the decomposition of dichloromethane on alumina (S_{sp} = 10 m^2 g^{-1}) was noted by Kovaleva et al.[56] The rate of decomposition then begins to fall. Simultaneously with the change in the degree of deposition of carbon, the specific surface of the decomposition catalyst initially increases and then falls.

The rate of the catalytic decomposition of dichloromethane depends on its concentration (with an exponent of unity) and has an activation energy of 105 kJ mol^{-1}.[57] Only carbon and hydrogen chloride were detected among the catalytic decomposition products[57] in accordance with the proposed reaction mechanism:

$$CH_2Cl_2 \rightarrow CHCl_{ads} + HCl,$$
$$CHCl_{ads} \rightarrow C + HCl$$

The study of the decomposition of chloromethanes in a fluidised activated charcoal bed was undertaken by Shatalov et al.[58] The qualitative results obtained agree with the decomposition reaction mechanisms proposed by Shilov and Sabirova.[46-48] The decomposition of mixtures of various chloromethanes and mixtures of methane with chloromethanes has also been studied.[58] For example, it has been noted that, in the presence of CH_4, the degree

of decomposition of tetrachloromethane increases, apparently as a result of the binding of chlorine.

A thermodynamic analysis of the reversible reactions in the formation of chloromethane has been carried out:[59]

$$CH_4 + CCl_4 \rightleftarrows CH_3Cl + CHCl_3,$$
$$CH_4 + CHCl_3 \rightleftarrows CH_3Cl + CH_2Cl_2,$$
$$CH_3Cl + CCl_4 \rightleftarrows CH_2Cl_2 + CHCl_3.$$

The highest equilibrium constant was obtained for the first reaction.

The study of the interaction of tetrachloromethane and methane showed that the experimental data are in satisfactory agreement with calculations based on the known constants for the elementary stages.[60] The exchange reaction has an order of 1.5 (0.5 with respect to CCl_4 and 1 with respect to CH_4) and the effective calculated rate constant given by

$$k = 10^{14.94} \exp(-205\,600/RT)\ \text{cm}^{1.5}\ \text{mol}^{-0.5}\ \text{s}^{-1}.$$

Thus the thermal stabilities of chloromethanes increase in the sequence $CHCl_3 < CH_2Cl_2 < CCl_4 < CH_3Cl$, and the pyrolytic carbon formed in the decomposition process can accelerate further decomposition. Apparently a proportion of the C_2 chlorohydrocarbon impurities are obtained from the radicals and biradicals formed on decomposition of chloromethanes.

IV. Benson's process

It is of interest that "undesirable" (in the synthesis of chloromethanes) reactions involving the decomposition of chloromethanes and the recombination of radicals have been used by Benson to develop a process for the preparation of hydrocarbons by the high-temperature interaction of chlorine with methane.[61] The process is carried out at atmospheric pressure, high temperatures (973–1983 K), methane : chlorine ratios ranging from 1:1 to 10:1, and short contact times counted in milliseconds. The combustion of a mixture of methane with chlorine results in the formation of ethane at temperatures of about 1000 K or of ethylene and hydrogen at temperatures of about 2000 K.

The method consists in chlorinating methane to chloromethane, the pyrolysis of chloromethane, and the formation of C_2 hydrocarbons as a result of the recombination of hydrocarbon radicals.[62]

The thermal reaction of a mixture of chlorine and methane has been investigated[63,64] at temperatures in the range 1081–1273 K, at pressures in the range 150–577 mm Hg, for a chlorine content in the mixture with methane of 0.42–1.2%, and for contact times of 0.8–1.6 s. The carbon-containing products are CH_3Cl, C_2H_4, C_2H_6, C_2H_2, and C_3H_6. The fraction of the non-chlorinated unsaturated hydrocarbons increases with increase in temperature and reaches 77% at 1273 K. The following radical process mechanism, divided into several stages, has been proposed:

I. Initial ethane

Initiation:

$$CH_4 \rightarrow \dot{C}H_3 + H^{\cdot},$$
$$Cl_2 + M \rightarrow 2\,Cl^{\cdot} + M.$$

Chain transfer:

$$H^{\cdot} + CH_4 \rightarrow H_2 + \dot{C}H_3,$$
$$H^{\cdot} + Cl_2 \rightarrow HCl + Cl^{\cdot}.$$

Chain propagation:

$$\dot{C}H_3 + Cl_2 \rightarrow CH_3Cl + Cl^{\cdot},$$
$$Cl^{\cdot} + CH_4 \rightarrow HCl + \dot{C}H_3.$$

Chain termination:

$$2\,\dot{C}H_3 \rightarrow C_2H_6. \qquad (3)$$

Chain termination is also possible (to a lesser extent) via the reaction:

$$\dot{C}H_3 + Cl^{\cdot} \rightarrow CH_3Cl,$$
$$\dot{C}H_3 + H^{\cdot} \rightarrow CH_4. \qquad (4)$$

The first stage can be characterised by the overall equations:

$$2\,CH_4 + Cl_2 \rightarrow C_2H_6 + 2HCl,$$
$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl.$$

II. Second stage

$$\dot{C}H_2Cl + RH \rightleftarrows CH_3Cl + R^{\cdot},$$
$$\dot{C}H_2Cl + Cl_2 \rightarrow CH_2Cl_2 + Cl^{\cdot},$$
$$\dot{C}_2H_5 \rightarrow C_2H_4 + H^{\cdot},$$
$$\dot{C}_2H_5 + RH \rightleftarrows C_2H_6 + R^{\cdot},$$
$$\dot{C}_2H_5 + Cl_2 \rightarrow C_2H_5Cl + Cl^{\cdot},$$
$$\dot{C}H_3 + \dot{C}H_2Cl \rightarrow C_2H_5Cl, \qquad (5)$$
$$2\,\dot{C}H_2Cl \rightarrow CH_2Cl{-}CH_2Cl. \qquad (6)$$

The concentration of the $CH_2Cl^{\cdot}$ radicals is negligible compared with the $CH_3^{\cdot}$ concentration so that the chain termination via reactions (5) and (6) is insignificant compared with the termination via reaction (3).

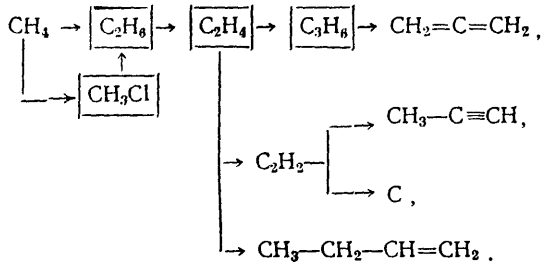
III. Third stage

$$\dot{C}H_3 + C_2H_4 \rightleftarrows CH_3{-}CH_2{-}\dot{C}H_2,$$
$$\dot{C}_2H_5 + C_2H_4 \rightarrow CH_3{-}CH_2{-}CH_2{-}\dot{C}H_2,$$
$$CH_3{-}CH_2{-}\dot{C}H_2 \rightarrow CH_3{-}CH{=}CH_2 + H^{\cdot},$$
$$CH_3{-}CH_2{-}CH_2{-}\dot{C}H_2 \rightarrow CH_3{-}CH_2{-}CH{=}CH_2 + H^{\cdot},$$
$$R^{\cdot} + C_2H_4 \rightarrow RH + \dot{C}_2H_3,$$
$$\dot{C}_2H_3 \rightarrow C_2H_2 + H^{\cdot}.$$

IV. Fourth stage

$$\dot{C}H_3 + C_2H_2 \rightleftarrows CH_3{-}CH{=}\dot{C}H,$$
$$R^{\cdot} + CH_3{-}CH{=}CH_2 \rightarrow RH + \dot{C}H_2{-}CH{=}CH,$$
$$R^{\cdot} + C_2H_2 \rightarrow RH + CH{\equiv}C^{\cdot},$$
$$CH_3{-}CH{=}\dot{C}H \rightarrow CH_3{-}C{\equiv}CH + H^{\cdot},$$
$$CH{\equiv}C^{\cdot} \rightarrow 2C + H^{\cdot},$$
$$\dot{C}H_2{-}CH{=}CH_2 \rightarrow CH_2{=}C{=}CH_2 + H^{\cdot}.$$

Under the conditions indicated, Benson's process can be summarised by means of the scheme presented below, the main products being ethane, ethylene, chloromethane, and propene, while the rest are present as impurities:



In our view, in the scheme for the initial stage it is necessary to make provision for the decomposition of methyl chloride, i.e. the reaction which is the reverse of reaction (4), as a result of which the $\dot{C}H_3$ and $Cl^{\cdot}$ radicals are returned to the reaction sphere and virtually the only possible termination involves the recombination of the $\dot{C}H_3$ radicals. Benson's process is based on the ease of dissociation of chlorine and the lower thermal stability of methyl chloride compared with methane.

V. Oxidative chlorination of methane and its chloro-derivatives

One of the deficiencies of the processes involving the direct chlorination of methane and its chloro-derivatives, not mentioned above, is the conversion of half of the chlorine used into hydrogen chloride. The necessity to utilise increasing amounts of the latter has been the cause of the development of a method for the oxidative chlorination of methane, where the chlorinating agent is a mixture of hydrogen chloride and oxygen.

The oxidative chlorination of methane is based on the oxidation of hydrogen chloride by oxygen to chlorine, which is usually carried out in the gas phase copper chloride-containing catalysts.

From the results of kinetic studies of the oxidative chlorination of methane, it has been concluded[14,23,65] that the oxidation of hydrogen chloride (also called the Deacon reaction) takes place at the same rate both in the presence and absence of methane, i.e. regardless of its subsequent chlorination. The oxidation of hydrogen chloride to chlorine is a reversible reaction, which usually occurs at temperatures in the range 623–723 K, the equilibrium constant K_e decreasing appreciably with increase in temperature. When the Deacon reaction and the methane chlorination reaction take place simultaneously, the equilibrium in the first reaction is displaced as a result of the consumption of chlorine, as can be seen from the data presented below:[2]

$$2n\,HCl + n/2O_2 \rightleftarrows n\,Cl_2 + n\,H_2O,\quad K_e(700\ K)\,8.3,$$
$$CH_4 + n\,Cl_2 \rightarrow CH_{4-n}Cl_n + n\,HCl$$
$$CH_4 + n\,HCl + n/2\,O_2 \rightarrow CH_{4-n}Cl_n + n\,H_2O,$$
$$K_e(700\ K)\,9.1\cdot10^{8} - 9.8\cdot10^{33}.$$

A number of recent publications have been devoted to the gas-phase heterogeneous-catalytic oxidative chlorination of hydrocarbons and their chloro-derivatives.[2,23,66]† The problem of the oxidative chlorination of methane will therefore be considered here in a more concise form.

Since, as can be seen from the above, the methane chlorination reaction at temperatures at which the Deacon reaction is carried out can proceed without the participation of a catalyst, the main task in the development of a process for the oxidative chlorination of methane is the selection of a catalytic system for the first stage.

Despite a number of advances achieved on these lines, copper(II) chloride, proposed as the catalyst for the oxidation of hydrogen chloride already in the past century, still remains the main component of catalysts for the Deacon and oxidative chlorination reactions.[67] Catalytic systems based on palladium, chromium, and iron chlorides proved to be less active.[68] Platinum(II)–platinum(IV) chloride complexes have been recently proposed as well as the complex $K_4Ru_2OCl_{10}$; being deposited on alumina or silicon dioxide, they catalyse the oxidative chlorination of methane in aqueous solutions or in the gas phase.[69,70] The catalysts obtained proved to be more active than catalysts based on copper and potassium chlorides. Our studies on catalysts which Tret'yakov et al.[69,70] prepared by adding a ruthenium complex to copper and potassium chlorides on α-alumina confirmed the higher activity of the ruthenium-containing catalyst. However, the addition of a lanthanide chloride[71] proved to be more effective.

It is noteworthy that catalysts for the oxidative chlorination of methane based on copper, alkali metal, and alkaline earth metal chlorides on a porous carrier constitute an extremely unusual system; apart from the traditional questions of activity, selectivity, and stability, problems associated with the volatility of copper chlorides in the formation of a melt of catalytically active salts under the reaction conditions arise here.

The addition of alkali metal chlorides to copper chloride diminishes the volatility of the latter.[72] The greatest decrease in volatility is observed when rubidium chloride is added, but, as regards the combination of efficiency with availability, preference was given to potassium chloride. The dependence of the volatility of copper chlorides and of the activity of the catalyst on the ratio $KCl:CuCl_2$ is illustrated in Fig.4. The equimolar ratio has been recognised as optimal in terms of the combination of activity and stability. The influence of the nature of the alkali metal (lithium, sodium, potassium, and caesium) and of the potassium : copper ratio in catalytic systems on the kinetic parameters of the hydrogen chloride oxidation reaction has been examined in detail.[23] The changes in these parameters are attributed to the formation of copper and alkali metal chlorides. It is most likely that this is also the cause of the decrease in the volatility of copper chlorides.

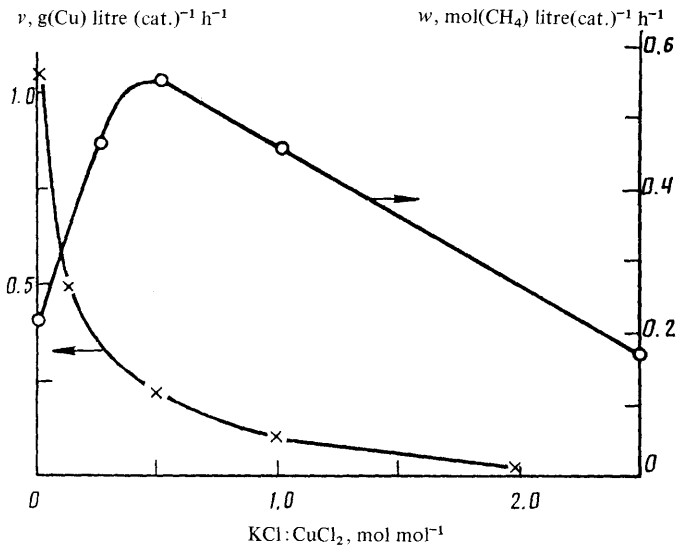


Figure 4. Dependence of the activity and stability of the catalysts for the oxidative chlorination of methane on the $KCl:CuCl_2$ ratio;[14,72] w—rate of overall conversion of methane at 648 K; r—rate of volatilisation of copper chlorides at 723 K.

†Yu A Treger, V N Rozanov, M R Flid, L M Kartashov, *Uspekhi Khim.*, 1988, **57** 577 [*Russ. Chem. Rev.*, 1988(4)]

The influence of potassium chloride on the activity of the catalyst based on copper chloride in the oxidative chlorination of methane has been investigated in detail in a recently published study.[73] The maximum activity was observed for the ratio potassium : copper = 1, the composition of the chloromethanes obtained varying as a function of the presence or absence of potassium chloride.

The attempts to bind copper in the spinel structure ($CuAl_2O_4$, $CuCr_2O_4$) in order to eliminate the volatility were unsuccessful, since, under the conditions of an excess of hydrogen chloride at an elevated temperature, these compounds gradually decompose with segregation of copper chloride as the active component of the catalyst.[68,74]

A melt of the active mass of the copper and potassium chlorides, on carriers of different chemical nature and with different specific surfaces, forms in the extensive pore system of the carrier isolated inclusions with a thickness equivalent to 10–200 molecular layers.[75,76]

The interaction of the salts with the carrier, the surface migration of the salt phases, and the change in the structure and surface area of the salt clusters have been demonstrated by electron microscopy and also by studying adsorption in conjunction with X-ray diffraction and differential thermal analysis.[77]

Porous substances with a wide range of specific surfaces are used as carriers for the catalysts of the oxidative chlorination of methane.[66] However, the choice of the carrier is fairly specific. For example, when the process is carried out in a fluidised catalyst bed, the use of carriers with a large specific surface proved preferable, since this ensures excellent fluidisation without bubbles and lumps.[78] However, on these catalysts the process selectivity, characterised by the degree of conversion of methane into chloromethanes relative to the overall conversion into chloromethanes and carbon oxides, is lower than in the case where inert carriers with a limited specific surface are used. At the same time, the catalysts on carriers with a limited specific surface in a fluidised bed form lumps probably owing to the partial emergence of the melt onto the surface. As a result, carriers with an average specific surface of 10–60 $m^2\ g^{-1}$ proved optimal.[78]

In the stationary catalyst bed, one can use carriers with a specific surface less than 10 $m^2\ g^{-1}$, but when it is reduced to 1 $m^2\ g^{-1}$ and less, the corrosion of the metallic walls of the reactor at the sites of contact intensifies sharply, which is also most probably associated with the presence of the melt.[79] Under these conditions, iron chloride, a corrosion product, enters the catalyst and increases the rate of the extensive oxidation of methane and chloromethanes to carbon oxides, while nickel and chromium chlorides hardly affect the activity and selectivity of the catalyst.[80]

Communications have been published recently concerning the possibility of carrying out the oxidative chlorination of methane at relatively low temperatures (less than 473 K) by using colloidal silicon dioxide as the carrier.[81]

The kinetics and mechanism of the oxidative chlorination of methane on traditional catalysts with copper chlorides have been described in greatest detail in Refs. 14, 23, 65, and 82. It was shown that the oxidation of HCl proceeds throughout the bulk of the salt melt with participation of copper chloride. The rate of the Deacon reaction is independent of the partial pressure of hydrogen chloride when it is above 0.04 atm, its observed reaction order with respect to oxygen is 0.5, and, when account is taken of the inhibiting effect of chlorine, it is unity. The observed activation energy on the catalyst containing an equimolar mixture of copper and potassium chlorides is 129 kJ mol^{-1}.

The process mechanism put forward by Slama and Kodajs[83] in connection with the observed second order of the oxygen absorption reaction with respect to Cu^+ assumes the following form:

$$2\,CuCl_2 \overset{\text{fast}}{\rightleftarrows} 2CuCl + Cl_2,$$
$$2\,CuCl + O_2 \xrightarrow{\text{slow}} Cu_2O_2Cl_2,$$
$$Cu_2O_2Cl_2 + 4HCl \xrightarrow{\text{fast}} 2CuCl_2 + Cl_2 + 2\,H_2O.$$

The following kinetic equation corresponds to this mechanism:

$$w = 4kK\,[CuCl_2]^2\ p_{O_2}/p_{Cl_2} = k'p_{O_2}/p_{Cl_2},$$

where k is the rate constant, K the equilibrium constant, and $k' = 4kK[CuCl_2]^2$.

The above mechanism may serve as an illustration of one of the first theories of catalysis, which explains the mechanism of the catalytic reaction by the formation of intermediate compounds which are then converted into the reaction products with regeneration of the initial catalysts. All the stages of the mechanism have been investigated separately and can proceed as independent reactions.[84,85]

On the basis of the results of the study of the adsorption of oxygen, Ruthven and Kenney[86] believe that the rate of the Deacon reaction is determined by the rate of oxidation of CuCl to $CuCl_2$ and is described by the equation

$$w = 4k\gamma^2K^2a^2p_{O_2}\{\gamma K + (p_{Cl_2})^{1/2}\}^2,$$

where K is the equilibrium constant of the thermal dissociation of copper chloride, a the mole fraction of copper in the melt, γ the ratio of the activity coefficients of Cu^{2+} and Cu^+, and k the rate constant for the absorption of oxygen.

When $(p_{Cl_2})^{1/2} \gg \gamma/K$, the familiar equation

$$w = k''p_{O_2}/p_{Cl_2},\ \text{where}\ k'' = 4k\gamma^2K^2a^2,$$

holds. Two probable mechanisms of the HCl oxidation reaction have been examined.[23] The author took into account primarily data (including his own) concerning the complex-forming properties of copper, which influence both the stage involving the formation of the active form of the catalyst and the stage in which the reactants are activated in the oxidation-reduction reaction. It is notable that the formation of complexes between copper and potassium chlorides, namely $KCuCl_3$, K_2CuCl_4, K_2CuCl_3, and $K_2Cu_2Cl_6$, has been noted by many investigators.[83–87]

The first mechanism is based on the fact that chlorine is formed in the copper(II) chloride decomposition stage, the copper(II) chloride being regenerated by reaction with oxygen and then with hydrogen chloride. In the second mechanism, chlorine is evolved in the stage involving the interaction of oxygen with copper(II) chloride which is promoted by the formation of complexes with HCl and KCl.

Subject to certain assumptions, the equations corresponding to both mechanisms simplify and are converted into

$$w = k'''(p_{O_2}/p_{Cl_2}).$$

Gel'bshtein[23] gave preference to the first mechanism.

The kinetics of the formation of chloromethanes proved to be the same both in the oxidative chlorination reaction and in the direct chlorination reaction in the presence of the $CuCl_2-KCl$ system.[14,65,82] Both reactions are characterised by the first kinetic order with respect to methane, a fractional order with respect to

chlorine, and virtually identical activation energies (113 kJ mol^{-1}). The rates of the oxidative chlorination and chlorination can be described with the same accuracy by an equation of the fractional-rational type:

$$w = \frac{kp_{CH_4} \cdot p_{Cl_2}}{1 + ap_{Cl_2} + bp_{O_2}},$$

where a and b are adsorption coefficients. Or they can be described by the equation

$$w = kp_{CH_4}\, p_{Cl_2}^{0.6}\, p_{O_2}^{-n},$$

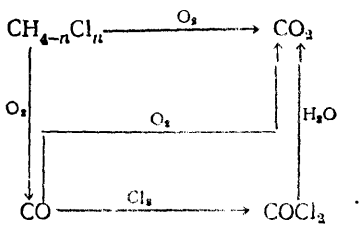
where n varies from 0.25 to 0 as the temperature increases.

It is of interest that the rate of chlorination is independent of the presence of copper in the salt composition, i.e. the presence of variable-valence metal cations in the centres on which chlorination takes place is not obligatory. It has been suggested[14,65,82] that the chlorination of methane at temperatures below 425 °C takes place on the surface of the melt preferentially as a result of the interaction with a polyhalide complex of the type ZCl_3 formed when molecular chlorine is chemisorbed by metal chlorides. An increase in temperature increases the contribution of the reaction involving the thermal volume chlorination by free chlorine.

Subsequently, evidence in support of the catalytic or heterogeneous-homogeneous chain mechanism of the chlorination of methane in the presence of oxidative chlorination catalysts was re-examined by Aglulin.[29] It was established that in a flow-circulation apparatus there is a possibility of additional chlorination in the free volume as a result of the contamination of the glass surface by volatile catalytic compounds (copper and iron chlorides) and also under the influence of light. The reduction of the distorting factors to a minimum enabled the authors[29] to support the heterogeneous-homogeneous mechanism of chlorination under the conditions of the oxidative methane chlorination reaction.

The use of semiconductor detectors, mass-spectrometric and molecular beam methods made it possible to develop these ideas.[88] On interaction with molecular chlorine, the carrier or catalyst generates atomic chlorine in space and subsequent chlorination proceeds via the usual chain mechanism.

The kinetics of the side reactions in the oxidation of methane and its chloro-derivatives have been established.[82] The mechanism of the formation of carbon oxides assumes the following form:



The rates of formation of carbon oxides are described by the following equations at $p_{Cl_2} > 0.01$ atm:

$$w_{CO} = \frac{k_i^{CO}\, p_i\, p_{O_2}\, p_{HCl}}{1 + Kp_{HCl}},$$

$$w_{CO_2} = \frac{k_i^{CO_2} p_i p_{O_2}}{1 + Kp_{HCl}},$$

where k_i and p_i are the rate constants and partial pressures of methane and chloromethanes respectively and K is the equilibrium constant for the absorption of hydrogen chloride.

At $p_{Cl_2} < 0.01$ atm, the rates of formation of carbon oxides depend also on $p_{Cl_2}^{0.5}$. The ratios of the rates of oxidation of methane and chloromethanes are CH_3Cl:CH_2Cl_2:$CHCl_3$:CH_4:CCl_4 = 1:0.5:0.33:0.18:0.033.

The mechanism of the extensive oxidation reactions has been hardly investigated. It is believed[89] that the oxidation reactions of hydrogen chloride and the reactions leading to the extensive oxidation of methane and chloromethanes are catalytic and that chlorination takes place mainly as a homogeneous process.

The view has been expressed[90] that the chlorination of methane occurs on the surface of the melt of copper chlorides. This is justified by the different selectivities in the formation of chloromethanes in catalytic and thermal chlorination processes and by the considerable difference between the rate of evolution of chlorine from the melt and the rate of chlorination. However, the activation energies obtained for the catalytic chlorination of methane (176 kJ mol^{-1}) and the oxidative chlorination of methane (172 kJ mol^{-1}) do not agree with the known values for the energy barriers in the gas-phase chlorination of methane (139 kJ mol^{-1}) and the oxidation of hydrogen chloride (126 kJ mol^{-1}), which can be associated with the change in the activity of the catalyst.

In conclusion one should note that the oxidative chlorination of methane has not been achieved on an industrial scale anywhere in the world. By virtue of the large amount of experimental and design studies, a balanced (with respect to chlorine) industrial manufacture of chloromethanes has been planned and is being established in the USSR, where the entire hydrogen chloride formed in the direct methane chlorination stage is processed in the oxidation chlorination stage. The report[91] concerning the construction of a plant for the preparation of chloromethanes by the oxidative chlorination of methane in fused salts was not confirmed—apparently technological difficulties arose.

VI. Interaction of methanol with hydrogen chloride

The heat of the reaction

$$CH_3OH + HCl \rightarrow CH_3Cl + H_2O$$

is low (32.9 kJ mol^{-1}). Dimethyl ether is formed as a side product:

$$2\,CH_3OH \rightarrow (CH_3)_2O + H_2O.$$

Dimethyl ether also interacts with hydrogen chloride:

$$(CH_3)_2O + 2HCl \rightarrow 2\,CH_3Cl + H_2O.$$

As a result, the selectivity in the formation of chloromethane is usually high and amounts to more than 99%.

Chloromethane can be synthesised from methanol and hydrogen chloride in both liquid and gas phases. Under laboratory conditions, chloromethane is obtained by refluxing methanol with hydrochloric acid without a catalyst. The kinetics of the reaction of hydrogen chloride with methanol at 363 K have been investigated.[92] When the initial hydrogen chloride concentration is varied from 0.115 to 1.623 M, the relative equilibrium degree of conversion of methanol changes only slightly—from 96.5 to 96.1%. The same method of synthesis has been proposed also for use in industry.[93,94] The process temperature is 343–423 K. Zinc chloride is usually employed as the catalyst of the liquid-phase process and a quaternary ammonium halide has been proposed for this purpose recently.[95]

However the majority of companies prefer to carry out the reaction of methanol with hydrogen chloride in the gas phase in the presence of a catalyst in the industrial manufacturing process.[4] Chloromethane is obtained in the USSR by the same method. The reaction is usually carried out in an excess of hydrogen chloride (about 30%), which suppresses the formation of dimethyl ether as the side product; the degree of conversion of methanol under these conditions is about 99%.

A comparative study of the catalytic activities of various salts (zinc, magnesium, calcium, strontium, barium, manganese, cobalt, nickel, copper, cadmium, bismuth, and mercury chlorides) in the reaction of methanol with hydrogen chloride has been carried out in a study for a dissertation.[96] It was shown that zinc chloride exhibits the highest catalytic activity. Comparative tests of various carriers (alumina, activated charcoal, silica gel) for the catalytically active zinc chloride mass led to the selection of activated alumina. The catalytic activity of pure alumina has also been studied.

The rate of reaction of methanol with hydrogen chloride is described by the equation

$$w_1 = k_1\, p_{CH_3OH}\, p_{HCl}.$$

The activation energy for the reaction in the presence of the catalyst containing 60% of zinc chloride on alumina is 36.5 kJ mol^{-1} and that on pure alumina is 51.5 kJ mol^{-1}, the pre-exponential factors being respectively 2.2×10^8 and 1.5×10^8 litre litre(cat.)$^{-1}$ h^{-1} atom^{-2}.

The kinetic equation for the side reaction involving the formation of dimethyl ether is

$$w_2 = k_2\, p^2_{CH_3OH}.$$

The activation energies for the side reactions in the presence of the same catalysts (60% $ZnCl_2/Al_2O_3$ and Al_2O_3) are 192 and 96 kJ mol^{-1} and the pre-exponential factors at 10^{19} and 2.5×10^{12} litre litre(cat.)$^{-1}$ h^{-1} atm^{-2} respectively.

The kinetics of the reaction of dimethyl ether with hydrogen chloride have also been studied.[96] It was found that the rate of reaction depends on the partial pressures of dimethyl ether and hydrogen chloride with an exponent of unity. It is suggested that the last reaction takes place consecutively—via a stage involving the interaction of dimethyl ether with one hydrogen chloride molecule:

$$w_0 = k\, p^0_{HCl}\, p^0_{CH_3OH}/\{1 + (K_{HCl}\, p^0_{HCl})^{1/4}\}^2,$$

and the methanol formed then reacts with another HCl molecule. Here we have $k_3 < k_1$.

Various possible mechanisms of the main reaction have been examined.[96] It has been suggested that a ternary complex of the metal chloride with methanol and HCl is formed as an intermediate[97] and then decomposes into the reaction products.

A correlation-regression analysis has been carried out[98-100] for the heterogeneous-catalytic reaction involving the synthesis of chloromethane from methanol and hydrogen chloride. Out of the 16 kinetic equations for the initial rate of reaction at temperatures in the range 423–473 K, the following equation was selected after resorting to IR spectroscopic data:

$$w_0 = k\; p^0_{HCl}\; p^0_{CH_3OH}/\{1 + (K_{HCl}\; p^0_{HCl})^{1/2}\}^2,$$

where p^0_{HCl} and $p^0_{CH_3OH}$ are the initial partial pressures of hydrogen chloride in methanol and K_{HCl} is the adsorption constant for hydrogen chloride.[99] It is suggested that the reaction takes place on the surface between the hydrogen chloride dissociatively adsorbed on activated charcoal and methanol from the gas phase.[100]

In a study of the kinetics of the reaction of hydrogen chloride with methanol over alumina,[101] it was found that the rate of reaction depends on the partial pressure of HCl with an exponent of unity and is independent of the partial pressure of methanol. The differential rate constant is proportional to the specific surface of the catalyst and is independent of its crystalline modification. Ageing of the catalyst takes place as a result of the deposition of carbon, its activity diminishing exponentially as a function of time.

Studies by Svetlanov[96] made it possible to develop and apply in an industrial process a stronger and more stable catalyst containing 35–38 wt.% of zinc chloride on active γ-alumina instead of the previously employed catalyst (zinc chloride on activated charcoal). The reaction kinetics were revised for the recommended catalyst and a mathematical model of the process was set up, which made it possible to design and recommend a two-compartment adiabatic reactor instead of the tubular reactor currently used.

An analogous catalyst ($ZnCl_2/Al_2O_3$) has been proposed in a patent.[102]

Nevertheless, even this improved catalyst, used nowadays in the industrial manufacture in the USSR,[103] has an appreciably shorter useful life (approximately half a year) compared with the useful life of catalysts of the best foreign companies (1–2 years). This stimulated further research into factors influencing the stability of the catalyst of the synthesis of chloromethane. One of the causes of the decrease in the activity of the catalyst with time is the volatilisation of its active component—zinc chloride.[104] It has been established that the carrier greatly retards the desorption of zinc chloride and that a limiting degree of desorption of zinc chloride corresponds to each temperature. The thermal desorption of zinc chloride from the carrier surface increases by a factor of 3–4 in the presence of reactants, in the first place methanol. Modifying additives have made it possible to reduce by a factor of 2–3 the loss of the active component.[104]

The gradual decrease in the rate of sublimation of zinc chloride as a function of time occurs, according to Grinberg et al.,[105] initially as a result of the slow establishment of the capillary equilibrium within the carrier pores and then as a result of the strengthening of the bond between the salt and the carrier surface.

In contrast to the above view,[105] according to which the surface of the catalyst working above the melting point of zinc chloride is the surface of melt menisci, fusion structures were not discovered in the study of Glazunova et al.[106] Apart from $ZnCl_2$, variable-composition zinc hydroxide chlorides as well as the structures resulting from the insertion of zinc into the spinel-type aluminium oxide lattice were detected by X-ray diffraction and thermal analyses.

Another factor influencing the stability of the operation of the catalyst of the synthesis of chloromethane is the deposition of carbon on its surface during the reaction. It has been observed[107] that the decrease in the specific surface of catalyst on deposition of carbon is associated with the reduction of the fraction of pores with effective dimensions less that 20 Å. A relation between the degree of deposition of carbon, on the one hand, and the surface acidity and the irreversible adsorption of methanol, on the other, has been demonstrated.

It is noteworthy that γ-alumina without salts is normally employed abroad in the manufacture of chloromethane from methanol and hydrogen chloride. Salt-free catalysts are used at a somewhat higher temperature, apparently in order to block the highly acid centres which are responsible for the deposition of carbon on the

catalyst and it is recommended that a small amout (0.05–2.0 wt.%) of an alkali metal oxide be introduced into the γ-alumina.[108]

It has been suggested that the reaction of methanol with hydrogen chloride be carried out in the presence of a natural or synthetic ion-exchange zeolite.[109] Chlorine-containing hydrogen chloride reacts with methanol in the gas phase and in the presence of alumina containing <0.5 wt.% of iron (as iron oxide).[110] A mixture obtained by chlorinating methane and containing methane, chloromethanes, nitrogen, and a small amount of chlorine is used in certain cases.[95,102]

In view of the difficulty of applying the oxidative chlorination of methane on an industrial scale, the reaction of methanol with hydrogen chloride has found extensive application abroad, as an HCl-consuming stage, in the industrial manufacture of chloromethanes from methanol and chlorine.[4] Chloromethane is chlorinated in the gas or liquid phase to di-, tri-, and tetrachloromethanes and the hydrogen chloride formed is used to synthesise chloromethanes from methanol. Although methanol is in fact more expensive than methane, the solution of the problem of the utilisation of hydrogen chloride by a relatively simple procedure compensates for the increased cost of the raw material.

VII. Hydrodechlorination of tetrachloromethane

The hydrodechlorination of tetrachloromethane has assumed major importance recently in connection with the positive imbalance which has arisen in the manufacture and consumption of tetrachloromethane. The large excess of tetrachloromethane is caused, firstly, by the cessation of its use as the raw material for the manufacture of Freons 11 and 12, which decompose the ozone layer; secondly, there has been a continuous growth of the processing of waste from organochlorine industries by exhaustive chlorination to perchlorocarbons (CCl_4 and C_2Cl_4). The presence of the stage involving the selective hydrodechlorination of tetrachloromethane to $CHCl_3$, CH_2Cl_2, and CH_3Cl combined with the direct chlorination of methane makes it possible to obtain chloromethanes in any required proportions.

Various methods are known for the reduction of tetrachloromethanes. For example, chloroform can be obtained by the slow (3–4 days) reduction of CCl_4 with iron and hydrochloric acid at 288 K or by treatment with zinc dust and a 50% NH_4Cl solution at 323–333 K and also by treatment with water, zinc, and nickel.[111]

Various methods for the reduction of organochlorine compounds have been examined in reviews.[112,113] In the electrochemical reduction,[114] two electrons are consumed in the dissociation of the carbon–chlorine bond, the half-wave potential being independent of the pH of the medium and the reactions being reversible overall. There is a linear relation between the half-wave potentials for the reactions

$$RCl + 2e + H^+ \rightarrow RH + Cl^-$$

and the R–Cl bond dissociation energies. With an increase in the number of chlorine atoms in the molecule, the reduction is facilitated as a result of the shift of the half-wave potential in the positive direction. Thus the half-wave potentials (relative to the saturated calomel electrode) for chloromethanes are respectively −3.23, −2.33, −1.67, and −0.78 V. The reduction of tetrachloromethane yields mainly di- and tri-chloromethanes. A publication[115] has also been devoted to the study of the adsorption and dehalogenation of chloromethanes on a platinised platinum electrode.

In a number of studies, the CCl_3 group has been reduced to $CHCl_2$ with the aid of hydrogen donors. Thus it has been shown[116] that the reduction by treatment with $(CH_3)_2C_6H_4$ or $(C_2H_5)SiH$ with participation of $Fe(CO)_5$ takes place selectively as far as the $CHCl_2$ group. Mercaptans, n- and t-C_4H_9SH, and $C_6H_5CH_2SH$ have been used[117] to reduce the CCl_3 group in the presence of the metal carbonyls $Mo(CO)_6$, $W(CO)_6$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $Fe(CO)_5$. The $Re_2(CO)_{10}-(C_2H_5)_3SiH$ system has been used for the same purposes.[118] The reduction of CCl_4 by isopropyl alcohol initiated with iron, molybdenum, and manganese carbonyls has been described.[119] The reaction of tetrachloromethane with alcohols, catalysed by metal complexes,[120,121] in particular dichlorotris-(triphenylphosphine)ruthenium(II) $RuCl_2(PPh_3)_3$ and also by rhodium, ruthenium, and iridium complexes immobilised on polystyrene,[122] has been investigated:

$$R^1R^2CHOH + CCl_4 \rightarrow R^1R^2CO + CHCl_3 + HCl$$

Strunkina and Brainina[123] used the zirconium and hafnium hydride complexes Cp_3ZrH, Cp_3HfH, and Cp_2ZrClH for the reduction of CCl_4. A review has been devoted[124] to new redox catalysts for the homolytic reduction of trichloromethyl compounds to dichloromethyl compounds.

However, the hydrodechlorination of tetrachloromethane with the aid of hydrogen donors is relatively unpromising from the practical point of view; in the industrial process, it is necessary to use hydrogen as the reductant. Few studies have been carried out on these lines.

The gas-phase hydrodechlorination of tetrachloromethane on the Pt/Al_2O_3 catalyst has been investigated at temperatures in the range 285–396 K.[125] The reaction products are methane, trichloromethane, and hydrogen chloride, trichloromethane being inactive in the hydrogenation reaction even when it is added to the initial mixture. The authors proposed a radical reaction mechanism in which hydrogen and tetrachloromethane dissociate on platinum and then two parallel reactions take place: CCl_3 interacts with H_2 or absorbs atomic hydrogen, affording tri-chloromethane. In the alternative reaction, CCl_3 is readsorbed on platinum and is not desorbed until it is converted into CH_3 and three molecules of hydrogen chloride. The reaction of the CH_3 radical with hydrogen gives rise to methane.

The hydrodechlorination of CCl_4 by hydrogen has been investigated[126] at 643 K over the nickel-containing zeolites NiNaY, NiCuNaY, NiCrNaY, NiCoNaY, and CuNaY. The amount of nickel was 30 wt.%.

In the reaction of tetrachloromethane with hydrogen on palladium membrane catalysts, the formation of tetrachloroethylene and hexachlorobuta-1,3-diene has been observed.[127]

A study of the interaction of tetrachloromethane with hydrogen by the pulse compression method in a free-piston apparatus with characteristic process times of 10^{-3} s showed that the reaction occurs in two regions.[128] At 1150 K (degree of conversion up to 20%), the process is relatively slow. By regulating the composition of the initial mixture and the process temperature, it is possible to obtain a 16% yield of trichloromethane with a selectivity close to 100%. In a certain temperature range, under the conditions corresponding to the self-inflammation of the mixture, the reaction can be directed to the preferential formation of tetrachloroethylene.

The gas-phase hydrodechlorination of tetrachloromethane over the palladium catalyst has two characteristic features according to Zanaveskin:[129] firstly, the reaction does not stop at an intermediate stage but proceeds as far as the formation of methane and, secondly, the catalyst is rapidly deactivated.

In order to maintain the stable operation of the catalyst (platinum on alumina) in the hydrodechlorination of trichloromethane to dichloromethane, it has been recommended[130] that water, which according to the authors promotes the removal of chlorine from alumina, preventing excess acidity and the associated rapid deposition of carbon, be added to the initial mixture. The addition of a small amount of H_2S lowers the initial activity of the catalyst but increases its stability.

The hydrodechlorination of tetrachloromethane has been studied[131] on palladium catalysts in the liquid phase at temperatures in the range 313–343 K. On palladium acetates with added acetic acid and using C_7–C_{12} paraffins, ethyl methyl ketone dimethylformamide, dioxan, and benzyl alcohol as the solvents, the only reaction product proved to be methane. By carrying out the reaction in isopropyl and t-butyl alcohols as solvents, it was possible to obtain trichloromethane and chloromethane as the main products, the yield of methane varying from trace amounts to 5%. The catalyst containing 4% of palladium on charcoal proved to be more active (approximately by a factor of 20). However, the activities of both catalysts fall appreciably during the experiment (5 h). Only the catalyst containing 0.1% of palladium and 1% of KOH on γ-alumina retains its activity during the experiment.

It has been found[132] that the palladium–cobalt catalysts on activated graphite are more active in the reactions involving liquid-phase hydrogenation with hydrogen than any non-prefused metals.

By passing the vapours of chloromethanes over metals (Ni, Co, Cu, Fe, Rh, Pd) or alloys (Ni–Cu, Ni–Pd), either in a pure form or in a mixture with hydrogen or H_2 + CO, it has been observed[133] that metals which are active in the Fischer–Tropsch reactions afford higher hydrocarbons both in the absence and in the presence of carbon monoxide.

VIII. Carbonylation of chlorohydrocarbons

The method of synthesis of carboxylic acid chlorides by carbonylating chlorohydrocarbons has been known for a long time.[134] It is best to use nickel carbonyl as the catalyst, but cobalt, iron, palladium, and rhodium compounds can also be used.[135] The following reaction mechanism has been proposed:

$$RX + Ni(CO)_4 \rightarrow RNi(CO)_2X + 2CO,$$
$$RNi(CO)_2X + CO \rightarrow RCONi(CO)_2X,$$
$$RCONi(CO)_2X + 2CO \rightarrow RCOX + Ni(CO)_4.$$

The process takes place at temperatures in the range 200–300 °C and pressures in the range 600–1000 atm; in the presence of tertiary amines or alkoxides in amounts equimolecular with the initial halide in the presence of the $NaCo(CO)_4$ catalyst, it is possible to attain a yield of 80% at 0–100 °C without using high pressure.[135]

The development of metal complex catalysis permitted the creation of catalytic systems, with the aid of which it is possible to obtain acetyl chloride by carbonylating methyl chloride:

$$CH_3Cl + CO \rightarrow CH_3COCl.$$

Table 3 presents examples illustrating the conditions in this reaction.

In the vapour-phase carbonylation of methyl chloride in the presence of catalysts—transition metal compounds deposited on activated charcoal—acetic acid with an admixture of methyl acetate is formed on treatment with water.[141]

The authors of a patent[142] describe a process leading to the formation of halogenoacetic acid halides from polyhalogenomethanes by a reaction with carbon monoxide in the presence of platinum and palladium catalysts. Most attention has been devoted to the synthesis of chloroacetyl chlorides by the reaction of polychloromethanes with carbon monoxide in the presence of palladium chloride at 20–250 °C and a carbon monoxide pressure of 30–300 atm:

$$CX_nH_{4-n} + CO \xrightarrow{PdCl} CX_{n-1}H_{4-n}C(=O)X$$
X=F, Cl, Br; $n = 2 - 4$.

The process is applicable to any polychloromethane having two or more halogen atoms of the same or different types.

Table 3. Carbonylation of methyl chloride with formation of acetyl chloride.

Catalytic system	Solvent	T, °C	Patm	t^*_{CO}, min	Yield, %	Refs.
$RhCl_3$, CH_3I, Bu_3P, Bu_3PO	toluene	150	20	120	45.5	[136]
$RhCl(CO)(PPh_3)_2$, CH_3I, Bu_3P	»	130	20	30	25	[137]
$RhCl_3$, $CrCl_3$, CH_3I, $(C_6H_5)_3PO$, $(C_6H_5)_3PCH_3I$	n-heptane	180	82.5	35	56	[138]
Ditto	»	180	75	60	54	[138]
$RhCl_3$, $[Re(CO)_5]_2$, $(C_4H_9)_3PCH_3I$, $(C_6H_5)_3PCH_3I$, CH_3I	»	180	75	35	62.8	[139]
$RhCl_3$, Li (CH_3COO), CH_3I, CH_3COOH, $(CH_3CO)_2O$	—	180	82.5	60	51.6	[140]

* t_{CO} is the time during which CO is passed through the system.

Any platinum or palladium group metals (Ru, Rh, Os, Ir, Pt, and Pd) or their compounds such as salts (nitrates, chlorides, bromides, benzoates, or acetates), oxides, or complexes with organic compounds for example, acetylacetonates) can be used as catalysts. Palladium halides ($PdCl_2$ or $PdBr_2$), which are relatively cheap and entirely effective, are preferred. It is recommended that other transition metal halides (Cu, Ni, Fe, and Co) be used as promoting agents. Inert organic solvents (hexane, octane, decane, benzene, toluene, etc.), are employed in the reaction, anhydrous solvents being preferred.

The use of phase transfer catalysts increases the activity of the catalytic system in reactions involving the cabonylation of organic halides.[143]

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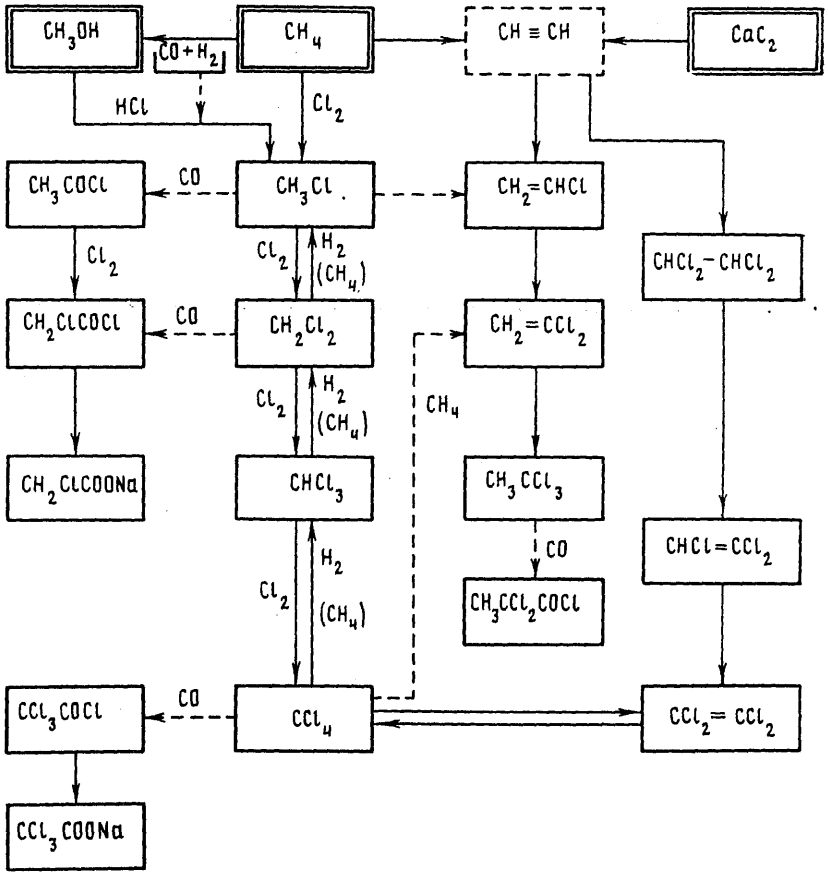


Figure 5. Schematic illustration of the synthesis of organochlorine compounds from one-carbon molecules.

The employment of one-carbon compounds such as methane, methanol, and carbon monoxide as starting material makes it possible to manufacture organochlorine compounds on an industrial scale both at the present time and probably in the future. The scheme presented in Fig. 5 illustrates the conversion of the one-carbon compounds into organochlorine compounds, the continuous lines indicating the reactions achieved in industry and the dashed lines the reactions so far attained only in the laboratory. The time when the latter will also become industrial processes is apparently not distant either.

References

1. Yu A Treger *Zhur. Vses, Khim. Obshch. im Mendeleeva,* 1985, **30** 242
2. Yu A Treger, L M Kartashov, N F Krishtal' *Osnovnye Khlororganicheskie Rastvoriteli* (Principal Organochlorine Solvents), Izd. Khimiya, Moscow, 1984, 224 pp
3. B A Krentsel' *Khlorirovanie Parafinovykh Uglevodorodov* (Chlorination of Paraffinic Hydrocarbons), Izd. Nauka, Moscow, 1964, 157 pp
4. I P Ermakova *Khim. Prom. za Rubezhom,* 1981, (3) 17
5. Z S Smolyan, P S Pyryalova, N A Kurdyumova *Uspekhi Khim.,* 1960, **29** 23 [*Russ. Chem. Rev.,* 1960(1)]
6. A S Bratolyubov *Uspekhi Khim.,* 1961, **30** 1391 [*Russ. Chem. Rev.,* 1961(6)]
7. G Chilts, P Goldfinger, G Huybrechts, G Verbeke *Chem. Rev.,* 1963, **63** 355
8. E T McBee, H B Hass *Ind. Eng. Chem.,* 1942, **34** 296
9. Yu G Belenko, E R Berlin, R M Flid, A L Englin *Zhur. Fiz. Khim.,* 1969, **43** 2126 [*Russ. J. Phys. Chem.,* 1969(8)]
10. T Arai, M Yoshida, S Shinoda *J. Chem. Soc. Japan. Ind. Chem. Soc.,* 1958, **61** 1231
11. P Johnson, J Parsons, L J Roberts *Ind. Eng. Chem.,* 1959, **51** 499
12. B N Gekhtman *Kinetika Mnogostupenchatykh Reaktsii* (Kinetics of Multistage Reactions), Izd. Nauka, Novosibirsk, 1980, 110 pp
13. B I Shatalov, V A Kernerman, A L Englin *Khim. Prom. Ukrainy,* 1970, (5) 37
14. A G Aglulin, Candidate's Thesis in Chemical Sciences, Karpov Physicochemical Institute, Moscow, 1979, 150 pp
15. Yu G Belenko, Candidate's Thesis in Chemical Sciences, GOSNIIKhLORPROEKT, Moscow, 1970, 156 pp

16. E N Smirnov, S I Kol'tsov, V B Aleskovskii *Zhur. Obshch. Khim.*, 1978, **48** 955
17. B I Shatalov *Khim. Tekhnol.*, 1982, (1) 6
18. *Encyclopedia of Chemical Processing*, 1979, Vol. 8, p. 236
19. A L Efron, B K Kravets, A V Ogorodnik, V P Kozlina *Vop. Khim. i Khim. Tekhnol.*, Khar'kov, 1978, (53) 115
20. A G Aglulin, Yu M Bakshi, A I Gel'bshtein *Kinet. Katal.*, 1983, **24** 519
21. V N Kondratiev *Comprehensive Chemical Kinetics* (Edited by C H Bamford and C F H Tipper), Elsevier, Amsterdam–London–New York, 1969, p. 81
22. Ya B Gorokhovatskii *Geterogenno-Gomogennye Reaktsii* (Heterogeneous-Homogeneous Reactions), Izd. Tekhnika, Kiev, 1972, 204 pp
23. A I Gel'bshtein *Vses. Shkola po Katalizatoram*, 1981, (3) 33
24. V N Kondrat'ev *Handbook, Konstanty Skorosti Gazofaznykh Reaktsii* (The Rate Constants for Gas-Phase Reactions), Izd. Nauka, Moscow, 1970, 350 pp
25. T N Bell, K A Perkins, P G Perkins *J. Phys. Chem.*, 1977, **81** 2610
26. N N Semenov *O Nekotorykh Problemakh Khimicheskoi Kinetiki i Reaktsionnoi Sposobnosti* (Some Problems of Chemical Kinetics and Reactivity), Izd. Akad. Nauk SSSR, Moscow–Leningrad, 1958, 686 pp
27. V A Aver'yanov, N N Lebedev, G F Lebedeva *Zhur. Fiz. Khim.*, 1977, **51** 2234 [*Russ. J. Phys. Chem.*, 1977(9)]
28. V A Aver'yanov, N N Lebedev, G F Lebedeva *Khimicheskaya Kinet. Katal.* (Chemical Kinetics and Catalysis) (Edited by V A Tulupov), Izd. Nauka, Moscow, 1979, p. 78
29. A G Aglulin Yu M Bakshi, A I Gel'bshtein, et al. *Kinet. Katal.*, 1985, **26**(1), 26
30. A I Rozlovskii, Yu A Treger *Kinet. Katal.*, 1979, **20** 1105
31. P A Khinkis, V A Kernerman *Ref. Sbornik 'Khlornaya Prom.'*, 1980, (5) 14
32. V I Skudaev, A B Solomonov, P P Gertsen, et al. *Zhur. Prikl. Khim.*, 1986, 839
33. B I Shatalov *Khim. Tekhnol.*, 1982, (1) 10
34. N Hitajima, J Schwartz *XVIII International Congress on Catalysis*, Verlag Chemie, Weinheim, 1984, Vol. 5, p. V-453
35. D D Lebedev, V V Gribkova, T I Trusova *Tezisy Dokladov IV Vsesoyuznoi Konferentsii 'Sovremennoe Sostoyanie i Perspektivy Razvitiya Teoreticheskikh Osnov Proizvodstva Khlororganicheskikh Produktov'* (Abstracts of Reports at the IVth All-Union Conference on 'The Present State and Prospects for the Development of the Theoretical Principles of the Manufacture of Organochlorine Products'), Izd. Azinneftekhim, Baku, 1985, Vol. 1, p. 63
36. A I Semenov, V V Lebedev *Tezisy Dokladov IV Vsesoyuznoi Konferentsii 'Sovremennoe Sostoyanie i Perspektivy Razvitiya Teoreticheskikh Osnov Proizvodstva Khlororganicheskikh Produktov'* (Abstracts of Reports at the IVth All-Union Conference on 'The Present State and Prospects for the Development of the Theoretical Principles of the Manufacture of Organochlorine Products'), Izd. Azinneftekhim, Baku, 1985, Vol. 1, p. 33
37. G B Sergeev, A V Pukhovskii *Tezisy Dokladov III Vsesoyuznoi Konferentsii 'Sovremennoe Sostoyanie i Perspektivy Razvitiya Teoreticheskikh Osnov Proizvodstva Khlororganicheskikh Produktov'* (Abstracts of Reports at the IIIrd All-Union Conference on 'The Present State and Prospects for the Development of the Theoretical Principles of the Manufacture of Organochlorine Products'), Izd. Azinneftekhim, Baku, 1981, p. 25
38. E B Svetlanov, V N Rozanov, Yu A Treger, see Ref. 35, p. 88
39. A G Nikitenko, V G Martur, V S Dmitrukha, M Kh Aizenshtadt *Khim. Prom.*, 1969, (3) 26
40. E V Gvozd, T V Gorozhankina, V N Rozanov, *Ref. Sbornik 'Khlornaya Prom.'*, 1982, (4) 3
41. B I Shatalov, Yu P Geid, I N Novikov, et al. *Khim. Prom.*, 1979, (2) 82
42. *Chem. Econ. Eng. Rev.*, 1970, **2**(2) 34
43. *Chem. Ind. Develop.*, 1976, **10**(6) 31–32
44. M M Guseinov, M S Salakhov, A M Rzaev *Azerb. Neft. Khoz.*, 1975, (12) 45
45. B I Shatlov *Khim. Tekhnol.*, 1981, (1) 3–6
46. A E Shilov, R D Sabirova *Dokl. Akad. Nauk SSSR*, 1957, **114** 1058
47. A E Shilov, R D Sabirova *Zhur. Fiz. Khim.*, 1959, **33** 1365 [see *Russ. J. Phys. Chem., Abs.*, **33**(1–6)]
48. A E Shilov, R D Sabirova *Zhur. Fiz. Khim.*, 1960, **34** 860 [*Russ. J. Phys. Chem.*, 1960(5)]
49. G P Sameluk, H B Bernstein *J. Amer. Chem. Soc.*, 1954, **75** 3793
50. K P Schug, H G Wagner, F Zabel *Ber. Bunsenges. Phys. Chem.*, 1979, **83** 167
51. M R Hoare, R G W Norrish, G Whittingham *Proc. Roy. Soc.*, 1959, **250A** 180
52. G S Dasaeva, Yu A Treger, *Ref. Sbornik 'Khlornaya Prom'*, 1982, (4) 34
53. E V Denisevich, P A Tesner *Neftekhimiya*, 1981, 552
54. E V Denisevich, P A Tesner *Neftekhimiya*, 1983, **23** 211
55. V T Amorebieta, A J Colussi *Int. J. Chem. Kinet.*, 1985, **17**(8), 849
56. T A Kovaleva, V L Kucher, V N Rozanov, see Ref. 35, p. 177
57. V N Rozanov, N F Babich, T A Kovaleva, see Ref. 37, p. 101
58. B I Shatalov, S S Gutenko, G A Obremskaya, I L Starykh *Khim. Tekhnol.*, 1974, (2) 5
59. S V Levanova, R M Rodova, V I Shishinova, see Ref. 37, p. 19
60. V N Rozanov, A I Rozlovskii, Yu A Treger, N F Babich *Dokl. Akad. Nauk SSSR*, 1983, **264** 1126
61. S W Benson, US P. 4 199 533
62. M Weissmann, S Benson *Int. J. Chem. Kinet.*, 1984, (16) 307
63. M Chambon, P-M Marquaire, G-M Come *Mol. Chem.*, 1987, **2**(1) 47
64. M Chambon, P-M Marquaire, G-M Come *Can. J. Chem.*, 1987, **65** 1491
65. A G Aglulin, Yu M Bakshi, A I Gel'bshtein *Kinetika i Kataliz*, 1976, **17** 670
66. M M Mallikarjunan, S Z Hussain *J. Sci. Ind. Res.*, 1983, **42** 209
67. J A Allen, A J Clark *Rev. Pure Appl. Chem.*, 1971, **21** 145
68. V N Rozanov, E V Gvozd, Yu A Treger, N F Babich *Khim. Prom.*, 1983, 584
69. V P Tret'yakov, E S Rudakov, A N Osetskii *IV Mezhdunarodnyi Simpozium po Gomogennomu Katalizu* (The IVth International Symposium on Homogeneous Catalysis), Leningrad, 1984, Vol. 3, p. 47
70. V P Tret'yakov, E S Rudakov, A N Osetskii *Kataliz i Katalizatory*, 1984, (22) 3
71. USSR P. 343 416; *Byul. Izobret.*, 1972, (20) 202
72. N F Babich, T A Kovaleva, V N Rozanov, see Ref. 37, p. 19

73. C L Garcia, D E Resasco *Appl. Catal.*, 1987, **29**(1) 55
74. V M Vlasenko, L V Feshchenko, Ya V Zhigailo, V L Chernobrivets *Kataliz i Katalizatory*, 1984, (22) 28
75. I I Kurlyandskaya, T F Kudryavtseva, Yu A Treger, et al. *Khim. Prom.*, 1979, (5) 15
76. J A Little, C N Kenney *J. Catal.*, 1985, **93**(1) 23–29
77. I I Kurlyandskaya, M I Dashevskii, I G Solomonik, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1220
78. V N Rozanov, E V Gvozd, Yu A Treger, et al. *Khim. Prom.*, 1985, 717
79. N F Babich, Ya V Matliz, T A Kovaleva, V N Rozanov, *Ref. Sbornik 'Khlornaya Prom.'*, 1982, (5) 8
80. N F Babich, E V Gvozd, A A Dergachev, V N Rozanov, *Ref. Sbornik 'Khlornaya Prom.'*, 1982, (4) 7
81. W J M Pieters, W C Conner, E J Carlson *Appl. Catal.*, 1984, **11**(1) 35
82. Yu M Bakshi, A G Aglulin, M P Dmitrieva, A I Gel'bshtein *Kinetika i Kataliz*, 1977, **18** 1472
83. G Slama, L Kodajs *Collect. Czech. Chem. Comm.*, 1971, **36** 2691
84. C M Fontana, E Gorin, G A Kidder, R E Kinney *Ind. Eng. Chem.*, 1952, **44**, 369
85. L A Cherenev, V I Skudaev, A I Morozovskii, see Ref. 35, p. 163
86. D M Ruthven, C N Kenney *Chem. Eng. Sci.*, 1968, **23** 981
87. W M H Sachtler, J H Helle *Chemisorption and Catalysis* (Edited by P Hepple), London, 1972
88. A I Gel'bshtein, Yu M Bakshi, see Ref. 35, p. 21
89. G Caprara, G Mentorsi, G Lovatere *Chim. Ind.*, 1968, **50**, 200
90. J Ohtsuke, J Tamai *J. Catal.*, 1978, **51**(2) 169
91. *Chem. Econ. Eng. Rev.*, 1976, **8**(6) 25
92. V I Vigdorovich, I I Gorelkin *Zhur. Prikl. Khim.*, 1973, **46** 1083
93. French P. 2 270 224; *Bull. Off. Prod. Ind.*, 1976, (2), 313
94. Japanese Appl. 57-116 727; *Jap. Pat. Gaz.*, 1982, (42), E:2
95. Japanese Appl. 56-150 026; *Ref. Zhur. Khim.*, 1983, 7N16P
96. E B Svetlanov, Candidates Thesis in Chemical Sciences, GOSNIILKhLORPROEKT, Moscow, 1967.
97. A I Gel'bshtein, M I Siling, G G Shcheglova, I B Vasil'eva, *Kinet. Katal.*, 1964, 5 460
98. H J Pak, Y R Kim *Kwanagwon Tongbo. Bull. Acad. Sci. D. P. R. Korea*, 1979, (5) 14
99. H J Pak, Y R Kim *Kwanagwon Tongbo. Bull. Acad. Sci. D. P. R. Korea*, 1980, (2) 30
100. S S Chu, H J Pak, Y R Kim *Kwanagwon Tongbo. Bull. Acad. Sci. D. P. R. Korea*, 1980, (6) 16
101. E G Schlosser, M Rossberg, W Lendle *Chem. Ing. Techn.*, 1970, **42** 1215
102. BRD P. 3 110 165
103. E B Svetlanov, V A Kernerman, L Sh Genin, V I Kharitonov, see Ref. 37, p. 77
104. E B Svetlanov, S B Grinberg, F V Semenyuk, see Ref. 37, p. 49
105. S B Grinberg, E B Svetlanov, F V Semenyuk, et al. *Kinet. Katal.*, 1987, **28** 1273
106. E D Glazunova, I I Kurlyandskaya, I G Solomonik, V I Yakerson, see Ref. 35, p. 156
107. S B Grinberg, E B Svetlanov, F V Semenyuk, see Ref. 35, p. 114
108. Japanese P. 57-21 165; *Ref. Zhur. Khim.*, 1984, 8N13P
109. Japanese P. 58-27 644; *Ref. Zhur. Khim.*, 1984, 5N12P
110. Japanese P. 54-88 204; *Ref. Zhur. Khim.*, 1980, 10N15P
111. J Colon *J. Org. Chem.*, 1982, **47** 2622
112. A R Pinder *Synthesis*, 1980, 425
113. R A W Johnstone, A H Wilby, I D Entwistle *Chem. Rev.*, 1985, **85** 129
114. *Metody Elementoorganicheskoi Khimii. Khloralifaticheskie Soedineniya* (Methods of Organoelemental Chemistry. Aliphatic Chloro-Compounds), Izd. Nauka, Moscow, 1973, 750 pp
115. G L Arkharova, T A Bogdanovskii, Yu B Vasil'ev *Elektrokhimiya*, 1978, **14** 1052
116. R Kh Freidlina, E Ts Chukovskaya, N A Kuz'mina, A A Kamyshova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, 1319
117. G R Petrova, T D Churkina, I A Golikova, R Kh Freidlina *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 1816
118. R G Gasanov, L V Ivanova, N A Kuz'mina, E Ts Chukovskaya *Izv. Akad. Nauk SSSR, Ser. Khim.*, ? 2062
119. E Ts Chukovskaya, M A Rozhkova, N A Kuz'mina, R Kh Freidlina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 354
120. J Sasson, G L Kempel *Tetrahedron Lett.*, 1974, 3221
121. R Grigg, T R B Mitchell, S Satthivaiyakit *Tetrahedron Lett.*, 1979, 1067
122. G Migron, J Blum, J Sasson *J. Mol. Catal.*, 1983, (22) 187
123. L I Strunkina, E M Brainina *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 2160
124. R Kh Freidlina, R G Gasanov, N A Kuz'mina, E Ts Chukovskaya *Uspekhi Khim.*, 1985, **54** 1127 [*Russ. Chem. Rev.*, 1985(7)]
125. A H Weiss, B S Gambhir, R B Leon *J. Catal.*, 1971, (22) 245
126. A H Weiss *J. Catal.*, 1982, **74**(1) 136
127. A P Mishchenko, E V Senina *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1664
128. Yu A Kolbanovskii, A S Chernysheva *I Vsesoyuznyi Simpozium po Makroskopicheskoi Kinetike i Khimicheskoi Gazodinamike, Alma-Ata. Tezisy Dokladov* (The Ist All-Union Symposium on Macroscopic Kinetics and Chemical Gas Dynamics, Alma-Ata. Abstracts of Reports), Chernogolovka, 1984, Vol. 1, Part 2, p. 105
129. L M Zanaveskin, Candidate's Thesis in Chemical Sciences, GOSNIIKhLORPROEKT, Moscow, 1987, 126 pp
130. C J Noelke, H F Rase *Ind. Eng. Chem. Prod. Res. Dev.*, 1979, **18**(4) 325
131. G S Dasaeva, S M Velichko, Yu A Treger, I I Moiseev, see Ref. 35, p. 179
132. T Mallat, J Petro, S Szabo, J Sztatisz *React. Kinet. Catal. Lett.*, 1985, **29**(2) 353
133. W A A Van Barneveld, V Ponec *J. Catal.*, 1984, **88**(2) 382
134. W Reppe, H Kroper, H J Ristor, O Weissbarth *Annalen*, 1953, **582** 105
135. R F Heck *J Amer. Chem. Soc.*, 1963, **85** 2013
136. Japanese P. 53-63 307; *Ref. Zhur. Khim.*, 1979, 7N71P
137. Japanese P. 53-46 912; *Ref. Zhur. Khim.*, 1979, 15N65P
138. BRD P. 3 016 900
139. BRD P. 3 035 201
140. BRD P. 3 248 468
141. T Shikoda, H Jagita, K Fujimoto, H Tominaya *Appl. Catal.*, 1986, **22**(2) 377
142. US P. 3 454 632
143. T E Zhesko, G A Nikitina, E G Novikova, G N Gvozdovskii *Tezisy Dokladov V Mezhdunarodnogo Simpoziuma po Svyazi Mezhdu Gomogennym i Geterogennym Katalizom* (Abstracts of Reports at the Vth International Symposium on the Relation Between Homogeneous and Heterogeneous Catalysis), Novosibirsk, 1986, p. 88

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Thermodynamics of ionic micelles

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ABSTRACT. The present state of the thermodynamics of ionic micellar systems is examined and the principal characteristics of these systems are discussed: the charge and activity coefficients of the micelles, the concentration of the monomers and the degree of binding of the counterions, and the dependence of the critical micelle formation concentration on the length of the hydrocarbon chain of the surfactant and on the added electrolytes. The thermodynamics of the micellar cell and the methods for the calculation of the electrostatic contribution to its energy are described.

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I. Introduction

The formation of surfactant micelles is one of the most interesting phenomena in the physical chemistry of solutions. It is characteristic of colloidal surfactants in the molecules of which hydrophilic (polar, including ionogenic) and lipophilic (hydrophobic) groups (hydrocarbon or fluorocarbon chains usually play the function of such groups) are well balanced. The micelles are molecular or ionic aggregates whose size is about 3–100 nm and which arise after the attainment of the critical concentration for micelle formation (CCM). Micelles are formed over a fairly narrow concentration range. It appeared natural to explain the results of the first observations[1–5] by the fact that micelles are formed under the influence of the attractive forces between surfactant molecules. However, this is true only of micelles in non-polar media. The true cause of micelle formation in aqueous solutions is the hydrophobic effect—the tendency of water to liquidate internal cavities and to expel hydrophobic bodies (especially hydrocarbon groups), which is due to the intermolecular interactions and the structure of water. Treatment of micelle formation as the water aggregation process[6] was the first step in the elucidation of the hydrophobic effect, numerous manifestations of which (the formation of adsorption layers, membranes, vesicles, etc.) play an important role in the self-organisation processes in molecular systems. Micelles may be formed only above a temperature characteristic of its surfactant, called the Krafft point (crystallisation takes place below this temperature). In the equilibrium micellar solution, there is a stable distribution of micelles with respect to size, shape, and composition with an extremely sharp maximum, which is a feature in terms of which micellar systems resemble monodisperse systems.

The first advances in the theory of micelle formation[3–6] were associated with the application of the Law of Mass Action. In this approach (it can be called quasi-chemical), the surfactant aggregation process is regarded as a reversible chemical reaction of the type

$$\sum_i n_i A_i \rightleftarrows M, \qquad (1)$$

where n is the aggregation number, i.e. the number of molecules or ions of the given kind involved in the formation of a single micelle, A and i are the symbol and number of the micelle component, and M is the symbol for the micelle. The lifetime of the surfactant molecule in the micelle can be of the order of 10^{-7} s[7,8] and the half-life of the micelle is between 10^{-3} and 1 s,[9–11] so that reaction (1) should be assigned to the class of fast reactions. The aggregation numbers n_i, which play the role of stoichiometric coefficients in Eqn. (1), are not strictly speaking constant (they increase with increasing surfactant concentration), but in the region of the CCM their variation can be neglected. The observed sharp transition to micelle formation can then be readily accounted for on the basis of the Law of Mass Action by the large aggregation number (several tens and more).

Micelle formation resembles not only a chemical reaction but also a process involving the segregation of a new phase. If this is the pure surfactant phase, then the addition of the latter to the system should not alter its state. In order to justify the phase treatment of micelles, the phase rule and the apparent identity of the Krafft point and the triple point have been resorted to,[12,13] but these arguments proved to be erroneous†.[14–17] Furthermore, direct measurements of the surface tension of a micellar solution and of the activity coefficients of the surfactants[18,19] established that the parameters of state vary steadily with concentration, as in the usual solution, even above the CCM. However, the functions of state of molecular (ionic) and micellar solutions are different and the transition through the CCM can therefore be interpreted as a second order phase transition.[20] The concept of the macroscopic phase is inapplicable to an individual micelle, but it can be regarded as a kind of microphase and, using the concept of the thermodynamics of curved surfaces,[21] a definite pressure and surface tension can be attributed to it. It is significant that this microphase has no macroscopic analogue, because a micellar solution can exist under experimental conditions

† The phase rule cannot be extended automatically to disperse systems and the difference between the Krafft point and the triple point became evident after a more detailed investigation of phase diagrams.

in equilibrium with the solid or liquid crystals surfactant phases and micelles are evidently not nuclei of these phases.

In quasi-chemical and phase approaches, there is a tendency to describe the micelle as a molecule or as a phase respectively. However, the micelle occupies an intermediate position between them. Whereas in the thermodynamic description of the molecule as a component of the solution attention is concentrated usually on the external energy while in the description of the phase the internal energy is exclusively concentrated upon; for the micelle both are equally important. The quasi-chemical approach is useful when its external degrees of freedom are examined and many important properties of the micellar solution can be described on the hypothesis that the micelle is an unmodified entity. On the other hand, in the analysis of the internal state of the micelle (in the language of the quasi-chemical approach, this can mean, in particular, the calculation of the Law of Mass Action constant), the phase approach is entirely appropriate because the micelle is regarded as a microphase. The combination of both approaches makes it possible to describe rationally the thermodynamics of the micellar solution[22] and below we shall follow this recipe.

Micelles are of very considerable practical interest. It is sufficient to recall their wide-scale employment in micellar catalysis, emulsion polymerisation, and other fields of the solubilisation phenomenon, i.e. the dissolution by the micellar solution of substances which are sparingly soluble in an aqueous medium in the absence of micelles. Extensive experimental data on micelles (data for the CCM, the aggregation numbers, the diffusion coefficient, the size, charge, geometrical shape, and degree of dissociation of micelles, etc.) have been published in a series of reviews.[13,23-33] There are more data about ionic micelles with which the study of micelle formation began. The critical concentration for micelle formation from ionic surfactants is 1–2 orders of magnitude higher than for non-ionic surfactants and the number of parameters characterising micelles is greater than for molecular substances (the electrical parameters are added). The interpretation of the experimental results, which depend greatly also on the purity of the surfactant, is also correspondingly more complex. On the one hand, the theory of ionic micelles is based on the general theory of micelle formation in aqueous solutions, including the analysis of the hydrophobic effect, and, on the other, its task is to estimate the contribution of electrostatic interactions to the micelle formation process. This task, which has been recognised at least since 1956,[34] has been considered in a series of studies.[13,35-55] In its development, the theory of ionic micelles was based on the advances in the general theory of solutions of charged colloidal particles[56] and the theory of electrolyte solutions in relation to reacting mixtures[57-62] and polyelectrolytes.[63-69] Considerable progress in the thermodynamic theory of ionic micellar systems was attained in the 1980's. This can be explained by at least two causes: the rapid improvement of the computer techniques and the introduction of new experimental research methods. Wide-scale prospects have arisen, for example, from the direct measurement of the electrical potential of the surface of the micelle, essential for thermodynamic calculations, by the fluoroescent probe method[70] (previously only its charge was determined).

This review considers mainly ionic micelles—more precisely their specific properties which distinguish ionic surfactant micelles from all others. On the other hand, certain results are applicable also to the micelles of non-dissociating surfactants, in particular to zwitter-ionic surfactant micelles (lecithin, betaines, etc.), in the molecules of which the opposite charges of the dipole are separated by a considerable distance (for example, by several CH_2 groups).

II. The micellar system as an electrolyte solution

1. The aggregation number and charge of the micelle. Degree of binding of counterions

The quasi-chemical approach presupposes that the micellar system is single-phase, i.e. is a solution, and that any ionic micelle is no more than a large multicharged ion. Its size is determined by the size and aggregation number of the surface-active ion (or ions) and its charge is determined by the aggregation number and degree of binding of counterions. In a specific concentration range above the CCM (usually within the limits of variation of the concentration by 1–2 orders of magnitude) micelles are spherical in shape. The volume of the hydrocarbon core of the micelle is calculated as the volume of a sphere whose radius is equal to the length of the extended largest hydrocarbon group in the surfactant molecule and the aggregation number is found by dividing this volume by the overall volume of the groups of the surfactant molecule forming part of the core (if necessary, account is taken of the additional packing conditions[26,71-75]). Under the usual conditions, the maximum length (l_{max}, m) and volume (V, m^3) of the linear aliphatic group is determined from the formulae[26]

$$l_{max} = (1.5 + 1.265n_C)\cdot 10^{-10},$$
$$V = (27.4 + 26.9n_C)\cdot 10^{-30}. \quad (2)$$

where n_C is the number of carbon atoms in the group. Accordingly, when the surfactant molecule contains only one such group, the aggregation number n is defined as follows:

$$n = 4\pi l_{max}^3/3V = 4\pi(1.5 + 1.265n_C)^3/(27.4 + 26.9n_C). \quad (3)$$

It is seen from Eqn. (3) that n is an increasing function of n_C. For $n_C = 12$, we obtain $l_{max} = 1.67$ nm, $V = 0.350$ nm^3, and $n = 55.5$ from Eqns. (2) and (3). We may note that the theoretical value of the aggregation number cannot be regarded as either minimal or maximal. If the hydrocarbon chain is not fully uncoiled, then the aggregation number may be less. If a proportion of the chains are not wholly incorporated in the core and continue to remain in contact with water (this possibility is indicated by data for the permeation of water into the interior of micelles[76-83]), then the aggregation number can be actually greater. For the most thoroughly investigated ionic surfactant—sodium dodecyl sulphate (SDS)—n = 60–70 and above has been obtained in many experiments, but, in the assessment of the experimental results, the question of the possible admixtures increasing the aggregation number always arises. An unusually low aggregation number (n = 27) of thoroughly purified SDS has been reported.[84]

For a specified aggregation number, the charge of the micelle is determined by the degree of binding of counterions. The very concept of binding has many meanings.[41] It can be understood as the recombination of ions (binding via chemical forces) or as simple electrostatic attraction, which depends on distance. Even if the degree of dissociation of the micelle is known and the radial statistical distribution of the counterions has been found, one cannot state what proportion of such counterions can be regarded as bound. It is assumed arbitrarily, for example, that the counterions in the first coordination sphere can be regarded as bound.[39] The ambiguity of the concept of binding is manifested also in the interpretation of experimental data, which creates a considerable scatter in the degrees of dissociation of counterions (from 0.46 to 0.86 for SDS[85]). Since this concept originates from the idea of the micelle as a kinetic entity, it is logical to make an attempt to base the concept of the degree of binding on kinetic considerations. Although this approach

does not in fact permit the determination of the exact value of the degree of binding, it does create the possibility of discovering its dependence on the parameters of state.

The critical concentrations for the micelle formations for the majority of ionic surfactants are so low that, in the absence of micelle formation, the average energy of the Coulombic interaction of a pair of ions (u_{ik}), given by

$$u_{ik} = z_i z_k e^2/(4\pi\varepsilon_0\varepsilon\bar{r}) \tag{4}$$

[$z_i e$ and $z_k e$ are the charges of ions of the ith and kth kinds respectively, u is the elementary charge, $\bar{r}$ the average interionic distance, ε_0 the electrical constant (permittivity) and ε the dielectric constant], is less than the average energy of thermal motion. Thus, for an aqueous SDS solution at 25 °C, we have CCM = c_m = 8.1 M, $\bar{r} = (2c_m)^{-1/3} \simeq 46.8 \times 10^{-16}$ m, and, when $\varepsilon = 80$, we have the ratio $u_{ik}/kT \simeq 0.15$ (k is the Boltzmann constant and T the absolute temperature). Under these conditions, the binding of oppositely charged ions is impossible. In the presence of micelles, the situation changes. Suppose that the aggregation number is n, whence the energy of the interaction of the primary core of the micelle with an individual ion is greater by the factor n than the value calculated using Eqn. (4) and, whereas this energy is an order of magnitude smaller than kT for $n = 1$, when $n = 100$ it is already an order of magnitude greater than kT. Such a micellar core will bind the counterions. In the general case, the degree of binding is

$$\beta = -\sum_k n_k z_k \Big/ \sum_i n_i z_i > 0,$$

where n_i and n_k are the aggregation numbers of the surface-active ions and counterions respectively (the minus sign is due to the different signs of z_i and z_k). The charge on the micelle is given by the expression

$$q_M = e\left(\sum_i n_i z_i + \sum_k n_k z_k\right) = e(1-\beta)\sum_i n_i z_i, \tag{5}$$

and a sufficient condition for the absence of binding of counterions by the micelle is

$$e^2(1-\beta)|z_k|\sum_i n_i|z_i|/(4\pi\varepsilon_0\varepsilon\bar{r}kT) \lesssim 1, \tag{6}$$

where $z_k e$ is the greatest of the charges on the counterions (ions with a large charge interact more strongly with the core of the micelle and are the first to be bound).

Eqn. (6) must hold for a certain parameter $\beta < 1$, which indicates the presence of a charge on the ionic micelle. Thus, for SDS, condition (6) holds in the vicinity of the CCM for $\beta \geqslant 0.87$, which means that the real value of β is less than 0.87. If it is assumed that a certain constant value of b on the left-hand side of Eqn. (6) corresponds to the equilibrium degree of binding, then the expression

$$\beta = 1 - 4\pi b\varepsilon_0\varepsilon\bar{r}kT \Big/ \left(e^2|z_k|\sum_i n_i|z_i|\right) \tag{7}$$

makes it possible to determine β as the parameter of state, namely as a function of temperature, concentration, aggregation numbers, and ionic charges. The temperature dependence of β is expressed both explicitly and in terms of the slowly varying functions $\bar{r}(T)$ and $\varepsilon(T)$. As can be seen from Eqn. (7), β diminishes with increase in temperature but in the accessible temperature range this variation is fairly slight.

The concentration dependence of β is manifested mainly in terms of the quantity $\bar{r}$ (and at high concentrations also in terms of ε).

In the presence of micelles, we have

$$\bar{r} = \left(\sum_i c_{i1} + c_M\right)^{-1/3}, \tag{8}$$

where $\sum_i c_{i1}$ is the overall volume concentration of the monomeric ions of both signs and c_M is the concentration of micelles. Above the CCM, both these quantities depend only slightly on the overall surfactant concentration: c_{i1} varies slightly, because the substance is consumed mainly in the formation of micelles and c_M varies slightly because of the large aggregation number. This leads to a very weak dependence of β on the overall surfactant concentration. Thus at concentrations above the CCM for a uni-univalent electrolyte, where the aggregation number of the surface-active ion is n, the doubling of the concentration of the species requires an increase in the overall surfactant concentration by the factor $2n$, i.e. by 2–3 orders of magnitude; under these conditions, r diminishes only by 20% and β even less.

As can be seen from Eqn. (7), the degree of binding is greater the higher the valence of the counterion and the higher the primary charge on the micelle (in particular the larger the micelle). The size of the micelle, its aggregation number, and its primary charge increase, as we have seen, with increase in the length of the hydrocarbon chain in the homologous series of surfactants. However, this entails a decrease in the CCM and an increase in $\bar{r}$, so that the numerator and denominator in Eqn. (7) change in the same direction. Experiment shows[86] that the degree of binding β is independent of the length of the hydrocarbon chain in the range accessible to study. Measurements of the activity and self-diffusion coefficients as well as NMR data[41] confirm the qualitative relations which follow from Eqn. (7): for spherical micelles, β is almost independent of temperature and surfactant concentration and also of the concentration of an extraneous electrolyte, but it does increase on passing to cylindrical micelles, which is always accompanied by an increase in their size.[86] The approximate constancy of β and aggregation numbers makes the micelle resemble a chemical compound and gives rise to the possibility of a quasi-chemical approach to the description of micelle formation.

2. The chemical potential and the activity coefficient of micelles

Statistical mechanics yields the following expression for the chemical potential of the molecules or ions of the solute:

$$\mu_i = \mu_i^0 + w_i + kT\ln a_i\lambda_i^3 \equiv g_i^0 + kT\ln a_i\lambda_i^3, \tag{9}$$

where μ^0 is the contribution of internal degrees of freedom, w the work of introducing one molecule (ion) through a vacuum into the solvent, $a \equiv cf$ the activity (c is the concentration and f the activity coefficient), λ the average de Broglie wavelength for a single molecule (ion), g^0 the partial Gibbs free energy for a molecule (ion) in the solvent with the centre of gravity at rest, and the subscript i characterises the kind of species. The work of introducing a species w depends on the charge q of the species:[87]

$$w(q) = w(0) + q\varphi - qP_0/\varepsilon_0 - (q^2/8\pi\varepsilon_0 r)\cdot(1 - 1/\varepsilon + \varkappa/r). \tag{10}$$

where $w(0)$ is the work of introducing the species in the absence of charge, φ the electrical potential of the bulk phase, P_0 the excess polarisation of the solvent at a neutral species (the constant part of polarisation which is independent of the charge), $\varkappa q/8\pi r^2$ the induced part of polarisation, and r the radius of the species. Since not one ion but a neutral combination of ions (a molecule) is in fact introduced into the solvent, the second term on the right-hand side of

Eqn. (10) is insignificant. The remaining part $w(q)$, called the chemical work of solvation of the ion, depends appreciably on the nature of the latter.

By analogy with Eqn. (9), we shall formulate an expression for the chemical potential of the micelle:

$$\mu_M = G^0_M + kT \ln a_M \lambda^3_M, \quad (11)$$

where G^0_M is the Gibbs free energy of the micelle with its centre of gravity at rest in the specified solvent, $a_M \equiv c_M f_M$ the activity of the micelle (c_M is the volume concentration of micelles and f_M the micellar activity coefficient), and λ_M the average de Broglie wave length of an individual micelle:

$$\lambda_M \equiv h\,(2\pi m_M kT)^{-1/2}, \quad (12)$$

where $m_M \equiv \sum_i n_i m_i$ is the mass of the micelle and m_i the mass of an individual ion (molecule).

The formulation of the chemical potential μ in terms of its standard value μ_s, corresponding to a selected concentration c_s, is very widely used in physical chemistry. For solutions of colloidal surfactants, c_s = 1 M is generally adopted and the following expression is used:

$$\mu = \mu^*_s + kT \ln c' f,$$

where

$$\mu^*_s \equiv \mu_s - kT \ln f_s = g^0 + kT \ln c_s \lambda^3, \quad (13)$$

where c' is a dimensionless quantity numerically equal to the molarity and μ^*_s the chemical potential in the hypothetical ideal unimolar solution. In the treatment of the activity coefficient f, it is necessary to distinguish two cases where the micelles ar segregated and not segregated as an individual component. If the surfactant is a strong electrolyte dissociating via the reaction

$$A = \sum_i \nu_i A_i, \quad (14)$$

where ν_i are stoichiometric coefficients, then its average activity coefficient $f_\pm$ is usually defined by the identity

$$\ln f_\pm \equiv \sum_i (\nu_i/\nu) \ln f_i \quad (15)$$

(the terms f_i are the activity coefficients of the individual ions and $\nu = \sum_i \nu_i$ is the total number of ions formed on dissociation of one surfactant molecule). When the micelle is differentiated as a single ion, the same surfactant dissociation reaction assumes the form

$$A = \sum_i \nu_i (1 - \alpha_i) A_i + (\nu_j \alpha_j / n_j) M, \quad (16)$$

where $\alpha_i = n_i c_M / \nu_i c$ is the degree of micellar aggregation of the ith ion (c_M is the concentration of micelles and c the overall concentration of the surfactant) and the subscript j can be assigned to any ion. By analogy with Eqn. (15), one can write for the mean activity coefficient

$$\ln f^*_\pm \equiv \sum_i (\nu_i/\nu^*)(1 - \alpha_i) \ln f_i + (\nu_j \alpha_j / \nu^* n_j) \ln f_M,$$
$$\nu^* \equiv \nu - \sum_i \nu_i \alpha_i + \nu_j \alpha_j / n_j. \quad (17)$$

The number of ions ν^* formed on dissociation of one molecule is now less than ν and the activity coefficients in Eqn. (17) have a different significance than in Eqn. (15). On the other hand, if the activity coefficients of the individual ions f_i defined by Eqns. (15) and (17) are set equal to one another, then Eqn. (15) yields the mean activity coefficient of the surfactant in the monomeric form. In fact, the micellar solution can be formally regarded as a solution of two electrolytes where the molecules of the first are identical with those of the surfactant and yield on dissociation ν monomeric ions, while those of the second are neutral micelles which split off counterions on dissociation. The mean activity coefficient of the first electrolyte is in fact the quantity $f_\pm$ defined by Eqn. (15) when the real activity coefficients f_i of the individual ions are substituted in it. However, this is not the quantity determined experimentally in accordance with the stoichiometry of Eqn. (14): according to Eqn. (17), the coefficients f_i refer to the real concentrations of the ions $c\nu_i(1-\alpha_i)$, while the experimental values usually refer to the stoichiometric concentrations $c\nu_i$. This increases each ionic coefficient by the factor $1-\alpha_i$ and, if the additional contribution of the micelles themselves is affected [in the region of existence of spherical micelles, the coefficient $\nu_j\alpha_j/n_j$ in Eqns. (16) and (17) is very small], the experimental mean activity coefficient of the surfactant in the micellar solution $f^e_\pm$ satisfies the condition

$$f^e_\pm = \prod_i [(1 - \alpha_i) f_i]^{\nu_i/\nu} \quad (18)$$

For a 1–1 electrolyte, Eqn. (18) can be written in the form[52]

$$f^e_\pm = [(1 - \alpha)(1 - \alpha\beta) f_1 f_2]^{1/2}, \quad (19)$$

where $\alpha \equiv \alpha_1$, $\beta \equiv \alpha_2/\alpha$ is the counterion binding coefficient, the subscript 1 corresponds to the surface-active ion, and 2 corresponds to the counterion.

It has been shown[52,53] that the Guggenheim–Pitzer method,[57,66,88] usually used for concentrated solutions of simple electrolytes, is applicable to the description of the activity coefficients in a micellar system. The expressions for the activity coefficients of ions and micelles of a 1 : 1 electrolyte assume the form

$$\ln f_1 = \ln f_{1D} + B_{1\gamma}(1 - \alpha\beta)\, c,$$
$$\ln f_2 = \ln f_{2D} + B_{1\gamma}(1 - \alpha)\, c + B_{n\gamma}\alpha c/n,$$
$$\ln f_M = n^2\delta^2 (1 - \beta)^2 \ln f_{MD} + B_{n\gamma}(1 - \alpha\beta)\, c, \quad (20)$$

where the terms B_{ik} are the parameters of specific ionic interactions (the surfactant concentration c is expressed on the molal scale) and f_{iD} is the Debye component of the activity coefficient specified by standard expressions of the theory of electrolyte solutions:

$$\ln f_{iD} = -A_\gamma I^{1/2}/(1 + b_i I^{1/2}), \quad (21)$$

$$I \equiv [2 - \alpha - \alpha\beta + n\delta^2 (1 - \beta)^2 \alpha]\, c/2, \quad (22)$$

where I is the ionic strength, A_γ and b_i are constants (it is often assumed that $b_1 = b_2 = b_M = 1$) and δ is the so called micelle charge shielding factor— is actually an adjustable parameter for the description of micelles within the framework of the Debye–Hückel theory (the values $\beta = 0.77$ and $\delta = 0.52$ were used by Burchfield and Woolley[52]). It follows from Eqn. (22) that, with a specified overall surfactant concentration, the ionic strength of the solution increases with increase in the content of micelles if $n > (1 + \beta)/\delta^2(1 - \beta)^2$, whilst otherwise it decreases. Comparison of the quantities obtained on substituting the parameters defined by formula (20) in Eqn. (19) with the experimental values of the mean activity coefficients both above and below the CCM[19,85,89] (it is also possible to compare the osmotic coefficients[52]) permits the determination of the coefficients $B_{1\gamma}$ and $B_{n\gamma}$ (in particular,

$B_{1\gamma} = B_{n\gamma} = 0$ has been found for SDS[52]) and hence one can calculate various thermodynamic characteristics of micelle formation.[52-55]

3. The micellar equilibrium. Expression for the law of mass action constant

The equilibrium condition

$$\sum_i n_i\mu_i = \mu_M. \qquad (23)$$

corresponds to the chemical reaction (1). It can be shown (see, for example, Kuni and Rusanov[90]) that condition (23) is strictly applicable only to the aggregation equilibrium. The entire difference consists in the fact that, at chemical equilibrium, the quantities n_i are strictly constant (they are stoichiometric coefficients), whilst at aggregation equilibrium they are generally speaking variable, since the average aggregation numbers depend on the parameters of state. On the other hand, if one uses not the average numbers but the distribution of the micelles with respect to size, then for each size one can assume that the numbers n_i are constant (determining the type of molecular or ionic aggregate) and one can consider the micellar equilibrium similarly to a multistep chemical equilibrium with participation of many intermediates (see the relevant reviews[91,92]). Condition (23) then makes it possible to find the equilibrium distribution of micelles with respect to size.[22] Within the framework of the monodisperse approach, the numbers n_i are variable but their dependence on the surfactant concentration is weak, so that over a limited concentration range, for example, in the region of existence of spherical micelles, the numbers can be regarded as approximately constant.

Substitution of Eqns. (9) and (11) in Eqn. (23) leads to the relation

$$a_M \Big/ \prod_i a_{i1}^{n_i} = \left(\prod_i \lambda_i^{3n_i}/\lambda_M^3\right) \exp\left[\left(\sum_i n_i g_i^0 - G_M^0\right)\Big/kT\right] \equiv K_a. \qquad (24)$$

For a specified temperature, pressure, solvent composition, and aggregation numbers, the right-hand side of Eqn. (24) is constant. the equation expresses the Law of Mass Action for the micelle formation process in terms of activities. If one goes over to the traditional formulation of the Law of Mass Action with a constant K_c, which is strictly speaking not constant and depends on the concentration, then Eqn. (24) becomes

$$c_M \Big/ \prod_i c_{i1}^{n_i} = K_a \prod_i f_{i1}^{n_i}/f_M \equiv K_c. \qquad (25)$$

The presence of the second subscript 1 in Eqn. (24) and (25) emphasises the fact that the activities, concentrations, and activity coefficients refer to monomeric ions and molecules in solution.

In Eqns. (24) and (25), the constants K_a and K_c are dimensional. In order to go over to dimensionless constants, we introduce, as in Eqn. (13), a standard concentration c_s, divide both sides of Eqn. (25) by $c_s/\prod_i c_s^{n_i}$, and put c_s = 1 M. Eqn. (25) then retains its form subject to the condition that all the concentrations are expressed on molar scale (in reality these are dimensionless quantities numerically equal to the molarities) and the constant K_a, which is now dimensionless, is defined by the expression

$$K_a \equiv \left(\prod_i c_s^{n_i}\lambda_i^{3n_i}/c_s\lambda_M^3\right) \exp\left[\left(\sum_i n_i g_i^0 - G_M^0\right)\Big/kT\right]. \qquad (26)$$

Since the quantities λ refer not to a mole but to an individual species, on substitution of the standard concentration c_s = 1 M in Eqn. (26), it must be expressed in terms of the number of species per unit volume (the Avogadro number in 1 dm^3). According to Eqn. (25), the quantities K_a and K_c differ from one another by a multiplier which includes the activity coefficients. Having determined this multiplier as described in the previous subsection, for example, with the aid of Eqns. (20), and knowing the value of K_c (usually determined from the CCM), it is possible to find the constant K_a.

Expressing the concentration of ions and micelles in terms of the overall surfactant concentration c taking into account the degrees of aggregation α_i and the stoichiometric coefficients ν_i (the subscript 1 is assigned to the surface-active ion), we obtain from Eqn. (25)

$$\ln K_c = \ln(\alpha_1\nu_1/n_1) + (1-n)\ln c - \sum_i n_i \ln \nu_i - \sum_i n_i \ln(1-\alpha_i) \qquad (27)$$

Since the overall aggregation number $n \equiv \sum_i n_i$ is large, the first term on the right-hand side of Eqn. (27) is small compared with the second. Near the CCM, where the degree of aggregation is several per cent, the last term is also small and both these terms may be neglected. The third term automatically becomes zero if the surfactant molecule gives rise to one ion of each kind on dissociation.

The first successes of the micelle formation theory[3-6] were associated with the application of the Law of Mass Action in its traditional form [Eqn. (25)] on the assumption that K_c = const. The activity coefficients are neglected also in modern theory (see, for example, Mijnlieff[93]). This is to some extent justified by the fact that, firstly, when one is dealing with small concentrations, the activity coefficients are close to unity and, secondly, the interaction of the dissolved species with one another, leading to the activity coefficients differing from unity, is in the case of micelle formation a preliminary and not a decisive factor (micelle formation is caused by the hydrophobic effect).

The quantity $-kT \ln K_\alpha$ yields the standard Gibbs free energy of micelle formation per micelle and the quantity

$$\Delta G_a = -(RT/n_1)\ln K_a \qquad (28)$$

is calculated per gram-ion of the surface-active ion with an aggregation number n_1. When K_a is replaced by K_c, the standard Gibbs free energy of micelle formation is defined as follows:

$$\Delta G_c = -(RT/n_1)\ln K_c \simeq (RTn/n_1)\ln c_m + RT\sum_i (n_i/n_1)\ln \nu_i, \qquad (29)$$

where c_m is the CCM. For 1–1 electrolytes, we have

$$\Delta G_c \simeq RT(1+\beta)\ln c_m. \qquad (30)$$

This is perhaps the most familiar relation of the thermodynamics of micelle formation. Some workers express the CCM in terms of the mole fraction x_m in the calculation of ΔG_c, but, since at low concentrations $x_m \simeq c_m/c_0$ (c_0 is the solvent concentration), in practice this means a change in ΔG_c by the constant quantity $RT(1+\beta)\ln c_0$. The different physical significance of the Gibbs free energy in Eqns. (28) and (29) must be emphasised. Whereas ΔG_a is the isothermal-isobaric work of formation of micelles from one mole of the surfactant in a unimolar ideal solution, ΔG_c is the same work subject to the condition that the unimolar solution is not ideal but is characterised by activity coefficients which correspond to the CCM in the real solution. It is seen from Eqn. (25) that, in contrast to K_a, K_c depends on the concentration and ΔG_c is therefore strictly speaking not a standard quantity.

The use of the stoichiometrically mean activity

$$a_{\pm}^{e} = \sum_{i} a_{i1}^{\nu_i/\nu} = f_{\pm}^{e} c \tag{31}$$

in Eqn. (24) leads to the expression

$$\ln K_a \cong -(n_1\nu/\nu_1)\ln a_{\pm} + \sum_{i\geqslant 2}(n_1\nu_i/\nu_1 - n_i)\ln a_{i1} \tag{32}$$

(the term $\ln a_M$ is neglected), whose substitution in Eqn. (28) affords

$$\Delta G_a/RT \cong (\nu/\nu_1)\ln a_{\pm} + \sum_{i\geqslant 2}(n_t/n_1 - \nu_i/\nu_1)\ln a_{i1}. \tag{33}$$

The concept of the critical activity for micelle formation $a_{\pm m}^{\nu}$, corresponding to the CCM, was used by Nakagaki and Handa[94] and the following formula was proposed for the calculation of ΔG_a:

$$\Delta G_a/RT \simeq (\nu/\nu_1)\ln a_{\pm}, \tag{34}$$

However, as can be seen from Eqns. (33) and (34), it is fairly approximate.

The coefficients of $\ln a_{i1}$ in Eqn. (33) (for a 1-1 electrolyte, these are the β-1 coefficients) must be zero for an electrically neutral micelle. An approximate electroneutrality is attained either at the concentration several orders of magnitude higher than the CCM (but it is then not permissible to neglect the term $\ln a_M$) or in the presence of an excess of an extraneous electrolyte. Nevertheless, it has been shown[94] that the use of Eqn. (34) yields somewhat better results than those obtained from Eqn. (29).

4. Dependence of the critical concentration for micelle formation on the length of the hydrocarbon chain of the surfactant molecule

We shall characterise the length of the hydrocarbon chain by the number of carbon atoms n_c. Since micelle formation is caused by the hydrophobic effect, the derivative $\partial\Delta G_a/\partial n_c$ (the hydrophobic effect per chain unit) must be approximately constant for a sufficiently long chain and the same for different surfactants. Near the CCM, a similar rule should hold also for the derivative $\partial\Delta G_c/\partial n_c$ and, according to Eqn. (29), also for the derivative $\partial \ln c_m/\partial n_c$, and the absolute value of the latter for surfactants which do not generate ions ($n = n_1$) should be greater by the factor n/n_1 (by the factor $1 + \beta$, i.e. 1.5-2, for a 1-1 electrolyte) than for ionic surfactants. In fact, experiment shows that the slopes of the $\lg c_m$-n_c curves for non-ionic and zwitter-ionic surfactants are almost the same and close to -0.5 (the slope is -0.517 for alkyl hexaethylene glycol ethers and -0.49 for n-alkylbetaines[94]). Although the $\lg c_m$-n_c relations do remain linear for ionic surfactants, their slope is appreciably smaller: it amounts to -0.29 for alkyltrimethylammonium bromides, -0.30 for sodium alkyl sulphates, -0.28 for sodium alkanecarboxylates,[95] and -0.25 for sodium alkyl phosphates[94] (the smaller slope, in absolute magnitude, for sodium alkyl phosphates is evidently associated with the higher value of β induced by the presence of the doubly charged ion). There exist analogous data also for other homologous series of ionic surfactants.[96]

Since the activity coefficients of non-ionic and zwitter-ionic surfactants at the CCM are virtually unity, the above slope (about -0.5) is characteristic also of the linear relation between $\lg a_m$ and n_c, where a_m is the critical activity for micelle formation. An analogous approach to ionic surfactants with $a_m \equiv a_{\pm m}^{\nu}$[94] made it possible to establish the following values of the derivatives $\partial \lg a_{\pm m}^{\nu}/\partial n_c$ for the above four homologous series: -0.54, -0.58, -0.52, and -0.50 respectively. The closeness of these values to -0.5, which is characteristic of other types of surfactants, confirms that the nature of the micelle formation is the same.

5. The influence of added electrolytes on the CCM

To make the treatment concrete, we shall consider cases where the extraneous electrolyte and the surfactant have a common ion which is a counterion for the micelle. In the presence of an excess of counterions, the micelle is almost electrically neutral, the second term on the right-hand sides of Eqns. (32) and (33) disappears, and condition (34) holds to a high degree of approximation. From Eqn. (32), we have

$$\ln a_{\pm}^{\nu} \simeq -(\nu_1/n_1)\ln K_a \equiv \text{const}. \tag{35}$$

Suppose that the surfactant yields on dissociation only two kinds of ions ($i = 1, 2$, the subscript 1 corresponding to the surface-active ion and 2 to the counterion). On passing from the mean activities to the concentrations of the monomeric ions c_{11} and c_{21} in Eqn. (35), we obtain

$$\nu_1 \ln c_{11} + \nu_2 \ln c_{21} + \nu \ln f_{\pm} \cong -(\nu_1/n_1)\ln K_a. \tag{36}$$

We apply this condition to the CCM. Substitution of $c_{11} \simeq c_m\nu_1$ and $c_{21} \simeq c_m\nu_2 + c'\nu_2'$ (the quantities referring to the extraneous electrolyte are designated by a prime) leads to the expression

$$\ln c_m + (\nu/\nu_1)\ln f_{\pm} \simeq -(\nu_2/\nu_1)\ln(c_m\nu_2 + c'\nu_2') - (1/\nu_1)\ln K_a - \ln\nu_1. \tag{37}$$

Eqn. (37) indicates the dependence of the CCM for an ionic surfactant on the concentration of the extraneous electrolyte in the presence of a common ion. The left-hand side of Eqn. (37) is a linear function of $\ln(c_m\nu_2 + c'\nu_2')$, the slope of the straight line being determined by the coefficient $-\nu_2/\nu_1$. When Eqn. (37) was tested experimentally, the slopes of the linear relation proved to be -0.9 for SDS and potassium dodecanoate and -1.8 for sodium dodecyl phosphate[94] against the theoretical values of -1 and -2. Although a discrepancy, associated with some inaccuracy of Eqn. (37) itself, does exist, the ratio of the quantities obtained is as expected: in the presence of a doubly charged surface-active ion (dodecyl phosphate), the slope is twice as steep. We may note that, if no account is taken of the activity coefficient (as is usually in fact done), the dependence of $\ln c_m$ on $\ln(c_m\nu_2 + c'\nu_2')$, whilst remaining linear, ceases to correspond to the expected relation associated with the difference between the ionic charges. Thus the slope becomes -0.67 for SDS, -0.6 for potassium dodecanoate, and -0.9 for sodium dodecyl phosphate.[94]

6. Concentration of monomeric ions

The results of kinetic studies,[10] of direct measurements of activities by an e.m.f. method,[19] and of the determination of the self-diffusion coefficients[86,97] show that above the CCM the activity and concentration of the monomeric surface-active ions diminished after the addition of the surfactant to the solution. This finding, which appears at first sight to be improbable, is in reality thermodynamically legitimate and its prediction dates back to as early as 1935.[5] This theory has been formulated[41] within the framework of the electrostatic model, but, for the understanding of the essential feature of the problem, the general considerations associated with the Law of Mass Action are sufficient. As already mentioned in the Introduction, above the CCM the chemical potential and hence the mean activity of surfactants increase only slightly with increasing content of the surfactant in solution. This is consistent with the requirement for the thermodynamic stability of the solution but says nothing about the behaviour of the activities of

individual ions. We shall turn initially to the electroneutrality condition for a micellar solution:

$$c_M z_M = -\sum_i c_{i1} z_i, \tag{38}$$

where z_i is the charge of the monomeric ions and $z_M \equiv \sum_i n_i z_i$ is the charge of the micelle (the number of elementary charges). The overall charge of the micelles appears on the left-hand side of Eqn. (38), while the charge of the rest of the solution (we shall speak of the 'charge of the solution') is on the right-hand side. Surface-active ions predominate in the micelles and counterions predominate in the solution, so that the charges of the micelles and the solution have the opposite signs. However, condition (38) does not express this trivial fact alone. Since the number of micelles increases after the addition of the surfactant, there is a corresponding increase (in absolute magnitude) also in the charge of the solution and this means that the concentration of the monomeric counterions in the solution increases faster than the concentration of the monomeric surface-active ions. In order that the mean activity of the surfactant should increase with increase in its content, it is essential that the activity of at least one of the ions should increase and this ion is evidently the counterion.

In order to discover something about the surface-active ions, we turn to the Law of Mass Action in the form of Eqn. (24). Having first formulated the electroneutrality condition [Eqn. (38)] in terms of the activities, i.e.

$$a_M z_M / f_M = -\sum_i a_{i1} z_i / f_i, \tag{39}$$

and having eliminated a_M from Eqns. (24) and (39), we obtain

$$f_M \sum_i a_{i1} z_i / f_i = -z_M K_a \prod_i a_{i1}^{n_i} \tag{40}$$

or

$$\sum_i c_{i1} z_i = -z_M K_c \prod_i c_{i1}^{n_i}. \tag{41}$$

The activities of the monomeric ions a_{i1} appear on both sides of Eqn. (40), but, whereas the left-hand side depends only slightly on these quantities, on the right-hand side, where there are power functions with large power exponents, such dependence is very marked. Clearly Eqn. (40) cannot hold if all the activities vary in the same direction, i.e. if they all increase with increase in the overall surfactant concentration. A compensation effect on the right-hand side of Eqn. (40) is necessary—some of the activities must increase whilst others must decrease and, since we know that the activity of the counterions increases, then the activity of the surface-active ions must in fact decrease. Analogous reasoning is possible also in terms of Eqn. (41) for the concentration of the monomeric ions, assuming that the quantity K_c is a weak function of concentrations (with activity coefficients close to unity). Thus the conclusion that the concentrations and activities of the monomeric surface-active ions decrease above the CCM can be regarded as thermodynamically justified.

The foregoing can be illustrated by the simplest specific example. Assuming to a very rough approximation that

$$K_c = (n_1 + n_2) \ln c_m = \text{const},$$

and adopting $c_m = 8.3 \times 10^{-3}$, $n_1 = 65$, and $n_2 = 39$ (for $\beta = 0.6$[86]) for SDS, we obtain from Eqn. (41) the equation

$$\ln (c_2 - c_1) = 520.74 + 65 \ln c_1 + 39 \ln c_2, \tag{42}$$

from which it is possible to calculate the concentrations of the monomeric dodecyl sulphate ion (c_1), the monomeric sodium ion (c_2), and the micelles (c_M) as a function of the overall surfactant concentrations $c = c_1 + \nu_1 c_M = c_2 + \nu_2 c_M$. It is seen from Table 1 that the functions $c_2(c)$ and $c_M(c)$ increase monotonically over the entire concentration range, whereas the function $c_1(c)$ has a maximum near the CCM.

Table 1. The concentrations (10^{-3} M) of monomeric ions and micelles in aqueous sodium dodecyl sulphate solution calculated from Eqn. (42).

c	c_1	c_2	c_M
6.01	5.98	5.99	$3.85 \cdot 10^{-4}$
6.33	6.09	6.19	$3.85 \cdot 10^{-3}$
6.82	6.40	6.56	$6.46 \cdot 10^{-3}$
8.4	5.91	6.91	$3.85 \cdot 10^{-2}$
17.7	4.85	10	0.20
248	1.27	10^2	3.80

III. Thermodynamics of the micellar cell

The Gibbs free energy of the micelle G_M^0 with the centre of gravity at rest plays an important role in Eqns. (24) and (26) for the Law of Mass Action constant. We shall now proceed to its analysis. The quantity G_M^0 includes the work of introducing the micelle into the solution to which the energy changes not only in the micelle itself but also in the surrounding solution contribute. We shall therefore define the concept of the micellar cell as the combination of the micelle and its environment. In principle, the entire micellar solution, containing, apart from the differentiated micelle at rest, also other (moving) micelles, can be included in the micellar cell. The micellar cell is electrically neutral and represents an autonomous thermodynamic system which can be regarded as a two-phase system. The hydrocarbon (fluorocarbon) core of the micelle is usually regarded as the internal phase (α) while the solution surrounding the micelle is treated as the external phase (β), an interfacial tension σ being attributed to the interface between them containing the electrical double layer (EDL). The interfacial tension satisfies, as usual, the Laplace equation

$$p^\alpha - p^\beta = \sigma (c_1 + c_2), \tag{43}$$

where p is the pressure and c_1 and c_2 are the principal curvatures of the selected interface. We may note that in general the applicability of the macroscopic condition (43) to small objects such as micelles is not open to doubt only for spherical micelles (the mechanics of spherical micelles have been described in detail[98]). For micelles of more complex shape, there is a possibility of the appearance of anisotropy in the interfacial tension and of effects which are non-linear in terms of curvature. In the most general case, the Laplace equation can be replaced by the equation

$$p^\alpha - p^\beta = \sigma_1 c_1 + \sigma_2 c_2 + C_1 c_1^2 + C_2 c_2^2, \tag{44}$$

where σ_1 and σ_2 are the interfacial tensions along the principal

directions and C_1 and C_2 are certain coefficients. If the micelles are spherical ($\sigma_1 = \sigma_2$, $c_1 = c_2$, and $C_1 = C_2$), it is possible to eliminate the quadratic terms by selecting a special position on the interface, which Gibbs called the tension surface. The case of a cylindrical ($c_2 = 0$) micelle with spheroidal ends (in the mechanics of a cylindrical micelle, the interfacial tension is usually assumed to be isotropic)[99] is also favourable in this respect. However, in the very widely used ellipsoidal micelle model, the neglect of the quadratic terms in Eqn. (44) is hardly permissible.

1. Fundamental equations for the Gibbs free energy

For computational purposes, it is essential that the micelle at rest considered should be characterised by the same aggregation number as the moving micelles in the solution. However, the existence of the micelle in the state at rest cannot fail to affect its chemical potential and hence the fixation of the micelle displaces it from equilibrium with the solution. In studying the thermodynamics of a micellar cell, one should therefore make provision for the case where the micelle proper is not in diffusional equilibrium with the solution [the thermal and mechanical equilibria, defined by Eqn. (44), can be regarded as attained] and in essence plays the role of only a source of an external field in relation to its environment. In this case, the components of the micelle are formally segregated in a special group although they do consist of the same species as the solution. When account is taken of this factor, the joint formulation of the First and Second Laws of Thermodynamics leads to the following fundamental equations for the Gibbs free energy G of the micellar cell:

$$dG = -SdT + Vdp^{\beta} + \sum_i \mu_i dN_i + \sum_i \mu_i^0 dn_i, \tag{45}$$

$$G = -(p^{\alpha} - p^{\beta})V_M + \sigma A + \sum_i \mu_i N_i + \sum_i \mu_i^0 n_i, \tag{46}$$

where S is the entropy, T the temperature, and V the volume of the micellar cell, μ_i and μ_i^0 are the chemical potentials respectively in solution and in the micelle with the centre of gravity at rest, N_i is the number of species of the ith kind in the solution, n_i their aggregation number, A the area of the micelle interface, and V_M the volume which the interface encloses.

If the micelle is spherical, then condition (43) converts Eqn. (46) into the form

$$G = \sigma A/3 + \sum_i \mu_i N_i + \sum_i \mu_i^0 n_i. \tag{47}$$

Yet another equation (of the Gibbs–Duhem type) follows from a comparison of Eqn.s (47) and (45):[22]

$$d(\sigma A/3) = -SdT + Vdp^{\beta} - \sum_i N_i d\mu_i - \sum_i n_i d\mu_i^0. \tag{48}$$

Eqns. (45)–(48) refer to the micellar cell. We define the Gibbs free energy of the micelle proper by the equations

$$G_M^0 = G - \sum_i \mu_i N_i = \sigma A/3 + \sum_i \mu_i^0 n_i, \tag{49}$$

$$dG_M^0 = -SdT + Vdp^{\beta} - \sum_i N_i d\mu_i + \sum_i \mu_i^0 dn_i. \tag{50}$$

On subtracting the Gibbs–Duhem equation (51) for the solution (phase β)

$$0 = -S^{\beta}dT + V^{\beta}dp^{\beta} - \sum_i N_i^{\beta} d\mu_i \tag{51}$$

from Eqns. (50) and (48), we obtain the fundamental equations in terms of excess quantities:

$$dG_M^0 = -\bar{S}_M^0 dT + V_M dp^{\beta} - \sum_i \bar{N}_i d\mu_i + \sum_i \mu_i^0 dn_i, \tag{52}$$

$$d(\sigma A/3) = -\bar{S}_M^0 dT + V_M dp^{\beta} - \sum_i \bar{N}_i d\mu_i - \sum_i n_i d\mu_i^0, \tag{53}$$

where $\bar{S}_M^0 \equiv S - S^{\beta} = S_M^0 + \bar{S}$ includes the entropy of the micelle S_M^0 and the excess entropy $\bar{S}$ contributed by the solution and $\bar{N}_i$ is the excess number of species of the ith kind at the surface of the micelle. By analogy with $\bar{S}_M^0$, it is possible to introduce a quantity G_M^0 intermediate between G[Eqn. (47)] and G_M^0 [Eqn. (49)]:

$$\bar{G}_M^0 = G_M^0 + \bar{G} = \sigma A/3 + \sum_i \mu_i \bar{N}_i + \sum_i \mu_i^0 n_i \tag{54}$$

and to formulate the fundamental equation

$$d\bar{G}_M^0 = -\bar{S}_M^0 dT + V_M dp^{\beta} + \sum_i \mu_i d\bar{N}_i + \sum_i \mu_i^0 dn_i. \tag{55}$$

The excess quantities $\bar{G}$, $\bar{S}$, and $\bar{N}_i$ are associated with the fact that the structure of the solution changes near the micelle. Statistical mechanics yields the following useful relations for the quantity $\bar{N}_i$:

$$(\bar{N}_i + \delta_{iM})/kT = \partial \ln c_M/\partial \mu_i = \partial c_i/c_M \partial \mu_M, \tag{56}$$

where c is the concentration and δ_{iM} the Kronecker symbol (the case $i = M$ corresponds to the distribution of mobile micelles in the field of th micelle at rest).

The fundamental equations for the internal energy ($U = G + TS - p^{\beta}V$), the [Helmholtz] free energy ($F = G - p^{\beta}V$), the enthalpy ($H = G + TS$), and the grand thermodynamic potential

$$\left(\Omega = G - p^{\beta}V - \sum_i \mu_i N_i\right)$$

of the micellar cell, can be readily obtained from the above equations for the Gibbs free energy.

2. Thermodynamics of the charging of the micellar cell

A characteristic feature of the ionic micellar cell is the presence of the ionic EDL and of a Coulombic contribution to the Gibbs free energy. There exist different methods for estimating the contribution. The commonest is the artificial procedure, proposed by Debye, involving the imaginary charging of the ion (for a more detailed description, see Deryagin[56]). If for a specified number of ions the charges of the latter $e\xi_i$ can be varied smoothly (from zero to ez_i), new variables ξ_i appear in eqns. (45), (48), (50), (52), (53) and (55) together with the additional term (on the right-hand side)

$$e\sum_i (N_i + n_i)\varphi_i d\xi_i, \tag{57}$$

where φ_i is the average electrical potential generated by all the ions in the system with the exception of one ion of the ith kind. In an inhomogeneous system, like the micellar cell, we have

$$\varphi_i = (N_i + n_i)^{-1} \int\int\int \varphi_i(\mathbf{r})\, c_i(\mathbf{r})\, d\mathbf{r}, \tag{58}$$

where $\varphi_i(\mathbf{r})$ is the average force potential generated by all the ions except one ion of the ith kind at the point $\mathbf{r}$ in space and $c_i(\mathbf{r})$ is the local concentration of ions of the ith kind; the integration is carried out over the entire volume of the system.

A similar additional term [formula (57)] appears in the fundamental equations for the energy, the [Helmholtz] free energy, the

enthalpy, and the grand thermodynamic potential. The work of charging the micellar cell is found by integrating Eqns. (45), (52), and others for fixed characteristic variables:

$$(\Delta G^{el})_{T,p\beta,N_i,n_i} = (\Delta G^{el}_{M})_{T,p\beta,\mu_i,n_i} =$$
$$= (\Delta U^{el})_{S,V,N_i,n_i} = (\Delta F^{el})_{T,V,N_i,n_i} =$$
$$= (\Delta H^{el})_{S,p\beta,N_i,n_i} = (\Delta\Omega^{el})_{T,V,\mu_i,n_i} =$$
$$= e\sum_i (N_i + n_i)\int_0^{z_i} \varphi_i d\xi_i. \qquad (59)$$

Here the symbol Δ denotes the change in the corresponding thermodynamic function and the superscript *el* shows that the change is due to the appearance of electrical charges. A chain of equations (59) naturally does not imply that the electrical contributions to different thermodynamic functions are always the same: they are the same under different external conditions and therefore differ under the same conditions. Thus under isothermal conditions we have

$$\Delta U = \Delta F + T\Delta S \qquad (60)$$

and, whereas ΔF is specified by Eqn. (59), ΔU now has a different value. Here it is appropriate to point out a common error in the use of Eqn. (60) for the calculation of the electrostatic contribution to the [Helmholtz] free energy: it is assumed that the Coulombic energy (apparently the very term provokes an error) is always ΔU and ΔF is found by substituting ΔU in Eqn. (60). Nevertheless, the Coulombic energy [the right-hand side of Eqn. (59)] is equal to the energy change ΔU only for an isentropic charging process, while Eqn. (60) is isothermal and one cannot substitute in it ΔU defined by Eqn. (59). When Eqn. (60) is used correctly, the Coulombic energy is set equal not to ΔU but to ΔF and substitution of ΔF, defined by Eqn. (59), makes it possible to calculate by this formula the unknown value of ΔU for the isothermal charging process (naturally provided that ΔS is known).

An analogous comment can also be made concerning the Gibbs–Helmholtz equation:

$$\Delta U = d(\Delta F/T)/d(1/T), \qquad (61)$$

which follows from Eqn. (60), provided that account is taken of the thermodynamic relation

$$\Delta S = -\partial\Delta F/\partial T. \qquad (62)$$

Integration of Eqn. (61) yields

$$\Delta F = T\int_0^{1/T} \Delta U d(1/T). \qquad (63)$$

The use of Eqn. (63) for the calculation of the electrostatic contribution to the [Helmholtz] free energy (see, for example, the study of Jönsson and Wennerström[42]) would be significant if the isothermal contribution to the energy were known [as in the initial formula (60), ΔU in Eqns. (61) and (63) refers to an isothermal process], but Eqn. (59) does not allow the determination of these contributions. Thus it must be recognised that Eqns. (60) and (63) are relatively unsuitable for the calculation of the electrostatic [Helmholtz] free energy ΔF^{el} (for condensed phases, $\Delta F^{el} \simeq \Delta G^{el}$). Furthermore, there is no need for them, since the quantities ΔF^{el} and ΔG^{el} can be determined directly from Eqn. (59).

Eqns. (59) yield the total change in the thermodynamic functions during the charging process with allowance for all possible concomitant phenomana (solvent polarisation, changes in the steric structure of the system, etc.). If the distribution in space of all the charged species, and not only the micelle ions (we recall that a micelle is in a state of rest), had been kept unchanged during such a process, then, by virtue of the linear relation between φ_i and ξ_i, the right-hand side of Eqn. (59) would have been determined by the elementary electrostatic relation

$$e\sum_i (N_i + n_i)\int_0^{z_i} \varphi_i d\xi_i = (e/2)\sum_i (N_i + n_i)\varphi_i z_i =$$
$$= (1/2)\iiint \sum_i \varphi_i(\mathbf{r})\rho_i(\mathbf{r})\,d\mathbf{r}, \qquad (64)$$

in which Eqn. (58) and the quantity $\rho_i(\mathbf{r}) = ez_i c_i(\mathbf{r})$—the local charge density generated by ions of the ith kind—are used. In fact, however, the positions of the ions change during the charging process and the linear relation between φ_i and ξ_i is lost. There are also other difficulties which preclude the calculation of the right-hand side of Eqn. (59) in a general form. A number of artificial procedures and approximations, to which we shall now turn, make it possible to obtain simpler expressions for the electrostatic component of the thermodynamic functions (to make the treatment concrete, we shall consider the Gibbs free energy).

3. A two-stage charging process

We imagine that the charging process is divided into two stages. We assume that initially, before charging, an amount of work ΔG_0 was performed under isothermal-isobaric conditions to achieve a reversible rearrangement of the system to the situation which corresponds to the final state of equilibrium in the presence of charges on the species. In the second stage, the charging of the species takes place for their specified distribution in space. The work of the second stage is defined by Eqn. (64) and one can then write

$$\Delta G^{el} = \Delta G_0 + (1/2)\iiint \sum_i \varphi_i(\mathbf{r})\rho_i(\mathbf{r})\,d\mathbf{r} \qquad (65)$$

(here and henceforth the subscripts to ΔG^{el} will be omitted).

For a spherical micelle, the use of Eqn. (47) and the change to spherical coordinates permit the formulation

$$\Delta G^{el} = \Delta(\sigma A/3)^{el} + \sum_i N_i \Delta\mu_i^{el} + \sum_i n_i (\Delta\mu_i^0)^{el} \qquad (66)$$

or, when account is taken of Eqn. (65),

$$\Delta G^{el} = \Delta(\sigma A/3)_0 + \sum_i N_i(\Delta\mu_i)_0 + \sum_i n_i(\Delta\mu_i^0)_0 +$$
$$+ 2\pi\int_0^R \sum_i \varphi_i(r)\rho_i(r)\,r^2 dr, \qquad (67)$$

where R is the radius of the micellar cell in its "charged" state (for $r = R$, there exists a virtually homogeneous phase β). The quantity

$$(\Delta\mu_i)_0 = (4\pi/N_i)\int_0^R \Delta\mu_i(r)\,c_i(r)\,r^2 dr \qquad (68)$$

has the significance of the average change in the chemical potential of the species of the ith kind, since in the first stage the rearrangement links the system to a non-equilibrium state (for this reason, $\Delta G_0 > 0$), while the chemical potential has different values at different points.

According to Eqn. (13),

$$\Delta\mu_i(r) = kT\ln[c_i(r)/c_{i0}(r)] + kT\Delta\ln f_{i0}(r), \qquad (69)$$

where the subscript 0 indicates the absence of charge. Whereas the concentration components of $\Delta\mu_i(\mathbf{r})$ and $\Delta\mu_i^{el}$ at the specified point

in space are the same, the force components are significantly different. Unspecified dispersion forces, whose overall balance is relatively insensitive to the position of the species in solution, contribute to the quantities $\Delta \ln f_{i0}(r)$ and $\Delta(\sigma A/3)_0$, while the main force contribution to the quantities $\Delta\mu_i^{el}$ and $\Delta(\sigma A/3)^{el}$ comes from the strong Coulombic interactions (one can easily imagine that $\Delta\mu_i^{el} > 0$ and $\Delta(\sigma A/3)^{el} < 0$). The approximation

$$|kT\,\Delta \ln f_{i0}(r)| \ll \Delta\mu_i^{el},\ |\Delta(\sigma A/3)_0| \ll |\Delta(\sigma A/3)^{el}|, \tag{70}$$

is suggested, and, when it is valid, Eqn. (67) reduces to the form

$$\Delta G^{el} \cong 4\pi kT \sum_i \int_0^R c_i(r) \ln [c_i(r)/c_{i0}(r)]\, r^2 dr + 2\pi \int_0^R \sum_i \varphi_i(r)\rho_i(r)\, r^2 dr. \tag{71}$$

4. The average field approximation

In order to evaluate the integral in Eqn. (71), one must know the functions $\varphi_i(r)$ and $\rho_i(r)$, the determination of which constitutes an extremely complex electrostatic problem. Even for homogeneous solution, it cannot be regarded as solved. In the modern versions of the Debye–Hückel theory, the quantity φ_i is calculated for low concentrations as the potential generated by the ionic atmosphere around the specified ion with the centre of gravity at rest. Account is thereby taken approximately of the two-particle correlations of the ions in the solution. However, the system which we shall be examining is much more complex. At the centre of the micellar cell, we have the micelle with the centre of gravity at rest, which generates a field in which the ions of the micellar cell, forming the ionic atmosphere of the micelle, move. If one imagines that one of these ions has been stopped and the potential generated by the ionic cloud is sought, then in essence this implies allowance for three-particle correlations with participation of the micelle. Here a reasonable approximation involves the neglect of the correlations of the ions in the strong field of the micelle, i.e. the neglect of the perturbation of the ionic atmosphere of the micelle arising as a result of the arrest of one of the ions. In terms of this approximation, the potential $\varphi_i(r)$ is replaced by the average potential $\varphi(r)$ generated by all the ions of the micellar cell without exception. The potential $\varphi(r)$ "no longer senses" the individual components of the system and in the summation with respect to i is taken outside the summation sign.

In terms of the approximation indicated, Eqn. (59) for ΔG^{el} assumes the form

$$\Delta G^{el} \approx 4\pi e \sum_i \int_0^{z_i} d\xi_i \int_0^R \varphi(r)\, c_i(r)\, r^2 dr = = 4\pi \int_0^1 (d\lambda/\lambda) \int_0^R \varphi(r,\lambda)\,\rho(r,\lambda)\, r^2 dr, \tag{72}$$

where $\lambda \equiv \xi_i/z_i$ is the Debye parameter of the "switching on" of the charge ($0 \leqslant l \leqslant 1$) and $\rho(r,\lambda) \equiv \sum \xi_i c_i(r,\lambda)$ is the variable charge density. The formulation of Eqn. (71) is simplified correspondingly:

$$\Delta G^{el} \cong 4\pi kT \sum_i \int_0^R c_i(r) \ln [c_i(r)/c_{i0}(r)]\, r^2 dr + 2\pi \int_0^R \varphi(r)\rho(r)\, r^2 dr, \tag{73}$$

where $c_i(r)$, $\varphi(r)$, and $\rho(r)$ correspond to $\lambda = 1$. As can be seen from Eqn. (73), by virtue of the electroneutrality of the micellar cell, the potential $\varphi(r)$ is determined to within an arbitrary constant—it is usually reckoned from the value of φ^β in the bulk phase β. We may note that the transition to the average potential immediately converts ΔG^{el} into an excess quantity, since in the bulk phase the integrand expression now becomes zero. For this reason, one can put $R = \infty$ in Eqns. (72) and (73).

5. The switching on of the hydrophobic interaction

Eqns. (72) and (73) have been derived by the method involving the imaginary charging of ions in the presence of a complete micelle. Since micelles exist by virtue of the hydrophobic effect, one may say that we have "switched on" the charge for a constant hydrophobic interaction. Conversely, we shall now try to achieve the imaginary "switching on" of the hydrophobic interaction for a constant ionic charge so that the ions gradually pass from the solution to the micelle. Although the charges of the ions themselves remain unchanged in this process, the charge on the micelle gradually increases and the same work which we calculated by the ion charging method is expended on the formation of the EDL.

If the assembly of the micelle from the ions of the solution proceeds with a constant overall number of ions, then, according to Eqn. (45),

$$(dG)_{T,p^\beta,N_i+n_i} = \sum_i (\mu_i^0 - \mu_i)\, dn_i, \tag{74}$$

and if it takes place for constant chemical potentials of the solution, then, according to Eqn. (50),

$$(dG_M^0)_{T,p^\beta,\mu_i} = \sum_i \mu_i^0 dn_i. \tag{75}$$

In terms of the average field potential, where the electrical component of the electrochemical potential is represented approximately by the term $ez_i\varphi$, the electrostatic contributions on the right-hand sides of Eqns. (74) and (75) are the same, since the bulk phase β, to which μ_i refers, does not participate in these contributions by virtue of its electroneutrality. Assuming now that

$$\sum_i (\mu_i^0 - \mu_i)^{el} dn_i \simeq \sum_i (\mu_i^0)^{el} dn_i \simeq \approx e \sum_i z_i \varphi_M dn_i = \varphi_M dq_M, \tag{76}$$

where φ_M and q_M are respectively the average potential and the charge of the micelle, we obtain, after integrating Eqns. (74) and (75),

$$(\Delta G^{el})_{T,p^\beta,N_i+n_i} = (\Delta G_M^{el})_{T,p^\beta,\mu_i} = = (\Delta U^{el})_{S,V,N_i+n_i} = (\Delta F^{el})_{T,V,N_i+n_i} = = (\Delta H^{el})_{S,p^\beta,N_i+n_i} = (\Delta\Omega^{el})_{T,V,\mu_i} \cong \int_0^{q_M} \varphi_M dq_M. \tag{77}$$

An expression of this type for the [Helmholtz] free energy of a charged colloidal particle was proposed previously by Deryagin.[56,100] If the micelle has a single-layer charge and φ_M is identical with the potential φ_l of the surface of a micelle with a radius l, then the right-hand side of Eqn. (77) can be transformed into[56]

$$\int_0^{q_M} \varphi_1 dq_M = (1/2) \int_l^\infty \varepsilon\, (r d\varphi/dr)^2 dr - 4\pi \int_0^\rho d\rho \int_l^\infty \varphi(r)\, r^2 dr. \tag{78}$$

In the general case of a complex charge structure of the micelle, we have

$$\varphi_M = (1/q_M) \int_l^{l+\delta} \varphi(r)\,\rho(r)\, r^2 dr, \tag{79}$$

where δ is the thickness of the charged layer. For a two-layer charge on spheres with radii l and $l + \delta$, one can write for the

average potential of the micelle

$$\varphi_M = (\varphi_1 q_1 + \varphi_2 q_2)/(q_1 + q_2), \quad (80)$$

where the subscripts 1 and 2 refer to the coordinates l and $l + \delta$ respectively.

IV. Model calculations of the electrostatic contribution to the Gibbs free energy of the micellar cell

Eqns. (72), (73), and (77) provide three ways of calculating the electrostatic contribution to the Gibbs free energy of the micellar cell, but, in order to be able to use them, one must know the functions $\varphi(r)$ and $\rho(r)$. The relation between them is given by the Poisson equation, which assumes the following form for a spherically symmetrical system:

$$(\varepsilon_0/r^2)\, d(r^2 \varepsilon d\varphi/dr)/dr = -\rho = -e \sum_i z_i c_i, \quad (81)$$

where $\varepsilon = \varepsilon(r)$ is the dielectric constant and ε_0 the electrical constant (permittivity). However, the functions $\varphi(r)$ and $\rho(r)$ themselves are not then determined. In order to find them, one must have at least one other relation or one must specify the functions $c_i = c_i(r)$ and hence $\rho(r)$ in an explicit form. This is done in model approaches to the consideration of which we shall now proceed.

1. Static models

In static models, the distribution of ions in space is assumed to be specified and constant. In this case Eqns. (72) and (73) become identical:

$$\Delta G^{el} \simeq 2\pi \int_0^R \varphi(r)\, \rho(r)\, r^2 dr, \quad (82)$$

and, bearing in mind the proportionality between the charge and potential characteristic of static models, Eqn. (77) can be written in the form

$$\Delta G^{el} \cong \varphi_M q_M/2, \quad (83)$$

which is equivalent to Eqn. (82).

As an example, we shall consider the spherical condenser model. If the charges are distributed in the form of two oppositely charged thin concentric layers with radii l and $l + \delta$, it follows from Eqns. (82) and (83) that

$$\Delta G^{el} \cong (q_1^2/8\pi\varepsilon_0\varepsilon)\,[1/l - 1/(l+\delta)], \quad (84)$$

where q_1 is the charge of the primary plate. For ionic micelles, Eqn. (84) is naturally too rough, but it can constitute a satisfactory approximation for non-ionic micelles with a dipolar EDL. Then $q_1 = \sum_i n_i D_i/\delta_i$, where D_i and δ_i are the dipole moment and the distance between the centres of the opposite charges of the dipole of the ith kind respectively. The spherical condenser model is satisfactorily applicable to zwitter-ionic surfactants. The opposite charges in their molecules are separated from one other and a distinct spherical condenser is created in the micelles with an energy close to that of ionic micelles.

The determination of the effective dielectric constant in the dipolar ELD constitutes an interesting problem. Water molecules naturally cannot become wedged between the charges of the same dipole but they can enter the EDL—can be located between the dipoles. Their presence influences the capacitance of the dipolar condenser, so that the dielectric constant ε retains its significance. The attempt to estimate this quantity by the spectral probe method, i.e. by introducing into the micelles small amounts of added substances (for example, dodecypyridinium iodide), whose spectra are sensitive to the polarity of the medium, led to the following values of ε:- $\varepsilon = 46$ for octyl β-D-glucoside $C_8H_{17}OCHC_5H_{10}O_5$, $\varepsilon = 36$ for the dodecyl ether of tricosaethylene glycol $C_{12}H_{25}.(OCH_2CH_2)_{23}OH$, and $\varepsilon = 37$ for *N*-dodecylbetaine $C_{12}H_{25}N^+.(CH_3)_2CH_2COO^-$.[82]

When applied to an ionic micelle, Eqn. (84) corresponds to the model with total binding of the counterions ($\beta = 1$). We obtain $\Delta G^{el}/nkT \simeq 2.2$ for SDS with $n = 56$, $T = 293$ K, $\varepsilon = 80$, $l = 1.97$ nm, and $\delta = 0.55$ nm (diameter of the hydrated sodium ion). The opposite case is represented by the model in which there is no binding of the counterions ($\beta = 0$). With the aid of this simplest and most approximate for the models, which, however, is used for calculations (see, for example, Eriksson et al.[101]) we obtain $\Delta G^{el}/nkT \simeq 10.2$ for SDS having assumed that $\delta = \infty$ in Eqn. (84). Since the real distribution of ions in the EDL is intermediate between these cases, the first and second models yield electrostatic contributions to the Gibbs free energy which are respectively too low and too high. More accurate values are obtained using the Boltzmann distribution.

2. The linearised Poisson–Boltzmann equation

As an additional equation relating φ and c_i, which enter into the Poisson equation (81), the Boltzmann formula is normally employed, i.e.

$$c_i(r) = c_i^\beta \exp[-ez_i\varphi(r)/kT], \quad (85)$$

which follows from the equilibrium condition $\mu_i(r) = \text{const.}$ [see Eqn. (9)] for

$$w_i + kT \ln f_i \cong ez_i\varphi.$$

In static mechanics, the Boltzmann formula can be rigorously justified only for low concentrations when the average energy of the Coulombic interaction of the species is much smaller than kT and only the first term of the series expansion of the exponential function on the right-hand side of Eqn. (85) need be retained:

$$c_i(r) = c_i^\beta [1 - ez_i\varphi(r)/kT]. \quad (86)$$

Substitution of Eqn. (86) in Eqn. (81) yields the linearised Poisson–Boltzmann equation

$$(\varepsilon_0/r^2)\, d(r^2 \varepsilon d\varphi/dr)/dr = \varphi e^2 \sum_i c_i^\beta z_i^2/kT, \quad (87)$$

from the solution of which for a specified function $\varepsilon(r)$ it is possible to find the distribution of the potential φ in the micellar cell. It is usually assumed that $\varepsilon = \text{const.}$ and Eqn. (87) is written in the form

$$(1/r^2)\, d(r^2 d\varphi/dr)/dr = \varphi \left[e^2 \sum_i c_i^\beta z_i^2/\varepsilon_0 \varepsilon kT \right] \equiv \varphi/\delta_D^2, \quad (88)$$

where δ_D is the Debye radius. The solution of Eqn. (88) for the micellar cell represents a trivial repetition of the Debye–Hückel theory. The final result depends on the part of the counterions and the part of the space of the micellar cell to which the Boltzmann formula is applied. We shall consider three cases.

Case 1. The Boltzmann formula is applied to the entire space with the exception of the primary core of the micelle with the charge q_1 localised on a sphere with a radius l. Then, according to the Debye–Hückel theory, we have

$$\varphi(r) = \varphi_1 \equiv \varphi(l) = q_1\delta_D/4\pi\varepsilon_0\varepsilon l(l+\delta_D), \quad (89)$$

for $r \leqslant l$ and

$$\varphi(r) = [q_1\delta_D/4\pi\varepsilon_0\varepsilon(l+\delta_D)\,r]\exp[-(r-l)/\delta_D], \quad (90)$$

for $r \geqslant l$;

$$\rho(r) = -\varepsilon_0\varepsilon\varphi(r)/\delta_D^2. \quad (91)$$

The charge q_1 is generated either by the surface-active ions of the micelle alone or jointly by the latter with the bound counterions. the latter situation is apparently a characteristic of spherical micelles in which the packing of the functional groups is least dense compared with micelles of other shapes and leaves room for the permeation of counterions.[102]

It is simplest to use Eqn. (77) for the calculation of ΔG^{el} with $q_M = q_1$ and $\varphi_M = \varphi_1$, for which it is necessary to know only φ_1 determined from Eqn. (89). Since according to Eqn. (89) φ_1 and q_1 are proportional to each other, we obtain

$$\Delta G^{el} \cong \int_0^{q_1} \varphi_1 dq_1 = \varphi_1 q_1/2 = (q_1^2/8\pi\varepsilon_0\varepsilon)\,[1/l - 1/(l+\delta_D)]. \quad (92)$$

From Eqn. (72), the same result can be arrived at by a much longer procedure.[103] The analogy between Eqns. (92) and (84) shows that, in the model described by the linearised Poisson–Boltzmann equation, the diffuse part of the EDL can be effectively reduced to the dense outer plate of a spherical condenser. For SDS ($n = 56$, $l = 1.97$ nm, $\delta_D = 3.33$ nm at the CCM, $T = 293$ K), we obtain $\Delta G^{el}/nkT \simeq 509/\varepsilon$ on the assumption that the counterions are not involved in the generation of the charge ($q_1 = -en$), which yields $\Delta G^{el}/nkT \simeq 6.36$ for $\varepsilon = 80$. On the other hand, if all the bound counterions also contribute to q_1 [$q_1 = -en(1-\beta)$], we have $\Delta G^{el}/nkT \simeq 1$ (evidently this is the smallest value for the given model) for $\beta = 0.6$[86] and $\varepsilon = 80$.

Case 2. The Boltzmann formula is applied starting with a distance $l + \delta_1$ from the centre of the micellar cell, although the primary charge is again on a sphere with a radius l. The parameter δ_1 has the significance of the distance of closest approach of free counterions (the bound counterions can be located on a sphere with a radius l). Evidently Eqn. (90) remains in force but l is replaced by $l + \delta_1$. The electrostatic contribution to the Gibbs free energy is correspondingly given by the expression[45]

$$\Delta G^{el} \simeq (q_1^2/8\pi\varepsilon_0\varepsilon)\,[1/l - 1/(l+\delta_1+\delta_D)], \quad (93)$$

which differs trivially from Eqn. (92) by the shift of the outer plate of the condenser by a distance δ_1.

Case 3. The Boltzmann formula is again applied starting with the distance $l + \delta_1$ but under conditions where the bound counterions can also be located in the second layer of charges. In the two-layer model, $q_M = q_1 + q_2$ and φ_M is specified by Eqn. (80). The surface potential of the micelle (this is now φ_2) is specified by the right-hand side of Eqn. (89) with l replaced by $l + \delta_1$ and q_1 replaced by q_M. We obtain accordingly

$$\varphi_M = q_1^2\delta_1/4\pi\varepsilon_0\varepsilon_1 q_M l(l+\delta_1) + q_M\delta_D/4\pi\varepsilon_0\varepsilon(l+\delta_1)(l+\delta_1+\delta_D), \quad (94)$$

where ε_1 is the effective dielectric constant in the $l \leqslant r \leqslant l + \delta_1$ layer. Hence

$$\Delta G^{el} \simeq \frac{\varphi_M q_M}{2} = \frac{q_1^2}{8\pi\varepsilon_0\varepsilon_1}\left(\frac{1}{l} - \frac{1}{l+\delta_1}\right) + \frac{q_M^2}{8\pi\varepsilon_0\varepsilon}\left(\frac{1}{l+\delta_1} - \frac{1}{l+\delta_1+\delta_D}\right). \quad (95)$$

In this case ΔG^{el} is interpreted as the electrical energy of two condensers with the charges $\pm q_1$ and $\pm q_M$ on their plates. Formulae for more complex micellar structures can be obtained analogously.

3. The non-linearised Poisson–Boltzmann equation

Substitution of Eqn. (85) in Eqn. (81) yields the non-linearised Poisson–Boltzmann equation

$$(\varepsilon_0/r^2)\,d(r^2\varepsilon d\varphi/dr)/dr = -e\sum_i z_i c_i^\beta \exp[-ez_i\varphi/kT]. \quad (96)$$

Sufficiently accurate solutions of this equation can be achieved by numerical methods (the details of the calculations can be found in a number of communications[35,41,67,68,104]), but if one is interested not in the detailed description of the EDL of the micellar cell but only in its energy relations (which in fact control the micelle formation process), then, with the aid of the non-linearised Poisson–Boltzmann equation (96) with ε = const., it is possible to transform Eqn. (73) into a form which does not require the knowledge of the entire function $\varphi(r)$. Since the Boltzmann formula is inapplicable to the central part of the micellar cell, we shall divide the integration region in Eqn. (73) into two parts: from zero to $l + \delta_1$ and from $l + \delta_1$ to R. The contribution to the first integral by the region $r < l + \delta_1$ will be neglected, since the change in concentration in it can be associated solely with the volume charging effect, which we shall assume to be small. The rest of the first integral in eqn. (73) will be formulated using Eqn. (85) as follows (assuming that $R = \infty$):

$$kT\int_{l+\delta_1}^{\infty}\sum_i c_i(r)\ln[c_i(r)/c_i^\beta]\,r^2dr = -\int_{l+\delta_1}^{\infty}\varphi(r)\rho(r)\,r^2dr, \quad (97)$$

after which Eqn. (73) assumes the form

$$\Delta G^{el} \cong 2\pi\int_0^{l+\delta_1}\varphi(r)\rho(r)\,r^2dr - 2\pi\int_{l+\delta_1}^{\infty}\varphi(r)\rho(r)\,r^2dr. \quad (98)$$

The first term will be estimated, in conformity with Eqn. (79), as $\varphi_M q_M/2$, which can be calculated by the following procedure.[41] We multiply both sides of Eqn. (96) by $r^3 d\varphi/dr$ and write their integrals in the form

$$\frac{\varepsilon_0}{2}\int_{r=l+\delta_1}^{r=\infty}\frac{1}{\varepsilon r}d\left(\varepsilon r^2\frac{d\varphi}{dr}\right)^2 = kT\sum_i c_i^\beta\int_{r=l+\delta_1}^{r=\infty} r^3 d[\exp(-ez_i\varphi/kT)]. \quad (99)$$

Integration by parts, taking into account the boundary condition $d\varphi/dr = -q_M/4\pi\varepsilon_0\varepsilon_1(l+\delta_1)^2$ with $r = l + \delta_1$ and $\varphi = 0$, $d\varphi/dr = 0$, $r^2 d\varphi/dr = 0$, and $r^3\varphi = 0$ for $r = \infty$ yields

$$-q_M^2/8\pi\varepsilon_0\varepsilon_1(l+\delta_1) + 2\pi\varepsilon_0\int_{r=l+\delta_1}^{r=\infty}(rd\varphi/dr)^2\,d(\varepsilon r) =$$

$$= -3kT\sum_i\{V_M[c_i(l+\delta_1) - c_i^\beta] + \overline{N}_i\}, \quad (100)$$

where $V_M \equiv (4\pi/3)(l+\delta_1)^3$ and $\overline{N}_i$ is the excess (relative to the bulk phase β) number of ions of the ith kind in the diffuse plate of the

EDL:

$$\bar{N}_i = 4\pi \int_{l+\delta_1}^{\infty} (c_i - c_i^{\beta}) r^2 dr. \quad (101)$$

The relation between the second integral in Eqn. (98) and the integral in Eqn. (100) is found by integration by parts using the Poisson equation (81):

$$2\pi \int_{l+\delta_1}^{\infty} \varphi\rho r^2 dr = -\varphi(l+\delta_1) q_M/2 + 2\pi\varepsilon_0 \int_{l+\delta_1}^{\infty} \varepsilon (rd\varphi/dr)^2 dr. \quad (102)$$

If it is assumed that, when $r > l + \delta_1$, the dielectric constant assumes a constant value, then the integrals in Eqn. (100) and on the right-hand side of Eqn. (102) become identical. On substituting Eqns. (100) and (102) in Eqn. (98), we then obtain

$$\Delta G^{el} \cong \varphi_M q_M/2 + \varphi(l+\delta_1) q_M/2 - q_M^2/8\pi\varepsilon_0\varepsilon_1 (l+\delta_1) + 3kT \sum_i \{V_M [c_i (l+\delta_1) - c_i^{\beta}] + \bar{N}_i\}. \quad (103)$$

In the special case where the micelle has a single-layer charge [$\delta_1 = 0$, $q_M = q_1$, and $\varphi_M = \varphi(l) \equiv \varphi_1$], we have

$$\Delta G^{el} \cong \varphi_1 q_1 - q_1^2/8\pi\varepsilon_0\varepsilon_1 l + 3kT \sum_i \{V_M [c_i(l) - c_i^{\beta}] + \bar{N}_i\}. \quad (104)$$

As an example, we shall consider the calculation of ΔG^{el} by Eqn. (104) for SDS at 20 °C. The numerical solution of Eqn. (96) for $\varepsilon = 79.7$, $n = 56$, $q_1 = 8.9 \times 10^{-18}$ C, and $l = 1.97$ nm yields $ez_1\varphi(l) \simeq 6.5\ kT$.[41] From the electroneutrality condition, we obtain $\bar{N}_2 \simeq 56$ and from the Boltzmann formula we have $c_2(l) - c_2^{\beta} \simeq 5.51$ M for $c_2 = 8.3 \times 10^{-3}$ M (CCM). From Eqn. (104), we then find $\Delta G^{el}/nkT \simeq 5.0$. Using the same initial data, we obtained above 6.36 by Eqn. (92), so that the linearised Poisson–Boltzmann equation yields a result which is too high.

4. A modified non-linearised Poisson–Boltzmann equation

If the dielectric constant in the Poisson–Boltzmann equation is assumed to be a function not of the spatial coordinates but of the electric field, then the very form of the equation changes. Such an equation is referred to as modified.[38,39] Apart from dielectric saturation, the intrinsic volume of the counterions is taken into account in it.

The dependence of the dielectric constant of a polar liquid on the electric field strength E is described by the expression[105]

$$\varepsilon(E) = n_0^2 + [4\pi cD(n_0^2+2)/3.3E] L(0.55(n_0^2+2)DE/kT), \quad (105)$$

where n_0 is the refractive index of the liquid (for long waves), c the number of its molecules per unit volume, D their dipole moment, and $L(x) \equiv \coth x - 1/x$ the Langevin function. For water, the effect of dielectric saturation begins to be manifested as $E = 10^8$ V m^{-1} is approached. At the surface of a micelle, $E = q_M/4\pi\varepsilon_0\varepsilon(l+\delta_1)^2$. If the counterions do not enter into the primary charge sphere, then $q_M = ezn$ and, taking into account Eqn. (2), we have

$$E = ezl_{max}^3/3\varepsilon_0\varepsilon(l+\delta_1)^2 v.$$

For members of a homologous series (excluding the initial members), $l_{max} \simeq l + \delta_1$ and $l_{max}/v \simeq$ const., so that all the micelles of the homologous series are characterised by approximately the same value of E. Its estimation for the specific case of SDS yields $E = 2.6 \times 10^8$ V m^{-1} for $n = 56$ and $\varepsilon = 80$, which means that in reality $\varepsilon < 80$: at the surface of the alkyl sulphate micelle dielectric saturation takes place. The substitution of $E = -\partial\varphi/\partial r \equiv -\varphi$ converts Eqn. (105) into

$$\varepsilon = n_0^2 - aL(-b\varphi')/\varphi', \quad (106)$$

where a and b are coefficients in Eqn. (105). The substitution of Eqn. (106) in Eqn. (81) yields in its turn a modified Poisson equation.

The presence of a strong electric field increases greatly the concentration of counterions at the surface of the micelle. Their intrinsic volume, which is not taken into account in the usual Boltzmann formula, becomes significant under these conditions. A refined Boltzmann formula has been proposed:[38]

$$c_j = c_{j_0} \exp(-z_j e\varphi/kT)/\{1 + (1/N) \times \times \sum_i' c_{oi} [\exp(-z_i e\varphi/kT) - 1]\}, \quad (107)$$

where N is the maximum possible occupation number by hydrated ions and the prime denotes summation with respect to ions having the same sign as that of the ion j (in this model only like ions are treated as hard spheres, while unlike ions are allowed to penetrate one another). The quantity N is assumed to be the same for all the ions; the ion with the maximum charge should be treated with greater precision [from Eqn. (107), it is also seen that N must be referred to unit volume].

Substitution of Eqns. (106) and (107) in Eqn. (96) leads to a modified non-linearised Poisson–Boltzmann equation. Its numerical solution for divalent counterions at a concentration of 1×10^{-3} M[38] shows that the influence of the intrinsic dimensions of the ions on their distribution near the surface of the micelle (in a layer 0.8 nm thick) begins to have an effect at a potential of the primary core of the micelle $\varphi_1 > 100$ mV and increases sharply with increase in the potential. For $\varphi_1 < 100$ mV, the use of the usual (unmodified) non-linearised Poisson–Boltzmann equation does not introduce an error. According to the data of Frahm et al.,[39] the values of φ_1 for sodium alkyl sulphate micelles at 35 °C are $\varphi_1 = -87$ mV for $n_c = 10$, $\varphi_1 = -120$ mV for $n_c = 12$, $\varphi_1 = 155$ mV for $n_c = 14$, and $\varphi_1 = -195$ mV for $n_c = 16$. For SDS at 25 °C in the region of the CCM, $\varphi_1 \simeq -130$ mV, but, since in this case the counterions are singly charged, one may hope that the application of the usual Poisson–Boltzmann equation still does not entail a large error.

If φ_1 has been determined experimentally (for example, by the fluoroescent probe method[39,70]), then the modified non-linearised Poisson–Boltzmann equation makes it possible to calculate the primary charge on the micelle and also the distributions $\varphi(r)$ and $c_i(r)$. Information about the primary charge is especially valuable, since, for a specified aggregation number, this makes it possible to find the number of counterions which have entered the primary plate of the EDL. According to Frahm et al.,[39] the primary charge on the SDS micelle for $n = 55$ and $l = 1.8$ nm is 26.8 ± 1.9 elementary charges, i.e. only half of the charge of the 55 surface-active ions. On the other hand, if it is assumed, as was done above, that $l = 1.97$ nm, then, for the potential $\varphi_1 = 130$ mV, the charge on the micelle is about 32 elementary charges, so that even in the primary plate of the EDL the degree of binding of the counterions reaches 42%. If apart from this one takes into account the additional shielding of the charge by the counterions in a shell 0.5 nm thick adjoining the core, then the degree of binding reaches $\beta = 0.55$ (Frahm et al.[39] obtained $\beta = 0.65$ for $l = 1.8$ nm). Accordingly, one can put forward the following picture of the distribution of the 55 counterions around the core of micelle: 23 enter into the primary layer of the EDL, 7 into the shell adjoining the core, and 25 into the

diffuse part of the EDL. In this case we are dealing with a two-layer charge on the micelle and the quantity ΔG^{el} can be calculated from Eqn. (103). However, the result of the calculation is sensitive to the postulated value of ε_1. The maximum value of $\Delta G^{el}/nkT \simeq 5.5$ is obtained for $\varepsilon_1 = 80$. On the other hand, if, for example, $\varepsilon_1 = 40$, then $\Delta G^{el}/nkT \simeq 4.2$.

The Poisson–Boltzmann equation has been modified[46] with the aid of the semiempirical relation[106]

$$\varepsilon(E) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)/(1 + BE^2), \qquad (108)$$

where the subscripts correspond to $E = 0$ and $E = \infty$ ($E_\infty = 6$) and B is a constant. Apart from the revised description of the EDL, Beunen and Ruckenstein[46] formulated the problem of the more accurate calculation of the work of formation of the primary plate of the EDL of the micelle. It is usually assumed that, when the ions are bound to one another, their contribution to the electrostatic energy vanishes. This would be the case if oppositely charged ions did indeed penetrate one another. In fact, they form dipoles, which interact with the surface-active ions of the micelle. The extent of such ion–dipole interaction can be estimated, for example, within the framework of the lattice model (taking into account the interaction of neighbours).[46] The values $\beta = 0.65$ for spherical micelles and $\beta = 0.88$ for cylindrical micelles were obtained by this method for SDS with $l = 2.03$ nm.

V. Conclusion

In terms of the average field approximation, the electrostatic contributions to the Gibbs free energy of the micellar cell and to the standard Gibbs free energy of micelle formation are the same, so that, by estimating ΔG^{el}, we thereby determine also the electrostatic contribution to the Law of Mass Action constant. If one takes into account the fact that the hydrophobic effect amounts to about $-1.5\ kT$ per CH_2 group, then the contribution by $\Delta G^{el}/nkT$ of the order of 4–5 must be recognised as relatively small. It is significant that $\Delta G^{el} > 0$ (while the main contribution by the hydrophobic effect is negative) and, as can be seen from Eqn. (30), this increases CCM (for $\Delta G^{el}/nkT = 4.6$, the critical concentration for micelle formation is 100 times greater than in the absence of the electrostatic contribution). It is necessary to note that the influence of ions on the micelle formation process can be mediated by the hydrophobic effect itself, because the dissolved ions influence the structure of water.[51,81] The marked dependence of the size of the dodecyl sulphate micelles on the nature of the counterion[51] provides an interesting illustration of this finding, although a theory of this phenomenon has not yet been developed.

In estimating the electrostatic contribution to the Gibbs free energy, we considered spherical micelles for which this contribution is a maximum. Analogous calculations can be performed also for cylindrical micelles, but in this case the electrostatic effects are smaller because of the denser packing of the surface-active ions and the greater degree of binding of the counterions. As regards the phenomenon of the polymorphic transformation of the micelles itself (from spherical to cylindrical and from cylindrical to lamellar), we confined ourselves only to a general comment in this review. Some workers (see, for example, Refs. 71 and 75) treat the phenomenon in terms of a purely geometrical aspect taking into account only the shape of the molecules and their packing. In reality, such processes are controlled by energy relations. A rigorous study of polymorphic transformations of micelles, like that of the polymorphic transformations of small crystals, is based on the generalised Gibbs–Curie principle[107] using [as in Eqns. (47) and (49)] the concept of surface tension. For the latter, as for many other thermodynamic quantities, it is also possible to differentiate and calculate in one way or another the electrostatic contribution characteristic of ionic micelles (see, for example, Rusanov[22]). However, a detailed examination of these questions is outside the framework of this review.

References

1. J W McBain, C S Salmon *J. Amer. Chem. Soc.*, 1920, **42** 426
2. P Ekwall *Acta Acad. Abo.*, 1927, **4** 1
3. E Jones, C R Bury *Philos. Mag.*, 1927, Ser. 7 **4** 841
4. B J Grindley, C R Bury *J. Chem. Soc.*, 1929, 679
5. R C Murray, G S Hartley *Trans. Faraday Soc.*, 1935, **31** 183
6. G S Hartley *Aqueous Solutions of Paraffin-Chain Salts, Hermann, Paris, 1936, 69 pp*
7. J Rassing, P J Sams, E Wyn-Jones *J. Chem. Soc., Faraday Trans. II*, 1974, **70** 1247
8. E A G Aniansson, S N Wall *J. Phys. Chem.*, 1975, **79** 857
9. M J Jaycock, R H Ottewill *Proceedings of the 4th International Congress on Surface Activity*, 1964, Vol. 2 p. 545
10. E A G Aniansson, S N Wall, M Almgren, et al. *J. Phys. Chem.*, 1976, **80** 905
11. T Okubo, H Kitano, T Ishiwatari, N Isem *Proc. Roy. Soc.*, 1979, **A366** 81
12. K. Shinoda, E Hutchinson *J. Phys. Chem.*, 1962, **66** 577
13. K Shinoda, T Nakagawa, B Tamamushi, T Isemura *Colloidal Surfactants: Some Physicochemical Properties* (Translated into Russian), Izd. Mir, Moscow, 1966, p.16
14. Y Moroi, R Sugii, R Matuura *J. Colloid Interface Sci.*, 1984, **98** 184
15. Y Moroi, N Ikeda, R Matuura *J. Colloid Interface Sci.*, 1984, **101** 285
16. G Charbit, F Dorion, R Gaboriaud *Fluid Phase Equil.*, 1985, **20** 233
17. A I Rusanov *Kolloid. Zhur.*, 1987, **49** 1129
18. P H Elworthy, K J Mysels *J. Colloid Interface Sci.*, 1966, **21** 331
19. S G Cutler, P Meares, D G Hall *J. Chem. Soc., Faraday Trans., I*, 1978, **74** 1758
20. D G Hall *J. Chem. Soc., Faraday Trans. II*, 1972, **68** 668
21. A I Rusanov *Fazovye Ravnovesiya i Poverkhnostnye Yavleniya* (Phase Equilibria and Surface Phenomena), Izd. Khimiya, Leningrad, 1967
22. A I Rusanov *Kolloid. Zhur.*, 1981, **43** 890
23. K Shinoda (Editor) *Solvent Properties of Surfactant Solutions*, Dekker, New York, 1967, pp.1, 27
24. P H Elworthy, A T Florence, C B Macfarlane *Solubilization by Surface-Active Agents*, Chapman and Hall, London, 1968
25. E W Anacker *Cationic Surfactants*, Dekker, New York, 1970, p. 203
26. C Tanford *The Hydrophobic Effect*, Wiley, New York, 1973, 200 pp
27. P Mukerjee *Enriching Topics from Colloid and Surface Science* (Edited by H van Olphen, K Mysels), Theorex, La Jolla, 1975, p.135

28. P Ekwall, P Stenius *Surface and Colloid Science* (Edited by M Kerker), Butterworth, London, 1975, p. 215
29. T Nakagawa, F Tokiwa *Surface and Colloid Science* (Edited by E Matijevic), Wiley, New York, 1976, Vol. 9 p.69
30. *Micelle Formation, Solubilisation, and Microemulsions* (Translated into Russian), Izd. Mir, Moscow, 1980
31. H Wennerström, B Lindman *Phys. Rep.*, 1979, **52** 1
32. B Lindman, H Wennerström *Topics in Current Chemistry* Springer, Berlin, 1980, Vol. 87 p. 1
33. T F Tadros (Editor) *Surfactants*, Acad. Press, New York, 1984 342 pp
34. J T G Overbeek, D Stigter *Rec. Trav. Chim.*, 1956, **75** 1263
35. A L Loeb, J T G Overbeek, P H Wiersema *The Electrical Double Layer Around a Spherical Colloid Particle*, MIT Press, Cambridge, 1961
36. M F Emerson, A Holtzer *J. Phys. Chem.*, 1965 , **69** 3718; 1967, **71** 1898
37. D Stigter *J. Colloid Interface Sci.*, 1974, **47** 473; *J. Phys. Chem.*, 1974, **78** 2480; 1975, **79** 1008, 1015
38. J Frahm, S Diekmann *J. Colloid Interface Sci.*, 1979, **70** 440
39. J Frahm, S Diekmann, A Haase *Ber. Bunsenges. Phys. Chem.*, 1980, **84** 566
40. P J Missel, N A Mazer, G B Benedek, C Y Young *J. Phys. Chem.*, 1980, **84** 1044
41. G Gunnarson, B Jönsson, H Wennerström *J. Phys. Chem.*, 1980, **84** 3114
42. B Jönsson, H Wennerström *J. Colloid Interface Sci.*, 1981, **80** 482
43. P Linse, G Gunnarson, B Jönsson *J. Phys. Chem.*, 1982, **86** 413
44. W C Cheu, P N Seu *J. Chem. Phys.*, 1982, **77** 2042
45. A V Konstantinovich, L A Al'bota *Kolloid. Khim.*, 1983, **45** 68
46. J A Beunen, E Ruckenstein *J. Colloid Interface Sci.*, 1983, **96** 469
47. D J Mitchell, B W Ninham *J. Phys. Chem.*, 1983, **87** 2996
48. D F Evans, B W Ninham *J. Phys. Chem.*, 1983, **87** 5025
49. D F Evans, D J Mitchell, B W Ninham *J. Phys. Chem.*, 1984, **88** 6344
50. H Akisada *J. Colloid Interface Sci.*, 1984, **97** 105
51. I Frahm, S Diekmann *Surfactants in Solution* (Edited by K L Mittal, B Lindman), Plenum Press, New York, 1984, Vol. 2 p. 897
52. T E Burchfield, E M Woolley *J. Phys. Chem.*, 1984, **88** 2149; *Fluid Phase Equil.*, 1985, **20** 207
53. E M Woolley, T E Burchfield *J. Phys. Chem.*, 1984, **88** 2155; 1985, **89** 714; *Fluid Phase Equil.*, 1985, **20** 225
54. M T Bashford, E M Woolley *J. Phys. Chem.*, 1985, **89** 3173
55. E M Woolley, M T Bashford *J. Phys. Chem.*, 1986, **90** 3038
56. B V Deryagin *Uspekhi Khim.*, 1979, **48**(4) 675 [*Russ. Chem Rev.*, 1979(4)]
57. E A Guggenheim *Philos. Mag.*, 1935, Ser. 7, **19** 588
58. P Van Russelberghe *J. Phys. Chem.*, 1935, **39** 403
59. K S Pitzer, L F Silvester *J. Solution Chem.*, 1976, **5** 269
60. K S Pitzer, R N Roy, L F Silvester *J. Amer. Chem. Soc.*, 1977, **99** 4930
61. C E Vanderzee *J. Chem. Therm.*, 1981, **13** 947; 1982, **14** 1051
62. J C Peiper, K S Pitzer *J. Chem. Therm.*, 1982, **14** 613
63. R M Fouss, A Katchalsky, S Lifson *Proc. Nat. Acad. Sci. USA*, 1951, **37** 579
64. R A Marcus *J. Chem. Phys.*, 1955, **23** 1057
65. F E Harris, S A Rice *J. Chem. Phys.*, 1956, **25** 955
66. A Katchalsky, Z Alexandrowicz, O Kedem *Chemical Physics of Ionic Solutions* (Edited by B E Conway, R G Barrads), Wiley, New York, 1966, p. 295
67. G M Bell, A J Dunning *Trans. Faraday Soc.*, 1970, **66** 500
68. M Mille, G Vanderkooi *J. Colloid Interface Sci.*, 1977, **59** 211
69. G Gunnarson, G Olofsson, H Wennerström, A Zacharov *J. Chem. Soc., Faraday Trans. I*, 1980, **76** 1287
70. M S Fernandez, P Fromherz *J. Phys. Chem.*, 1977, **81** 1755
71. J M Israelachvili, D J Mitchell, B W Ninham *J. Chem. Soc., Faraday Trans. II*, 1976, **72** 1525
72. D W R Gruen *J. Colloid Interface Sci.*, 1981, **84** 281
73. D W R Gruen, E H B de Lacey *Surfactants in Solution* (Edited by K L Mittal, B Lindman), Plenum Press, New York, 1984, Vol. 1, p.279
74. D W R Gruen *J. Phys. Chem.*, 1985, **89** 146, 153
75. J M Israelachvili *Physics of Amphiphiles: Micelles, Vesicles and Microemulsions*, North Holland, Amsterdam, 1985, p.24
76. N Müller, R H Birkhahn *J. Phys. Chem.*, 1967, **71** 957
77. B Svens, B Rosenhokm *J. Colloid Interface Sci.*, 1973, **44** 495
78. F Podo, A Ray, G Nemethy *J. Amer. Chem. Soc.*, 1973, **95** 6164
79. F M Menger, J M Jerkunica, J C Johnston *J. Amer. Chem. Soc.*, 1978, **100** 4678
80. B J Boyer, F M Menger *J. Amer. Chem. Soc.*, 1980, **102**, 5936
81. V D Yakovlev, L P Zaichenko, A A Abramzon *Zhur. Prikl. Khim. (Leningrad)*, 1979, **52** 2471
82. P Mukherjee, J R Cardinal, N R Desai *Proc. Int. Symp. "Micellization, Solubilization, Microemulsions"* [Edited by K L Mittal, **1** 241 (1976)]) (Translated into Russian), Izd. Mir, Moscow, 1980, p. 142
83. D G Whitten, J B S Bonolha, K S Schanze, J R Winkle *Surfactants in Solution* (Edited by K L Mittal, B Lindman), Plenum Press, New York, 1984, Vol. 1, p. 585
84. A Rohde, E Sackmann *J. Colloid Interface Sci.*, 1979, **70** 494
85. T Sasaki, M Hattori, J Sasaki, K Nukina *Bull. Chem. Soc. Japan*, 1975, **48** 1397
86. B Lindman *Surfactants* (Edited by T F Tadros), Acad. Press, New York, 1984, p. 83
87. A I Rusanov, F M Kuni *Zhur. Fiz. Khim.*, 1984, **58**(9) 2336 [*Russ. J. Phys. Chem*, 1984(9)]
88. K S Pitzer, L Brewer *Thermodynamics*, McGraw-Hill, New York, 1961
89. K M Kale, E L Cussler, D F Evans *J. Phys. Chem.*, 1980, **84** 593
90. F M Kuni, A I Rusanov *Teor. Mat. Fiz.*, 1970 **2** 265
91. H-F Eicke *Topics in Current Chemistry*, Springer, Berlin, 1980, Vol. 87, p.85
92. A Couper *Surfactants* (Edited by T F Tadros), Acad. Press, New York, 1984, p. 19
93. P F Mijnlieff *J. Colloid Interface Sci.*, 1970, **33** 255
94. M Nakagaki, T Handa *Structure/Performance Relationships in Surfactants* (Edited by M J Rosen), ACS, Washington, 1984, p. 73
95. P Mukerjee, K J Mysels *Critical Micelle Concentration of Aqueous Surfactant Systems*, NSRDS-NBS 36, US Nat. Bur. Stand, 1971
96. A A Abramzon, V D Yakovlev, A A Novozhenets *Zhur. Prikl. Khim. (Leningrad)*, 1985, **58**
97. B Lindman, M C Puyal, N Kamenka, et al *Phys. Chem.*, 1982, **86** 1702

98. J C Eriksson, S Ljunggren, U Henriksson *J. Chem. Soc., Faraday Trans. II*, 1985, **81** 833
99. J C Eriksson, S Ljunggren *J. Chem. Soc., Faraday Trans. II*, 1985, **81** 1209
100. B V Deryagin *Kolloid. Zhur.*, 1940, **6** 293; *Trans. Faraday Soc.*, 1940, **36** 203
101. F Eriksson, J C Eriksson, P Stenius *Colloids Surfaces*, 1981, **3** 339
102. D Stigter *J. Phys. Chem.*, 1964, **68** 3608
103. J T G Overbeek *The Science of Colloids* (Translated into Russian), Inostr. Lit., Moscow, 1955, Vol. 1, p. 207
104. N E Hoskin *Trans. Faraday Soc.*, 1953, **49** 1471
105. F Booth *J. Chem. Phys.*, 1955, **23** 453
106. R O James, T W Healy *J. Colloid Interface Sci.*, 1972, **40** 65
107. A I Rusanov *Dokl. Akad. Nauk SSSR*, 1980, **253** 917; *Kolloid Zhur.*, 1981, **43** 903

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Catalytic synthesis of organic compounds by the carbonylation of unsaturated hydrocarbons and alcohols

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ABSTRACT. The methods of synthesis of organic compounds by the carbonylation of acetylene, diene, and alkene hydrocarbons as well as alcohols in the presence of homogeneous and heterogeneous catalysts based on Group VIII metals and acid catalysts are examined. Data are presented on the synthesis of unsaturated and saturated mono- and di-carboxylic acids and their esters, lactones, and ketones from hydrocarbons and alcohols as well as the activities, selectivities, and stabilities of the catalytic systems in the carbonylation reaction.
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I. Introduction

During recent years, the world industrial output based on the use of carbon monoxide has expanded significantly. The synthesis of methanol and of liquid hydrocarbons from CO and H_2 (the synthesis gas), the hydroformylation of olefins, and the carbonylation of methanol with formation of acetic acid may be regarded as some of the processes carried out on a large scale.

The development of processes based on the use of carbon monoxide is associated with many factors. The principal of these is the necessity to employ new alternative sources of raw materials. Since the 1940s, petroleum has been the principal source of raw materials for the chemical industry, which led to the creation of an independent branch of industry—petrochemistry. However, in recent years a tendency has arisen towards a decrease in the rate of extraction of petroleum, the principal petroleum deposits tend to become exhausted, and there is a trend towards a shift of the main centres of petroleum extraction in the USSR to the regions of the North, the North West, and the Far West. These factors led to the increase in the cost of prospecting for and the extraction and transport of petroleum and hence has necessitated the search for new ways of replacing it. Since the USSR has enormous resources in coal, shale, and natural gas, the intensification of their chemical processing in order to obtain valuable organic compounds, which are nowadays produced on the basis of petroleum, is extremely promising.

In particular, carboxylic acids, hydroxyacids, acid anhydrides, lactones, alcohols, ethers and esters, and aldehydes and ketones can be obtained via carbonylation. Many of these reactions have been fairly thoroughly investigated but so far sufficiently active, selective, and stable catalytic systems, which would permit the introduction of promising processes into industry, have not been created in many instances.

The present review includes data on the latest advances in the catalytic syntheses of oxygen-containing compounds by the catalytic carbonylation of acetylene, dienes, olefins, and alcohols in the presence of homogeneous and heterogeneous catalysts based on Group VIII metals or acid catalysts.

II. Carbonylation of unsaturated hydrocarbons

A wide variety of carbonyl-containing products of practical value are obtained by the carbonylation of unsaturated compounds containing triple, double, or conjugated bonds. The interest in this reaction has grown particularly in recent years in connection with the necessity to create new technological methods for the synthesis of valuable chemical products on the basis of natural gas and coal from which mixtures of carbon monoxide and hydrogen can be readily obtained.

A series of monographs and reviews have been devoted to the carbonylation reactions of unsaturated compounds.[1-3] Below we shall therefore examine only the publications of recent years as well as problems of a general character.

The possibility of obtaining acetylene hydrocarbons from a non-petroleum raw material leads to good prospects for the application of processes involving the carbonylation of these substrates.

1. Carbonylation of acetylene hydrocarbons

The carbonylation of acetylene hydrocarbons usually leads to the formation of acrylic acid, its derivatives, and esters:[4-20]

$$R{-}C{\equiv}CH + CO{-}\begin{cases}\xrightarrow{H_2O} CH_2{=}C(R)COOH\\ \xrightarrow{R'OH} CH_2{=}C(R)\,COOR'.\end{cases}$$

For example, mixtures of maleic and fumaric acids have been obtained in 35–40% yield by the carbonylation of acetylene in the presence of H_2PdBr_6.[4] The reaction is carried out at atmospheric pressure and a temperature in the range 35–40 °C by passing a 4:1 mixture of CO and C_2H_2 through a hydrochloric acid solution. The maleic acid formed together with fumaric acid then isomerises fully to fumaric acid. When $PdBr_2$ mixed with oxidants [$FeCl_3.6H_2O$, $Fe_2(SO_4)_3.9H_2O$, O_2] is used as the catalyst, a mixture of fumaric and maleic acids and maleic anhydride is obtained from acetylene and its homologues.[5] The anhydride of phenylmaleic acid has been obtained from phenylacetylene under these conditions.

The carbonylation of acetylene and some of its homologues in the presence of palladium catalysts in the liquid phase containing HCl and HBr takes place with formation of acrylic acid and its esters and β-chloroacrylic acid and its esters. It has been studied in detail in a number of investigations.[6-12] *trans*-β-Chloroacrylic acid has been obtained in 62.5% yield from a 4:1 C_2H_2-CO mixture in HCl solution in the presence of $PdCl_2-HgCl_2$ with added NH_4Cl and $FeCl_3$ at 80.5 °C and atmospheric pressure.[6] Vinyl chloride and small amounts of acetaldehydes are formed as side products.

The carbonylation of acetylene also takes place in the presence of the $PdBr_2-HBr-$oxidant$-BuOH$ system with added PPh_3. $FeCl_3$, O_2, and quinone are used as oxidants.[7,8] In order to increase its rate, the reaction is carried out in carboxylic acid amides.[8]

The rate of carbonylation of acetylene (70 °C, atmospheric pressure) is described by the following equation when the $PdBr_2-P(OPh)_3-HBr.ROH$ catalytic system is used:[9]

$$r = k_1 p_{CO} p_{C_2H_2} / [H^+] \times (1 + k_2 p_{CO} p_{C_2H_2} + k_3 p_{C_2H_2}),$$

where k_1, k_2, and k_3 are constants and p_{CO} and $p_{C_2H_2}$ are the current partial pressures of carbon monoxide and acetylene respectively.

In the presence of the $PdI_2-LiI-HCl-ROH$ catalyst, the kinetics of the carbonylation of acetylene are described by a more complex equation.

The "alkoxide" reaction mechanism has been proposed:[9]

$$PdX_2 \underset{HX}{\overset{ROH}{\rightleftharpoons}} XPdOR \xrightarrow{CO} XPdCOOR \xrightarrow{C_2H_2} XPdCH{=}CHCOOR - \begin{cases} \xrightarrow{H^+} CH_2{=}CHCOOR + PdX_2, \\ \xrightarrow{CO,ROH} (ROOCCH{=})_2 + HX + Pd(0). \end{cases}$$

The activity of complexes of the type $Pd\{P(OR)_3\}X_2$ in the carbonylation of acetylene in hydrochloric acid and 1-butanol diminishes in the sequences $Cl^- > Br^- > I^- > SCN^-$ and $P(OCH_3)_3 > P(OC_2H_5)_3 > P(O\text{-iso-}C_3H_7)_3$. When the reaction is carried out in hydrobromic acid, the opposite sequences are observed. The addition of LiI to the reaction medium appreciably increases the activity of the catalytic system. Palladium complexes with ligands in the *trans*-positions possess a higher activity. The main product of the carbonylation of acetylene is the monoester of acrylic acid. The formation of dicarboxylic acid diesters is hardly observed.[10,11]

Quinone is an effective oxidant when the $PdI_2-LiI-HCl-BuOH$ catalytic system is used for the carbonylation of acetylene with formation of acrylic, propionic, maleic, fumaric, and succinic acid esters. The Pd^+ ion is then responsible for the catalysis. The activity of the complexes $MPdI_2.2H_2O$ (where M = Li or Cs) is significantly higher than that of the complexes $[Pd(CO)Cl]_n$ and $Cs[Pd(CO)Cl_2]$.[8]

The carbonylation of methylacetylene in the presence of a catalytic system containing $PdCl_2$ and HI in methanol and acetone at 50 °C and a pressure of 24 atm afforded methyl methacrylate and methyl crotonate in overall yields of 97.0 and 2.0% respectively.[12,14] The reaction takes place effectively not only in alcohol but also in other oxygen-containing compounds, for example, methyl and ethyl acetates, ethyl methyl ketone, tetrahydrofuran (THF), dioxan, and acetone.

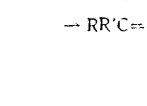
The carbonylation of acetylene, methylacetylene, phenylacetylene, and other alkyl- or aryl-acetylenes can be achieved in the presence of a wide range of palladium complex catalysts containing various ligands.[15,16] Thus acetylene reacts readily with CO and O_2 in the presence of PdX_2, where X = Cl, Br, or I, at temperatures in the range 0–70 °C and atmospheric pressure with added thiourea.

Methyl maleate with a small admixture of fumaric acid ester as well as the diesters of *cis,cis*-, *cis,trans*-, and *trans,trans*-muconic acids are mainly formed in methanol and acetone at 15 °C from CO, C_2H_2, and O_2 in proportions of 1:1:0.1 in the presence of $PdCl_2$ and thiourea.[15]

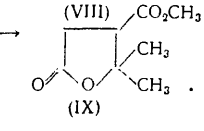
Maleic and fumaric acid esters are obtained from acetylene, CO, and O_2 at 20 °C and atmospheric pressure in the presence of $PdCl_2$ and ethanol with the following aminoacids as additives: DL-threonine, L-glutamic acid, DL-lysine.HCl, *N*-methylglycine, L-α-alanine, DL-β-phenyl-α-alanine, and DL-serine.[16]

Nickel catalysts are also effective in the carbonylation of acetylene. Ethyl 3,4-diacetoxy-2-methylenebutyrate, whose hydrolysis affords the valuable antibacterial preparation methyl βγ-dihydroxy-α-methylenebutyrate, is formed from 1,2-diacetoxybut-3-yne in solution in an alcohol–acetic acid (or an alcohol–benzene) mixture in the presence of nickel carbonyl under mild conditions (70 °C, atmospheric pressure).[17]

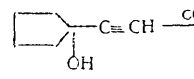
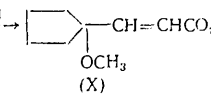
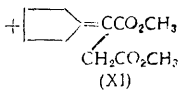
Derivatives of alkylidenesuccinic acids have been synthesised from acetylene alcohols having the general formula $RR'C(OH)C{\equiv}CH$ and carbon monoxide by carbonylation under pressure in the presence of palladium black and HI in benzene or in the presence of $CO_2(CO)_8$ with various additives.[18] The reaction proceeds in accordance with the mechanism

$$RR'C(OH)C{\equiv}CH + CO \rightarrow \underset{(I)}{[RR'C{=}C{=}CHCOOH]} \xrightarrow{CO,H_2O} \underset{(II)}{RR'C{=}C(COOH)CH_2COOH} \rightarrow RR'C{=}\underset{(III)}{\text{  }}.$$

The carbonylation of the alcohols (Ib) and (Ic) proceeds specifically. Thus a mixture of the aliphatic unsaturated methoxyacids (VI), (VII), and (VIII) as well as the lactone (IX) have been obtained from compound (Ib):

$$\underset{(Ib)}{(CH_3)_2C(OH)C{\equiv}CH} \begin{cases} \rightarrow (CH_3)_2C{=}C(CO_2CH_3)CH_2CO_2CH_3, \ (VI) \\ \rightarrow (CH_3)_2C(OCH_3)CH{=}CHCO_2CH_3, \ (VII) \\ \rightarrow (CH_3)_2C(OCH_3)C(CO_2CH_3){=}CHCO_2CH_3, \ (VIII) \\ \rightarrow \underset{(IX)}{\text{  }}. \end{cases}$$

The carbonylation of the alcohol (Ic) results in the formation of a mixture of the methoxymonoester (X) and the diester (XI):

$$\underset{(Ic)}{\text{  }} \xrightarrow{CO,CH_3OH} \underset{(X)}{\text{  }} + \underset{(XI)}{\text{  }}.$$

Acetylene alcohols having the formula (I), where R = R′ = H (Ia), R = R′ = CH_3 (Ib), R + R′ = $(-CH_2)_4$ (Ic), or R = CH_3 and R′ = C_6H_5 (Id) have been converted into the anhydrides of the corresponding dicarboxylic acids (II) (Table 1) on interaction with CO under a pressure of 100 atm in benzene in the presence of palladium black and HI.

On refluxing with water, the anhydrides (IIIb–d) are converted into the corresponding acids (IIb–d).

The carbonylation of compound (Ia) in methanol leads to the formation of dimethyl itaconate (IV) and dimethyl aconitate (V) in proportions of 6:1 in an overall yield of 35%. The reaction

proceeds in accordance with the mechanism

$$HC{\equiv}CCH_2OH \xrightarrow[-H_2O]{CO,CH_3OH} [CH_2{=}C{=}CHCO_2CH_3] \xrightarrow{CO,CH_3OH} CH_2{=}C(CO_2CH_3)CH_2CO_2CH_3 \quad (IV)$$

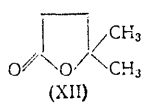
$$HC{\equiv}CCH_2OH \xrightarrow{CO,CH_3OH} CH_3O_2CCH{=}C(CO_2CH_3)CH_2OCH_3 \xrightarrow{CO} CH_3CO_2CH{=}C(CO_2CH_3)CH_2CO_2CH_3 \quad (V)$$

Table 1. Carbonylation of acetylene alcohols in benzene in the presence of palladium black and HI.[18]

Acetylene alcohol	T, °C	p_{CO}, atm	t, h	Reaction product	Yield of reaction product, %
(Ia)	30	20	1.5	tar	—
(Ib)	50	20	3.0	(IIIb)	45
(Ic)	70	50	5.0	(IIIc)	36
(Id)	30	50	2.0	(IIId)	51

The carbonylation of the alcohol (Ib) in the presence of $Co_2(CO)_8$ with various additives (see Table 2) affords tetraconic anhydride (IIb) and the diester (VII). 5,5-Dimethyl-$\Delta^{3,4}$-dihydrofuran-2-one (XII) was also obtained in small amounts:[18]

$$(CH_3)_2C(OH)C{\equiv}CH \xrightarrow{CO,H_2O} (CH_3)_2C(OH)CH{=}CHCOOH \rightarrow$$



(XII)

Table 2. Carbonylation of ethynyldimethylmethanol (Ib) in the presence of cobalt catalysts (150 °C, 100 atm CO).[18]

Catalytic system	Overall yield of compounds (IIb), (VII), and (XII), %	Relative yields, %		
		(IIb)	(VII)	(XII)
$Co_2(CO)_8+HI+CH_3OH$	53.4	42.1	50.4	7.5
$Co_2(CO)_8+HI+Py+CH_3OH$	49.2	25.6	32.3	42.1
$Co_2(CO)_8+C_6H_6$	15.3	—	—	100.0
80.7% CoNaY (SiO_2/Al_2O_3=4.4)	58.3	28.8	47.9	23.3

Butyl acrylate and propionate, the diesters of maleic and fumaric acids, and also crotonic acid esters can be obtained by carbonylating acetylene in the presence of $Pd(NH_3)_nX_2$ (where n = 2 or 4 and X = Cl or I) and HCl at 70 °C and atmospheric pressure in the liquid phase.[19,20] A 1 : 1 mixture of CO and C_2H_2 is used in the reaction. Palladium is regenerated by treating the reaction solution with a stream of dry NH_3 and subsequently isolating the palladium complex by filtration. Under the conditions indicated, the overall rate of formation of the carbonylation products is 1.45 mol litre^{-1} h^{-1}.[19]

Thus a wide variety of mono-, di-, and tri-carboxylic acids, their esters and anhydrides, lactones, and cyclic compounds can be obtained by carbonylating acetylene compounds and their homologues. However, the industrial application of these processes is prevented in the first place by the insufficient activity and selectivity of the proposed catalytic systems.

We may also note that complexes based on Group VIII noble metals are very costly, while nickel complexes are extremely toxic and volatile. In addition, the use of homogeneous complex systems requires the creation of complex regeneration schemes.

2. Carbonylation of dienes

When dienes interact with carbon monoxide in aqueous or alcoholic media, unsaturated monocarboxylic acids, saturated dicarboxylic acids, or their esters, lactones, and mono- and polyketones are formed.[1-3,21] Butadiene and its oligomers, allene, keten, the di- and tri-oligomers of cyclopentadiene are most often used as substrates in this reaction.

The carbonylation of the simplest diene (buta-1,3-diene) in methyl or ethyl formate takes place under mild conditions (120 °C, 30 atm) mainly with formation of the pent-3-enoic acid ester.[22] Pent-3-enoic acid itself is formed in small amounts. Cobalt carbonyl with added isoquinoline is used as the catalyst. The process selectivity increases after the introduction of amines with pK_a = 3–11 into the reaction zone as cocatalysts and also on raising the reaction temperature to 140 °C and the CO pressure to ~900 atm.[23] The presence of admixtures of acetylene hydrocarbons in buta-1,3-diene lowers the efficiency of the process. In the presence of $Co_2(CO)_8$ and pyridine, methyl pent-3-enoate can be obtained in 78% yield from buta-1,3-diene containing about 5% of vinylacetylene, CO, and methanol at 135 °C and a pressure of 900 atm. A decrease in the vinylacetylene content to 0.1% increases the yield of the product to 98%.

In the presence of the $Pd(OAc)_2-Ph_2P(CH_2)_2.PPh_2$ catalytic system (110 °C, 50 atm), a mixture of the isopropyl esters of pent-3-enoic and nona-3,8-dienoic acids is formed from buta-1,3-diene, CO, and isopropyl alcohol in 26.0 and 13.5% yields respectively.[24] The use of C_1–C_{12} aliphatic alcohols makes it possible to regenerate the palladium to the extent of 90%.

The selectivity of the carbonylation of buta-1,3-diene with formation of pen-3-enoate esters increases after the introduction of a mixture of pyridine and isoquinoline into the reaction zone together with $Co_2(CO)_8$. Under these conditions, mainly only the target product is formed from the butadiene at 100–140 °C. Side compounds—4-vinylcyclohexene, dibutyl ketone, methyl α-methylglutarate, and butenals—are formed in insignificant amounts.[25]

A method has been proposed for the synthesis of the phenyl esters of pent-3-enoic and pent-2-enoic acids by carbonylating buta-1,3-diene with carbon monoxide in the presence of compounds having the formula $HX.C_6RR^1R^2R^3R^4$, where X = O or S and R – R^4 = H, alkyl, alkoxy-group ($\leqslant C_6$), cycloalkyl, cycloalkoxy-group (C_3–C_{12}), aryl, and aryloxy-group (C_6–C_{12}), in the presence of $Co_2(CO)_8$ and nitrogen-containing bases with pK_a = 3–10, namely pyridine, γ-picoline, isoquinoline, or their mixtures.[26] The carbonylation of the butadiene is accompanied by dimerisation, which results in the formation of a nona-3,8-dienoate ester:

$$2CH_2{=}CHCH{=}CH_2 + CO + ROH \rightarrow CH_2{=}CH(CH_2)_3CH{=}CHCH_2COOR .$$

It has been suggested that the coupled dimerisation and carbonylation reactions be carried out in the presence of palladium salts or complexes together with sodium, lithium, and potassium acetates.

The catalytic systems are stabilised by arsines, stibines, or phosphines in aliphatic, cyclic or aromatic alcohols and heterocyclic compounds containing oxygen, sulphur, and nitrogen atoms: THF, tetrahydropyran, dioxan, lactones, diketones, tetrahydrothiophen, dibenzothiophen, benzo-1,3-dioxole, etc. Thus isopropyl nona-3,8-dienoate was formed in 85% yield from butadiene, CO, and isopropyl alcohol in the presence of $Pd(OAc)_2$ and PPh_3 at 110 °C and a CO pressure of 50 atm after 18 h.[27]

Allene is carbonylated in the presence of $(Et_2NH)_2NiI_2$ and Et_2NH under mild conditions (20 °C, 5–10 atm CO).[28] For the $(Et_2NH)_2\ NiI_2 : CH_2=C=CH_2 = 1:2$ ratio, a mixture of $Et_2NC(O).C(=CH_2)CH_2NEt_2$ and $Et_2NC(O)C(=CH_2)CH_2C(=CH_2)CH_2NEt_2$ is formed in 48 and 12% yields in solution in a THF–ether mixture. For the equimolar reactant ratio, the yields of these products are 57 and 0.9% respectively. They are formed from allene, Et_2NH, and CO via the intermediate $Et_2NC(O).(=CH_2)CH_2NiI(Et_2NH)_n$.[28] Alkyl esters of malonic acid, which are used in the industrial synthesis of malonic and barbituric acids and medicinal drugs, are obtained by the interaction of keten $CH_2=C=O$ with CO in nitrous acid esters RONO in the presence of phosphine-containing complexes L_2MX_2 (where M = Pt, Pd, Rh, Ru, or Ir and X = Cl, Br, or I), tin halides, and quaternary ammonium salts $R'_4N.X$.[29]

A process has been developed for the syntheis of formylvaleric acid by carbonylating buta-1,3-diene with subsequent hydroformylation of the pent-3-enoic acid ester formed in accordance with the scheme[30]

$$CH_2=CHCH=CH_2 + CO + ROH \rightarrow CH_2=CHCH_2CH_2COOR \rightarrow \xrightarrow{CO,\ H_2} HCOCH_2CH_2CH_2CH_2COOR\ .$$

The first stage is carried out at 135 °C and a CO pressure of 900 atm and the second stage is performed at 120 °C and a pressure of 200 atm. The methyl formylvalerate formed is used in the manufacture of plasticising agents, ε-caprolactam, ε-caprolactone, hexanediol, and adipic acid.

The selective carbonylation of dienes, in particular buta-1,3-diene,[31] can be achieved in a two-phase system consisting of a layer of a polar liquid (water, MeCN, DMF, DMSO, $MeNO_2$, *N*-methylpyrrolidinone, and C_1-C_4 alcohols) and a layer of a non-polar liquid with a dielectric constant $\varepsilon < 2.3$ (pentane, isopentane, hexane, iso-octane, cyclo-octane, tetradecane, etc.). The non-polar solvents then contain the reaction products and the layer of polar liquids contains the components of the catalytic system which are returned to the process. The catalysts are palladium and its compounds. Palladium catalysts on carriers promoted by nitrogen, phosphorus, and arsenic compounds and quaternary ammonium compounds, containing substances capable of generating hydrogen halides in the course of the reaction. Thus, ethyl esters of pentenoic acid (in 61.0% yield) as well as a mixture of diethyl α-methylglutarate and ethyl nona-3,8-dienoate are formed from buta-1,3-diene, CO, and ethanol in the presence of $(C_3H_4)_2PdCl_2$, Bu_4NCl, and 1-chlorobut-2-ene (source of HCl) at 120 °C and a pressure of 196 atm. After the treatment of the products with a mixture of hexane and methanol, the components of the catalytic system are extracted from the methanol phase and the reaction products are extracted from the hexane phase.

The esters of nona-3,8-dienoic acid are obtained selectively from butadiene in the presence of palladium complexes with phosphines and of a thiol as a stabiliser.[32] Thus methyl nona-3,8-dienoate has been obtained in 75% yield from buta-1,3-diene, CO, and methanol in the presence of the complex $Pd(OAc)_2.[P(iso\text{-}Pr)_3]_2$ with added $P(iso\text{-}Pr)_3$ and BuSh (stabiliser) at 100 °C and a pressure of 52.5 atm. Palladium black is not formed during the reaction, which indicates the stability of the catalytic complex.

Esters of but-2-ene-1,2-dicarboxylic acid have been obtained from butadiene under oxidative carbonylation conditions. The reaction is carried out in the presence of O_2, alkoxycycloalkenes, and alcohols. For example, treatment of butadiene with a mixture of carbon monoxide (7 atm) and O_2 (7 atm) in methanol and 1-methoxycyclohexene in the presence of $PdCl_2$, $CuCl_2$, and LiCl at 100 °C and a pressure of 126 atm gave rise after 2 h to dimethyl hex-3-enedioate in 84% yield for a diene conversion of 43%.[33,34]

Pent-3-enoic acid esters were obtained from butadiene, CO, and O_2 in the presence of $PdCl_2-CuCl_2$ as well as the additives PrCOONa and $HC(OMe)_3$. Thus *trans*-$(PhCH_2OOCCH_2CH=)_2$ is formed in ~80% yield in $PhCH_2OH$ at a CO pressure of 144 atm and a temperature of 60 °C.[35]

Pent-3-enoic acid diesters are obtained also without access of water and air in the presence of $PdCl_2$, $CuCl_2$, and alkali earth metal salts. The interaction of butadiene with CO in solution in anhydrous $CuCl_2$ in $PhCH_2OH$, NaOOCPr, and $HC(OMe)_3$ in the presence of $PdCl_2$ at 60 °C and a pressure of 3 atm resulted in the formation of the diester *trans*-$PhOOCCH_2CH=CHCH_2COOPh$.[36] This diester is hydrolysed to the unsaturated acid, which is then hydrogenated to adipic acid over a palladium catalyst.[36]

The selectivity of the conversion of butadiene into adipic acid diesters increases when mixtures of two bases of the pyridine and quinoline series, substituted by C_1-C_6 alkyls or alkenyls or by C_7-C_{10} alkylaryls or arylalkyls, are used as cocatalysts with $Co_2(CO)_8$. In the presence of the $Co_2(CO)_8$–pyridine–isoquinoline system butadiene interacts with CO and MeOH to form dimethyl adipate with a selectivity of 72.5% for a 100% conversion of the diene. When the $Co_2(CO)_8$–pyridine–γ-picoline catalytic system is used, the selectivity of the reaction with respect to the target product is 77.5%.[37]

A convenient technology has been proposed for the synthesis of adipic acid diesters via a two-stage scheme, where the first stage involves the preparation of the pent-3-enoic acid ester with utilisation of all the reaction side products and the regeneration of cobalt.[38–41] The catalyst is the $Co_2(CO)_8$, $HCo(CO)_4$ + pyridine (*N*-methylpyridine or *N*-methyldihydropyridine) system.

The synthesis of dimethyl butane-1,4-dicarboxylate from butadiene was improved by introducing the step involving the cooling to −5 °C of the products obtained in the first stage in the alcoholic phase (MeOH). This results in the formation of two phases: the reaction product (methyl pent-4-enoate) collects in the upper phase, while the lower, aqueous alcoholic phase contains up to about 98% of the cobalt catalyst, which is used in the second carbonylation stage.[41]

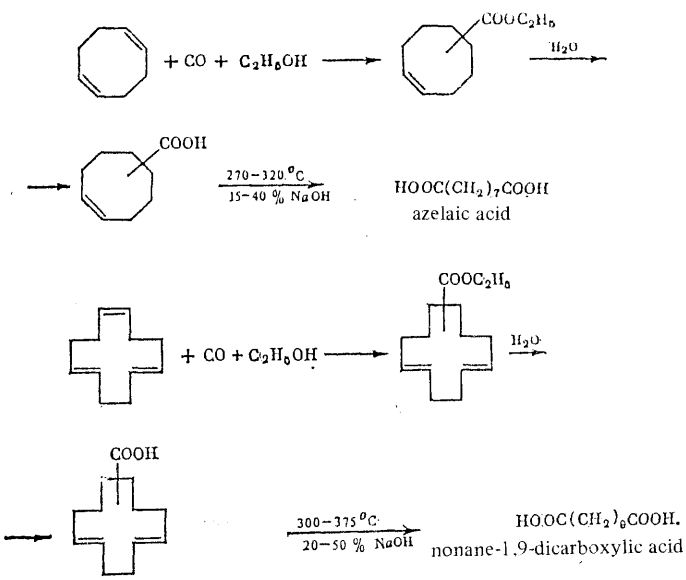
It has been shown[42] that the efficiency of the $Pd(OAc)_2-X_2$ (where X = phosphine) catalytic system in solution in amines [quinoline, lutidine, *NN*-diethylaniline, and 3,5-lutidine ($pK_a < 7$)] in the carbonylation of butadiene by carbon monoxide in an alcoholic phase (110 °C, 48 atm CO) with formation of the nona-3,8-dienoic acid ester increases with increasing basicity of the phosphines in the sequence $P(OPh)_3 < P(p\text{-}ClPh)_3 < PPh_3 < P(p\text{-}MePh)_3 < P(p\text{-}Bu)_3$. In the presence of tertiary amines with $pK_a > 7$ (*N*-methylmorpholine, *NN'*-dimethylpyridine, *NN'*-dimethylpiperazine, *N*-methylimidazole, etc.), the yield of the target products falls from 60–70 to 6–7%. The activity of the $Pd(OAc)_2$ $(PPh_3)_2$ catalytic system in amines with $pK_a < 7$ hardly changes after 32 cycles of its use, while the selectivity diminishes by 20%.

The structure and basicity of the ligands influence strongly the carbonylation of butadiene. For "strong" ligands ($pK_a < 6$), a ligand/Pd = 1–3 ratio is desirable, while for "weak" ligands ($pK_a < 6$) the ratio should be 4–100. Methyl nona-3,8-dienoate can be obtained in 60% yield from butadiene, CO, and methanol in the presence of $Pd(OAc)_2$, n-Bu_3P, and $(CNCC_2H_4)_3P$ at 90 °C and a CO pressure of 35 atm in the first stage for 2 h and at 110 °C in the second stage for 4 h.[43]

A continuous method has been developed for the synthesis of dialkyl adipates from butadiene, CO, and alcohols in the presence of the $Co_2(CO)_8$–pyridine–isoquinoline catalytic system with added hexane.[44] The first stage is carried out at 130 °C and a CO pressure of 300 atm, while the second stage is performed at 185 °C and 300 atm. The selectivity with respect to dimethyl adipate reaches 72.5%. In the absence of hexane, the selectivity is 66.4%.

Studies on the carbonylation of cyclic dienes (cyclo-octa-1,5-diene and cyclo-dodeca-1,5,9-triene), obtained from butadiene in the presence of nickel catalysts, are of great theoretical and practical interest.

A method has been proposed[45,46] for the preparation of azelaic acid from cyclo-octa-1,5-diene and of nonane-1,9-dicarboxylic acid from cyclododeca-1,5,9-triene by carbonylating dienes with formation of the corresponding unsaturated monocarboxylic acid esters and subsequent ring opening by refluxing in aqueous NaOH solutions.

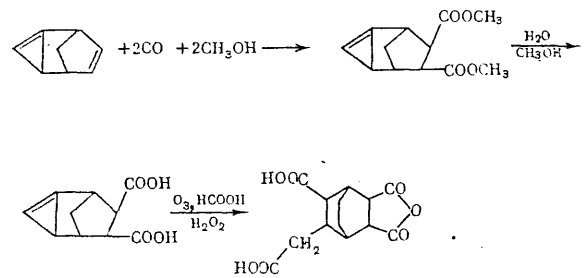


Cyclo-octa-1,5-diene is carbonylated in the presence of Rh(OAc).$(CO)(PPh_3)_2$ or Rh_2O using a 2 : 1–2 mixture of CO and H_2 at 70–85 °C and a pressure of 55–80 atm,[45] while cyclododeca-1,5,9-triene is carbonylated at 50–60 °C and a pressure of 250 to 300 atm.[46]

Ethyl cyclo-oct-4-ene-1-carboxylate has been obtained in yields up to 85–90% by carbonylating cyclo-octa-1,5-diene in the presence of $PdCl_2(PPh_3)_2$ and $AlCl_3$ in ethanol at 105–108 °C and a pressure of 100 atm.[47]

Cyclic di-, tri-, and tetra-carboxylic acids or their anhydrides, which are widely used in the industrial manufacture of plasticising agents, hardening agents for epoxy-resins, water-soluble polyester resins, and inks and dyes for printing and coatings, were obtained by carbonylating di- and tri-cyclopentadienes.[48–51]

The esters of dicyclopentadienedicarboxylic acids are obtained in high yields from dicyclopentadiene, CO, and alcohol in the presence of $Co_2(CO)_8$ and a pyridine base (pyridine, picoline, etc.). The process is carried out at a CO pressure of 20–40 atm in two stages: the first takes place at 100–120 °C and the second at 140–160 °C.[48] Dimethyldicyclopentenedicarboxylate is obtained by carboxylating dicyclopentadiene in the presence of $PdCl_2$, $CuCl_2$, and CH_3OH. It is then hydrolysed to the free acid, ozonised in formic acid, and oxidised to a tetracarboxylic acid and then further to the anhydride in accordance with the scheme[49]



The so called "tarry" carboxylic acids are obtained by carbonylating cyclopentadiene trimers and tetramers.[50] As in the carbonylation of dicyclopentadiene, which has the norbornadiene structure, in the presence of the $Co_2(CO)_8$ + pyridine catalytic system (50 atm CO, 80–140 °C) in methanol, methyl tricyclodecenecarboxylate and dimethyltricyclodecanedicarboxylate in porportions of 90 : 8 are obtained in an overall yield of ~80%.

The alkoxycarbonylation of butadiene is performed in isopropyl alcohol in the presence of $PdCl_2$ with added quaternary nitrogen-, phosphorus-, and arsenic-containing salts.[51] Extraction by saturated hydrocarbons to which the same quaternary salts have been added makes it possible to separate selectively methyl pent-3-enoate from the palladium catalyst present in the alcoholic layer. This ensures the stability of the catalytic system employed. The process takes place with a selectivity of 93.2%. The efficiency of the carbonylation of the cyclopentadiene trimer increases if some of the cyclopentadiene trimers or tetramers are hydrogenated in a preliminary step. The carbonylation of the partly hydrogenated cyclopentadiene trimer in the presence of NiI_2–H_2O (220 °C, 80 atm) yielded "tarry" carboxylic acids with a softening temperature of 42 °C.

In the carbonylation of buta-1,3-diene in the presence of $PdCl_2$ with addition of quaternary nitrogen-, phosphorus-, and arsenic-containing salts, 99% of the palladium passes to the isopropyl phase after the introduction into the reaction mixture of n-octane and Bu_4NCl. The specific activity of the catalytic system increases somewhat when it is reused. Analogous results have been obtained also in the carbonylation of butadiene in the presence of bis(π-allylpalladium dichloride) with the addition of the same salts and hydrogen halides.[52,53]

It has been suggested[54–56] that the products of the alkoxycarbonylation of dienes (including butadiene) in the presence of the $Co_2(CO)_8$–isoquinoline system be separated by distillation with subsequent refluxing of the separated product in benzene. The benzene layer is next treated with sulphuric acid and then with a Na_2CO_3 solution. The degree of extraction of cobalt is 99%.[52] Cobalt may be isolated from the reaction products also by treatment with air.[53]

3. Carbonylation of olefins

The interaction of olefins with CO and H_2O leads to the formation of unsaturated carboxylic acids having linear or branched structures. When water is replaced by alcohol, carboxylic acid esters are obtained. The structure of the acids formed depends primarily on the nature of the catalyst used and also on the conditions under which they are employed. In the presence of catalysts based on Group VIII metals, mainly mixtures of linear and branched α-methyl-substituted carboxylic acids are formed. When acid catalysts are used, the products are mainly branched αα-dialkyl-substituted carboxylic acids.

(a) Carbonylation of olefins in the presence of Group VIII metals and their complexes. When ethylene is carbonylated in the presence of metal complexes, propionic acid is formed.[58] The advantages of this method are its single-stage nature, high selectivity, and relative mild process conditions. Propionic acid is an important product used for the preparation of artificial fibres, the conservation of agricultural feed, and the manufacture of medicinal drugs and perfumes.

The synthesis of propionic acid by the carbonylation of ethylene has been achieved with a yield of 95% on the $Ni(OCOC_2H_5)_2$ catalyst at 285 °C and a pressure of 235 atm.[57] Nickel in the form of the carbonyl is extracted from the reaction mixture by treating it at 70–80 °C with an inert gas containing 3–10% of O_2. The acid obtained is used in the bread-baking industry.[58]

Effective catalysts based on mixtures of nickel and molybdenum or nickel and tungsten compounds have been proposed for the synthesis of propionic acid from C_2H_4, CO, and H_2O.[59] The reaction is carried out in the presence of iodine-containing promoting agents as well as amines or phosphines. Propionic acid has been obtained in 48.9% yield from ethylene (28 atm) and CO (28 atm) with added H_2 (3.5 atm) in the presence of $NiI_2.6H_2O$, $Mo(CO)_6$, and EtI at 175 °C in aqueous propionic acid. In the presence of NiI_2, $Mo(CO)_6$, and PPh_3, propionic acid is also formed in 56% yield from C_2H_4, CO, and H_2O.[60]

Together with heterogeneous palladium catalysts, homogeneous palladium systems are also effective in the carbonylation of C_2–C_4 olefins.[61–66] The $Pd(OAc)_2$, $Pd(OAc)_2(PPh_3)_2$, and Pd[poly-(2-vinylpyridine)]$_2Cl_2$ catalytic systems are active and selective in the carbonylation of ethylene (170 °C, 100 atm, C_2H_4/CO = 1). Propionic acid is formed in 65–70% yield.[61]

The reaction is carried out in acetic or propionic acid with the addition of Group I–III, VI, and VIII metals salts to the $Rh-Ru_3(CO)_{12}$ cluster and complexes based on it. The maximum yield of methyl esters of butyric acid is observed in the hexane–methanol–water mixture at 180 °C, an initial pressure of 28 atm, and a water concentration of 46.2 vol. %. The addition of $MoCl_6$ to the catalyst induces an increase in the activity of the system. It has been shown by UV spectroscopy that the change in activity is apparently associated with the formation of the $[Ru_3(CO)_{12-n}]Cl^{n-}$ anion stabilised by a M^{n+} metal ion.[62]

The carbonylation of olefins can occur in the presence of palladium catalysts obtained by the impregnation of zeolites or by ion exchange involving them.[61,63,64] High-silica zeolites, containing 0.5–1.0% of palladium, exhibit a high activity and selectivity in this reaction. Propionic acid has been obtained with a selectivity of 75–95% by carbonylating ethylene in aqueous acetic or propionic acid (140–190 °C, 20–80 atm). Partial hydration of ethylene results in the formation, together with propionic acid, of ethanol, from which ethyl acetate, ethyl propionate, and diethyl ketone are obtained with participation of ethylene. The optimum ethylene carbonylation conditions are created at a temperature of 170 °C and a pressure of 60 atm. Preliminary treatment of the Pd/NaM catalyst with air (350 °C, 5 h) and hydrogen (300 °C, 5 h) in succession increases the selectivity in the formation of propionic acid. The introduction of platinum instead of palladium into the zeolite increases sharply the degree of hydration of ethylene. Palladium-zeolite catalysts with a modulus $SiO_2/Al_2O_3 \geqslant 10$ are stable under the carbonylation conditions. In the presence of 1.2 wt. % of Pd/HSZ-1† (modulus = 47), propionic, butyric, and valeric acids have been obtained from CO and H_2O as well as C_2H_4, C_3H_6, and C_4H_8 respectively (170 °C, initial pressure 60 atm, 3 h). The degree of conversion then reached 98% and the overall selectivity in the formation of these three acids was 90–98%.[64]

The synthesis of cycloalkanecarboxylic acids from cyclo-olefins, CO, and H_2O is also of practical importance. These acids are used to synthesise medicinal drugs and preparations. Homogeneous palladium catalysts are active in the carbonylation of cyclopentene, cyclohexene, a 60 : 14 : 13 : 13 mixture of 1-methyl-, 3-methyl-, and 4-methyl-cyclopentenes and cyclohexene, as well as 1-methylcyclo-hexene, 4-methyl-cyclohexene, and 1-ethylcyclohexene with formation of the corresponding carboxylic acids.[65] The efficiency of the catalyst decreases in the sequence $Pd_3(CO)_3(PPh_3) > Pd(PPh_3)_2.(OAc)_2 > Pd(PPh_3)_2Cl_2 > Pd(OAc)_2 > PdCl_2$.

The carbonylation of cyclo-olefins in the presence of $Pd(PPh_3)_2Cl_2$ takes place most effectively in acetic acid. Mainly 2-methyl- and 3-methylcyclopentanecarboxylic acids are formed from a mixture of 1-, 3-, and 4-methylcyclopentenes. The formation of 1-methyl-cyclopentane-1-carboxylic acid is prevented by steric hindrance. A temperature of 150 °C and a CO pressure of 50–100 atm are optimal for the carbonylation of cyclo-olefins. Under these conditions, the yield of cyclic carboxylic acid is 80–90%.[65]

Acetals have been synthesised in high yields from olefins, CO, and H_2 in an alcoholic medium in the presence of cobalt carbonyl and added quaternary ammonium compounds. Thus the dimethyl acetal of tridecanal has been obtained with 90% selectivity and 10% conversion from dodec-1-ene and 1 : 1 mixture of CO and H_2 under pressure at 110 °C in methanol containing $Co_2(CO)_8$ and $PhCH_2M^+Me_3MeO^-$.[66]

The esters of branched carboxylic acids have been synthesised by carbonylating β-alkyl-α-olefins:[67] 2-ethylpent-1-ene, hex-1-ene, hept-1-ene, 2-butyloct-1-ene, 2-hexyldec-1-ene, 2-octyldec-1-ene, 2-hexyl-decyleicos-1-ene, or 3-propylhex-1-ene. The reactions were carried out at 180–200 °C and a pressure of CO with added H_2 of 50 to 250 atm in the presence of cobalt catalysts as well as nickel-containing compounds and pyridine bases as promoting agents. In the carbonylation of 2-ethyl-hex-1-ene in the presence of cobalt laurate and γ-picoline (185 °C, 180 atm) by carbon monoxide with added H_2 (3.5 atm) in methanol, the degree of conversion of the olefin was 90% and the selectivity with respect to methyl esters of nonanoic acids was 38%. The contents of the methyl esters of various acids in the mixture were 49.5% of the 4-methyloctanoate, 17% of the 6-methyloctanoate, and 18.5% of the 3-ethylheptanoate. The branched carboxylic acids obtained are widely used in the

†HSZ = high-silica zeolite.

synthesis of alcohols, amines, surfactants, emulsifying agents, plasticising agents, and components of synthesit lubricants.

A mixture of carboxylic acid esters has been obtained under analogous conditions from olefins, CO, and alcohols in the presence of the cobalt carbonyl–pyridine (alkylpyridine) catalytic system.[68] Their hydrogenation in the presence of a copper–chromium catalyst (250–350 atm, 180–220 °C) leads to the formation of alcohols which are intermediates in the synthesis of surfactants. Thus the carbonylation of a mixture of n-undecene, n-dodecene, and n-tridecene in methanol in the presence of cobalt carbonyl and γ-picoline yields a mixture of the methyl esters of C_{12}–C_{14} acids, which are hydrogenated to the corresponding C_{12}–C_{14} alcohols.[68]

The esters of linear saturated carboxylic acids are synthesised by carbonylating α-olefins and the esters of unsaturated carboxylic acids or the acids themselves are synthesised from dienes and acetylenes in the presence of palladium complexes $(R_3P)_2PdXR'$ (where R = alkyl, hydroxyalkyl, cycloalkyl, dialkylamine, thioalkyl, thioaryl, substituted or unsubstituted aryls, and piperidine or pyrrolidine groups and R′ = H, Cl, Br, C_1–C_5 alkyl, C_2–C_4 acyl, or arylalkyls up to C_{12}) and promoting agents—Ti, Tl, Ni, Fe, Cu, Mn, Cr, Pd, Zn, Co, or Sn chlorides. The interaction of hex-1-ene with CO (700 atm, 90 °C) in the presence of $PdCl_2(PPh_3)_2$ and $SnCl_2.2H_2O$ in ethanol results in the formation of C_7 acid esters consisting of 77% of the linear isomer.[69,70] The degree of conversion of hex-1-ene reaches 86%. C_7 acids, including 90% of oenanthic acid, are obtained in aqueous acetone (90 °C, 100 atm) from hex-1-ene in the presence of the $(PPh_3)_2PdCl_2.NH_2(CH_2)_2NH_2$ complex systems.[69,70]

Esters of linear carboxylic acids have been synthesised with a high selectivity under mild conditions in the presence of palladium complexes containing sterically hindered ligands.[71] Thus the esters of isopropanethiol with linear and α-methyl-substituted branched C_7 acids have been obtained in 78.8 and 7.1% yields respectively from hex-1-ene, CO, and alcohol in the presence of $Pd(OAc)_2$ and $(iso\text{-}Pr)_3P$ in solution in the $THF-(CH_3)_3CSH$ mixture (100 °C, 50 atm).

The isomeric composition of the esters formed in the methoxycarbonylation of hex-1-ene in the presence of $Co_2(CO)_8$ depends greatly on the nature of the medium, which also influences the rates of isomerisation and carbonylation of the olefin. For a methanol : hex-1-ene molar ratio of 10, the rates of isomerisation and carbonylation of hex-1-ene in pyridine are comparable (175–190 °C, 200–300 atm). In toluene, the rate of isomerisation of olefin is higher than the rate of its carbonylation, as a result of which esters of branched acids predominate in the products of the synthesis. The selectivity in the formation of the oenanthic acid ester increases with decrease in temperature and with increase in the CO pressure.[72]

Carboxylic acid esters are obtained[73,74] from α-olefins up to C_{12}–C_{13} in the presence of catalytic systems based on cobalt: $HCo(CO)_4$, $Co_2(CO)_8$, $Co_4(CO)_{12}$, or $Co(CO)_3A_3$, where A = Bu_3P, $(C_{10}H_{21})_3P$, $(PhCH_2)_3P$, pyridine, picoline, or an alkylpyridine. Phosphine, phosphine oxides, and phosphites having the general formula $RR'PHO$, RR^1POR^2, and $RR^1POC(OH)R^2R^3$, where R, R′, R^1, R^2, and R^3 are C_1–C_{20} alkyls, are also used as ligands. Thus a mixture of C_{13} aldehydes and carboxylic acids in proportions of 10 : 1 has been obtained from dec-1-ene in the presence of $Co_2(CO)_8$ and $(C_8H_{17})_2POH$ (150 °C, 70 atm, H_2/CO = 1) for an overall degree of conversion of the olefin of 97%.[74]

Olefins can be carbonylated in a tubular reactor at 180 °C and a pressure of 170 atm in the presence of cobalt naphthenate.[75] The olefin is fully converted into carboxylic acid esters. When a mixture of CO with 5–10% of H_2 was used, the methyl esters of C_{13} acids were obtained in 97% yield from dodec-1-ene. They included 74% of the linear acid ester and the degree of conversion of the olefin was 63%.

Nickel complexes with tertiary amines, promoted by iodine compounds, are also effective catalysts of the carbonylation of α-olefins.[76] Thus the carbonylation of hexadec-1-ene in the presence of the $NiI_2-Py-HI$ system in an aqueous medium (88 atm CO, 200 °C) results in the formation of a mixture of C_{17} acids (yield 94%) containing 31.0% of acids with a linear structure. The remaining acids (47.0, 13.0, and 9.0%) contain methyl, ethyl, and propyl groups in the α-position, relative to the carboxy-group. Mixtures of saturated and unsaturated carboxylic acids, which can be used as surfactants after hydrogenation, have been obtained from cracking olefins.

Carboxylic acid esters are also synthesised by carbonylating olefins in the presence of mixtures of nickel and molybdenum or nickel and tungsten compounds, a halogen promoting agent, and a phosphorus- or nitrogen-containing base.[77] Treatment of ethylene with carbon monoxide in a medium consisting of a mixture of methanol and ethyl propionate in the presence of the $NiI_2-Mo(CO)_6-EtI$ system and PPh_3 (150–200 °C, 10–100 atm CO) affords methyl propionate in a high yield.

The selective synthesis of carboxylic acids or their esters has been achieved by carbonylating olefins in the presence of copper compounds with palladium, rhodium, ruthenium, iridium, or cobalt compounds in protic hydrogen halide acids.[78] The interaction of dec-1-ene with CO and methanol in the presence of $PdCl_2$, $CuCl_2$, and HCl under mild conditions results in the selective formation of methyl undecanoate.

Olefins are carbonylated in alcohols or phenols also under mild conditions (70–120 °C, 1–40 atm CO) in the presence of palladium complexes, phosphines, and peroxide compounds (H_2O_2, peracids). The presence of peroxides facilitates the coordination of the substrates to the palladium complexes and also promotes the oxidation of phosphines.[79]

The selectivity of the propene carbonylation process and the activity of Ru–Fe carbonyl clusters increase after the addition of $CuCl_2$ to the catalytic system. The main reaction products are methyl butyrate and butyric acid.[80]

Not only acids and their esters but also ketones can be obtained from olefins and CO. Diethyl ketone was formed from a mixture of C_2H_4, CO, and H_2O in the presence of the catalyst formed as a result of the rapid thermal decomposition of $Co_2(CO)_8$ on a carbon carrier at 150 °C and atmospheric pressure.[81]

Ketones have also been synthesised by carbonylating higher olefins (C_3–C_{20}) in a mixture with ethylene in the presence of H_2 on rhodium or cobalt catalysts at 150–250 °C and a pressure of 150 to 350 atm in various solvents, especially butanol.[82] The molar ratio of the catalyst and the mixture of ethylene with a higher olefin must be between 100 and 10 000 and that of the alcohol and the olefin must be between 0.3 and 2.0. Thus the interaction of ethylene and propene with CO in butanol at a pressure of 120 atm leads to the formation of a mixture of the ketones $EtCOCHMe_2$, PrCOEt, $(MeCH)_2CO$, $PrCOCHMe_2$, and Pr_2CO.

Ketones are also obtained by the reaction of olefins with CO and H_2O in the presence of cobalt carbonyl compounds and phosphines. For example, the reaction of C_3H_6 with CO and H_2O in the presence of $Co_2(CO)_8$ and $Ph_2PCH_2PPh_2$ at 165 °C and a pressure of 100 atm led to the formation of a mixture of the ketones Pr_2CO, $(Me_2CH)_2CO$, n-$PrCOCHMe_2$, and $PrCHO + Me_2CHCHO$.[83]

Homogeneous palladium catalysts deposited on polymers are active in the carbonylation of α-olefins. Thus the catalyst in the presence of which ethyl hexanoate was formed from pent-1-ene, styrene, and CO (120 °C, 28 atm CO) with 94% selectivity for an olefin conversion of 26.3% has been obtained from a copolymer of styrene with 1% of divinylbenzene (after bromination and treatment with $LiPPh_2$ in THF) by its interaction with $(PhCN)_2PdCl_2$.[84]

Palladium–anion exchanger catalysts, containing 0.4–0.75% of palladium on the Soviet produced anion-exchange resins AN-221, AN-251, and AN-511, possess a high activity, selectivity, and stability in the carbonylation of hex-1-ene.[85,86] Such catalysts can be used repeatedly (up to 10 times), retaining 0.35–0.4% of Pd under these conditions. Catalysts with a higher palladium content are less stable. Under optimum conditions (170 °C, 100 atm CO), C_7 acids are formed in an overall yield of 75–95%, the selectivity in the formation of oenanthic acid amounting to 50–60%.[86]

When $SnCl_2.2H_2O$ is added to palladium–anion exchanger catalysts (0.4% Pd/AN-221, 0.75% Pd/AN-511, and 0.4% Pd/AN-251) (atomic ratio Sn/Pd = 5–30), the selectivity in the formation of oenanthic acid increases to 94.5% with a simultaneous decrease the degree of conversion of the olefin to 30–35%.[86]

It has been suggested that the bimetallic complexes of $SnCl_2$ with chromium, molybdenum, or tungsten carbonyls can be used as catalysts of the carbonylation of olefins with formation of carboxylic acid esters (molar ratio 1–1.5 : 1, temperature 150–200 °C, CO pressure 250–300 atm).[87] These catalysts are less toxic than the nickel catalysts.

The carbonylation of isobutene or isobutyl alcohol in the presence of the $Rh(PR_3)_2X_2$ system, where X = Cl, Br, I, or another univalent anion and R = alkyl, aryl, or cycloalkyl, results in the selective formation of isovaleric acid. Such a reaction occurs, for example, in the interaction of iso-C_4H_8 with CO and H_2O at 18 to 20 °C and atmospheric pressure in the presence of $RhCl_2.[P(C_6H_{11})_3]_2$.[88] Palladium complexes with aminophosphine and phosphine ligands have been proposed as catalysts for the synthesis of isobutyric acid from propene, CO, and H_2O.[89] The process takes place selectively at 75–150 °C and a pressure of 20–350 atm. Isobutyric acid is formed in 79.5% yield from C_3H_6, CO, and H_2O in the presence of $Pd(OAc)_2$ and $(Me_2N)_3P$ in acetic acid and 38% HCl (110 °C, 315 atm).

The carbonylation of propene with formation of isobutyric acid and small amounts of n-butyric acid as well as a certain amount of $(CH_3)_2CHCl$ has been achieved on the $Pd(OAc)_2-Ph_3As-HCl$ catalyst at 75–150 °C and a CO pressure of 20–50 atm.[90]

The addition of n-Pr_3N to $Co_4(CO)_{12}$ increases the activity of the system in the hydrosilylation of α-olefins by a factor of 70 compared with the activity of $Co_2(CO)_8$.[91]

Isobutyric acid esters are obtained by carbonylating C_3H_6 in the presence of $Pd(PPh_3)_4$, PPh_3, and CF_3SO_3H (105 °C, 138 atm) in alcohol.[92]

Carboxylic acids and their esters are formed from C_{10}–C_{20} olefins or their mixtures in the presence of the $Co_2(CO)_8$–pyridine (or alkylpyridine) catalyst in C_2–C_{20} carboxylic acid at a pressure of 200 atm and a temperature of 150–200 °C.[93,94] The carbonylation is carried out in two stages. Initially the reaction is performed at 220 °C and the yield is then about 90%. The second stage, in which the yield of acids from the olefins is 10–12%, is performed at 180–190 °C. The fraction of linear acids formed in the first and second stages is 70–75% and 40–70% respectively. Water is added continuously to the reaction zone in order to increase the selectivity in the formation of linear carboxylic acids. In the carbonylation of a mixture of olefins, the contents of α-olefins in the first and second stages were 90 and 10.8% respectively. The carboxylic acids obtained are used in the manufacture of plastics, lubricants, and surfactants.

The carbonylation of π-olefins has been investigated[95–98] in the presence of homogeneous palladium catalysts at a low pressure of CO or the synthesis gas. The carbonylation of hept-1-ene on the $PdCl_2(PPh_3)_2-SnCl_2$ catalytic system in dioxan (185 °C, 20 atm, CO/H_2 = 1) takes place quantitatively with a selectivity of 85% in the formation of octanoic acid.[95]

In the carbonylation of non-1-ene in the presence of the $PdCl_2.(PPh_3)_2-PPh_3$ system in aqueous acetone (volume ratio acetone : water = 1 : 27, molar ratio olefin : Pd = 117, 13 atm, 90 °C, 6 h), the selectivity in the formation of capric acid increases to 88% with increase in the PPh_3/Pd ratio to 15. In the absence of PPh_3, the selectivity remains unchanged as the pressure is raised from 3 to 24 atm. The carbonylation products are a mixture of capric and α-methylpelargonic acid as well as a small amount (~4%) of α-ethylcaprylic acid.

The selectivity in the formation of linear acid increases when the CO pressure is reduced to 3 atm for the molar ratio PPh_3/Pd = 4.5.[96] With increase in the water concentration in acetone, the overall yield of carboxylic acid diminishes and the carbonylation process ceases with the volume ratio acetone : water = 3.

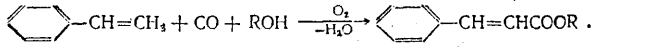
The influence of CO pressure on the carbonylation of non-1-ene is different in solution in the acetone–methanol mixture in the presence of the same $PdCl_2(PPh_3)_2$ catalytic system. With increase in the CO pressure from 7 to 24 atm and also with increase in the PPh_3/Pd ratio, the yield of methyl caprate also rises.[97]

The selectivity in the formation of octanoic acid from hept-1-ene in the presence of $PdCl_2(PPh_3).PR_3$ (where R = aryl or alkyl) in dioxan increases with increasing basicity of the phosphine ligand.[98]

The methyl esters of C_{12}–C_{17} carboxylic acids are obtained by carbonylating C_{11}–C_{16} olefins in methanol in the presence of the $Co_2(CO)_8$–pyridine–isoquinoline catalytic system at 140 °C and a CO pressure of 250–300 atm.[99] Thus methyl dodecanoate has been obtained with a selectivity of 93% from undec-1-ene, CO, and CH_3OH (140 °C, 300 atm). Cobalt carbonyl compounds are removed from the reaction products by oxidising them with oxygen or air in the liquid phase at a pressure of 3 atm and a temperature of 50 °C.

Higher C_{10}–C_{20} carboxylic acids are obtained by carbonylating C_9–C_{19} olefins under the same conditions using the catalysts described by Katsnel'son and Bel'nik.[99] The processes are carried out in a solvent with vigorous stirring of the reaction mixture.[100]

The synthesis of cinnamic acid esters by the oxidative carbonylation of styrene has been described:[101–106]



The catalysts used are 2% Pd/C[101,102] as well as Pd, Pt, Rh, Ir, Ru, and Os compounds or their mixtures with Cu^{2+} and Fe^{2+}.[103,104] Tertiary amines or bases—alkali or alkaline earth metal salts of organic or inorganic acids—are also used as additives. Aluminium powder[105] and aliphatic polyamines—ethylenediamine, piperazine, etc.[106]—can be added to compounds of the platinum group metals.

Cinnamic acid esters, which are widely used in the manufacture of medicinal drugs and perfumes, plant protecting agents, and light-sensitive resins, are obtained from styrene at CO and O_2 partial pressures ⩽18 atm and ⩽7 atm respectively in alcohol at 120 to 170 °C.[105] The yield of the target products is between 26 and

82.4% for a degree of conversion of styrene from 35 to 75.8%. La, Nd, Ce, Eu, V, and Pr oxides and acetates are effective process cocatalysts. The Pd : Cu (or Pd : Fe) atomic ratios range from 1 : 10 to 1 : 30, while the Cu : Ln (or Fe : Mn) atomic ratios are between 1 : 0.1 and 1 : 50.[105]

The carbonylation of styrene in the presence of the complex $PdCl_2.(PPh_3)_2$ in dioxan results in the formation of α-phenylpropionic acid with a selectivity of 99% for a degree of conversion of the olefin amounting to 93%. The replacement of carbon monoxide by the synthesis gas does not alter the overall yield of carboxylic acids but it does induce an increase in the process selectivity in the direction of the formation of β-phenylpropionic acid.[107]

An improved method has been proposed for the carbonylation of α-olefins, which makes it possible to obtain carboxylic acids or their ester with an increased content of linear products at 80–120 °C.[108] For this purpose, one uses palladium–sulphonic acid catalysts with phosphines, containing added perfluorosulphonic acids (CF_3SO_3H, $C_2H_5SO_3H$, $C_4H_9SO_3H$, and $C_8H_{17}SO_3H$) and polymeric perfluorosulphonic acids having molecular weights in excess of 5000, as promoting agents. Thus the carbonylation of propene in methanol in the presence of $Pd(PPh_3)_4$, PPh_3, and the additive CF_3SO_3H (molar ratio Pd/CF_3SO_3H = 1/2, 105°, 138 atm, CO, 2 h) results in the formation of methyl esters of butyric acids in 53.4% yield. The selectivity in the formation of the n-butyric acid ester is 69.2%. An increase in the amount of the CF_3SO_3H additive increases the degree of conversion of propene into butyric acid esters to 92.5%.

α-Olefins or diolefins are hydrocarboxylated under mild conditions in the presence of $PdCl_2-CuCl_2$ and O_2 in alcohol to which gaseous HCl has been added.[109] Mainly esters of branched carboxylic acids are formed. Olefins with an inner double bond afford carboxylic acid esters branched at the carbon atom which is closer to the end of the carbon chain. Thus $CH_3O_2CCH(CH_3)(CH_2)_4CH(CH_3)CO_2CH_3$ is formed quantitatively from octa-1,7-diene. Cyclic olefins also readily enter into the carbonylation reaction .[109]

Catalytic systems based on $Co_2(CO)_8$ and alkylpyridines (with the exception of pyridines having an *ortho*-substituent) capable of carbonylating selectively olefins with an inner double bond (for example, dodecenes) to form linear carboxylic acids have been devised.[110,111] Under the reaction conditions (180 °C, ratio of promoting agent and catalyst 10 : 1, 180 atm CO), the initial olefins with an inner double bond isomerise to α-olefins, which are in fact carbonylated. The initial α-olefins are obtained by the dehydrochlorination of the chlorinated paraffins. The process can be carried out in the presence of paraffins (up to 75%) and carbon monoxide containing up to 10% of H_2. The cobalt catalyst is normally employed as the acetate, naphthenate, 2-ethylhexanoate, or stearate, which are converted into cobalt carbonyl, while the promoting agents are β- or γ-picolines, 3,4- or 3,5-lutidines, or ethylpyridines in an amount of 3–25 moles per mole of the cobalt compound. Thus the carbonylation of a mixture of dodecenes in the presence of cobalt naphthenate and γ-picoline (molar ratio 1 : 10) in methanol (180 °C, 180 atm CO, 2% H_2 in CO) leads to the formation of a mixture of methyl esters of tridecanoic acids in 60% yield and a selectivity with respect to the linear isomer of 74%. Cobalt carbonyl is removed from the reaction products by treatment with air at 40–60 °C, cobalt oxides being isolated and returned to the cycle. The process is carried out under continuous conditions.[111]

The selective hydromethoxycarbonylation of higher olefins takes place with a high molar ratio of alkylpyridines and the cobalt catalyst (10–100). Otherwise there is a sharp increase in the yield of branched carboxylic acid esters. The productivity of the catalytic systems described above is 300–500 g of the ester per litre of the reaction solution per hour. Calculations have demonstrated the economic efficiency of the given method of synthesis of esters and acids having a linear structure.[112]

In order to reduce the yield of high-boiling products, it has been suggested either to remove water from the initial reactants by azeotropic distillation[113] or to replace the large amount of alkylpyridines by high-boiling residues isolated after distilling off the reaction products.[114] It has been suggested that the selective methoxycarbonylation of α-olefins and alkylenenitriles be carried out in the presence of cobalt catalysts with added ruthenium compounds and tertiary nitrogen-containing bases.[115] Hex-1-ene is selectively converted into methyl oenanthate in methanol in the presence of $Co_2(CO)_8$, isoquinoline, and $Ru_3(CO)_{12}$.

Dialkyl ketones can be obtained from ethylene (or propene), CO, and H_2 in the presence of the $Pd(OAc)_2-PPh_3$ catalytic system under mild conditions (30–70 °C, 1 atm) in aqueous trifluoroacetic acid.[116] Butyric acid, butyraldehyde, paraffins, and CO_2 are formed in small amounts. The rate of reaction and the isomeric composition of dialkyl ketones depend on the concentration of water in the reaction mixture. For a water content less than 5 vol. %, a mixture of 2,4-dimethyl-3-pentanone, 2-methyl-3-hexanone, and 4-heptanone is formed in proportions of 1 : 2 : 1. At a water concentration of 25–30 vol. %, the above ratios change to 1 : 5 : 1. It has been suggested that the ketones are synthesised via the intermediate formation of the Pd–H hydride complexes, formed as a result of the heterolytic capture of hydrogen by the palladium complex.

A method has been proposed for the carbonylation of olefinic compounds under mild conditions in the presence of a cobalt catalyst and disubstituted phosphines RR′ – PH as promoting agents.[117] The catalytic system is separated from the reaction products (acids or esters) by distilling off the latter.

Pent-3-enoic acid esters, which are intermediates in the synthesis of adipic acid diesters, are synthesised from butadiene, CO, and alcohols in the presence of $Co_2(CO)_8$ promoted by pyridine, quinoline, isoquinoline, both unsubstituted and substituted C_1-C_6 alkyls or alkenyls, aryls, and C_7-C_{10} arylalkyls or alkylaryls.[118] The process is carried out in the presence of the polymerisation inhibitors Ph_2NH, (Ph)(Me)NH, *NN′*-tetraethyl-*p*-phenylenediamine, *NN′*-di-β-naphthyl-*p*-phenylenediamine, benzoquinone, anthraquinone, or chloramine. Thus methyl pent-3-enoate is formed with a selectivity of 98.5% from butadiene, CO, and methanol in the presence of $Co_2(CO)_8$, pyridine, and *NN′*-di-β-naphthyl-*p*-phenylenediamine (120 °C, 300 atm CO, 1.5 h). The degree of conversion of the diolefin reaches 99.5%.

In the presence of the $PdCl_2$ catalyst, the carbonylation of a disubstituted but-2-ene proceeds with formation of the diester of an unsaturated C_6 dicarboxylic acid:

$$RCH_2CH{=}CHCH_2R + CO \rightarrow RCOCH_2CH{=}CHCH_2COR\ ;$$
$$R = OAc,\ OMe,\ OH \text{ or } Cl.$$

The selectivity of the reaction increases in the presence of polar and non-basic solvents.[119]

Dicarboxylic acid esters are obtained by treating unsaturated C_5-C_{15} carboxylic acids with carbon monoxide in the presence of C_1-C_3 alcohols using as the catalyst cobalt carbonyl with added water (up to 50% of the alcohol) and alkanes to separate the reaction products from the catalyst. Thus the interaction of the methyl ester of tricyclo[5.2.1.$0^{2,6}$]dec-3(or 4)-ene-8(or 9)-carboxylic

acid with CO (100 atm, 160 °C) in the presence of $Co_2(CO)_8$ in aqueous methanol with added cyclohexane results in the formation of dimethyl ester of tricyclodecanedicarboxylic acid in 79.3% yield.[120]

Together with olefins, other unsaturated compounds enter into the carbonylation reaction. A series of processes involving the carbonylation of unsaturated alcohols with formation of lactones[121] in the presence of $PdCl_2$, CO, O_2, and concentrated HCl in dry THF at room temperature and atmospheric pressure have been described. For example, but-3-enol is converted in 60% yield into α-methyl-γ-butyrolactone, while 2-methylbut-3-en-1-ol is converted into a 2:1 mixture of *trans*- and *cis*-2,3-dimethyl-γ-lactones. Pent-4-en-1-ol is converted into α-methyl-δ-valerolactone in 75% yield. In the presence of $Co_2(CO)_8$, the corresponding lactones are formed from saturated alcohols in yields ranging from 3 to 51%. The process takes place under fairly severe conditions—at 240 °C and a CO pressure of 900 atm.

Succinic acid diesters have been obtained by carbonylating acrylic acid esters in the presence of cobalt-containing catalysts and pyridines. Thus the interaction of methyl acrylate with CO and methanol in the presence of $Co_2(CO)_8$–Py in toluene (130 °C, 120–130 atm CO) affords dimethyl succinate in 94.2% yield. Dibutyl and dicyclohexyl succinates are obtained analogously in 91.2 and 90.0% yields respectively.[122]

In the methoxycarbonylation of 3-(β-cyanoethoxy)propene (110–120 °C, 200 atm CO) in the presence of $Co_2(CO)_8$, the addition of pyridine and CH_3ONa does not affect the rate of reaction or lower it.[123] The selectivity in the formation of methyl 4-(β-cyanoethoxy)butyrate then increases from 52 to 60–70%, while the selectivity in the formation of methyl 3-(β-cyanoethoxy)-isobutyrate rises from 1.7 to 3.3%. The addition of $PdCl_2$ to $Co_2(CO)_8$ in the absence of pyridine increases the rate of reaction by a factor of 10, while in its presence the increase is by a factor of 15–17. The addition of $PdCl_2$ has a similar effect on the carbonylation of propene in the presence of pyridine (140–160 °C, 200 atm CO). The introduction of up to 7.5% of H_2 into carbon monoxide acts effectively on the carbonylation process. The addition of $PdCl_2$ to $Co_2(CO)_8$ also influences the carbonylation of acetonitrile [140 °C, 200 atm CO, $Co_2(CO)_8$–pyridine mixture in proportions of 1:2]: an increase in the degree of conversion of acetonitrile from 28 to 80% is observed with the simultaneous rise in the yields of methyl γ- β-, and α-cyanobutyrates from 18.0, 3.4, and 4.9% to 52.0, 8.8, and 17.0% respectively.[123]

The carbonylation of CN-containing olefinic hydrocarbons with formation of the esters of the corresponding carboxylic acids has been described.[124–128] The esters are used for the synthesis of aminoacids, which have found extensive application in industry, agriculture, medicine, and biology. Complexes based on cobalt, palladium, and ruthenium are effective catalysts. Thus the carbonylation of acetonitrile in the presence of cobalt or ruthenium carbonyls and polyamines [poly(vinylpyrrolidinone)] as ligands leads to the formation of methyl α-cyanopropionate in 55.4% yield.[124]

The cobalt catalysts are promoted by γ-picoline oxide[125] and also by the oxides of various substituted pyridines.[126] The substituents can be not only alkyl or hydroxyalkyl groups but also the $(CH_2)_nCN$, $(CH_2)_mOR$, $(CH_2)_fCOOH$, or $(CH_2)_pCOOR$ groups.[125] Not only pyridine oxides but also phosphine oxides, sulphide oxides (sulphoxides?), or sulphones are effective ligands.[126] Unsaturated compounds are carbonylated in nitriles or dinitriles. The carbonylation of acetonitrile (97.5 °C, 70 atm, CO/H_2 = 1) in the presence of $Co_2(CO)_8$ and γ-picoline oxide in adipodinitrile with added CH_3OH resulted in a degree of conversion of 84.4%, the mixture of products consisting of 97.5% of methyl γ-cyanopropionate.[127,128] The catalytic system is extracted from the reaction mixture with a fourfold excess of C_5–C_8 alkanes and is returned to the reaction cycle.

A method has been proposed for the selective synthesis of isobutyric acid by carbonylating propene in the presence of a catalytic system containing palladium(II) compounds as well as arsenic compounds in the inorganic aicds HBr, HCl, H_2SO_4, HI, H_3PO_4, or HBF_4.[129] When propene is carbonylated in an autoclave with glass-lined walls (105 °C, 60 atm CO, 1.5 h) in the presence of $Pd(OAc)_2$, $AsPh_3$, and HCl (molar ratios 1:40:90) in aqueous isobutyric acid, isobutyric acid is formed with a selectivity of 74.9% for a 100% conversion of the olefin.

δ-Cyanovaleric acid esters are obtained in 75% yield by carbonylating 3-cyanobut-1-ene in alcohol and acetone (160 °C, 200 atm CO) in the presence of the $Co_2(CO)_8$–pyridine catalytic system.[130]

The carbonylation of acetonitrile in the presence of $Co_2(CO)_8$ with formation of methyl α-cyano-α-methylacetate and β-cyanopropionate (120–140 °C, 260–300 atm, CO/H_2 = 8–10) has been described.[131] Their hydrolysis affords respectively methylmalonic and succinic acids. The cyanoethylation of methyl α-cyano-α-methylacetate gives rise to $NCC(COOCH_3)(CH_3)CH_2CH_2CN$, which is hydrolysed to α-methylglutaric acid. The hydrogenation of the β-cyanopropionic acid ester results in the formation of α-pyrrolidinone in 95–98% yield. The reactions proceed in accordance with the following schemes:

$$NCCH{=}CH_2 + CO + CH_3OH \xrightarrow{Co_2(CO)_8,\ H_2} \begin{cases} \longrightarrow NCCH(CH_3)COOCH_3 \xrightarrow{H_2O} NH_3 + \\ \quad + HOOCCH(CH_3)COOH + CH_3OH + CO_2, \\ \quad \alpha\text{-methylmalonic acid} \\ \longrightarrow NCCH_2CH_2COOCH_3 \xrightarrow{H_2O} NH_3 + \\ \quad + HOOCCH_2CH_2COOH + CH_3OH; \\ \quad \text{succinic acid} \end{cases}$$

$$NCCH(CH_3)COOCH_3 + NCCH{=}CH_2 \rightarrow NCC(COOCH_3)(CH_3)CH_2CH_2CN \xrightarrow{H_2O} \rightarrow 2NH_3 + 2CO_2 + HOOCCH(CH_3)CH_2CH_2COOH;$$

α-methylglutaric acid

$$NCCH_2CH_2COOCH_3 \xrightarrow[150-300^\circ C\ 2-21\ atm]{H_2,\ NH_3} \underset{\text{α-pyrrolidinone}}{\overset{H_2C-CH_2}{\underset{CO}{H_2C\quad NH}}}$$

Methyl 5-cyanovalerate has been obtained with a selectivity of 92% for a conversion of the initial compound of 92% by carbonylating *cis*-pent-2-enylnitrile in the presence of $Co_2(CO)_8$ (180 °C, 310 atm) in a mixture of tetramethylene sulphone and methanol.[132]

α-Acyloxypropionic acids, whose hydrolysis affords lactic acid, are formed from the vinyl esters of carboxylic acids in the presence of $Pd(PR_3)_4$ in an excess of PR_3 (R is an aromatic group).[133] A characteristic feature of the process is a rigorously specified amount of water necessary for the formation of the product, its concentration in the mixture amounting to about 1.0 wt.%. The carbonylation of vinyl acetate (150 °C, 49 atm CO, H_2O concentration 0.9%) in the presence of $[(CH_2{=}CHCH_2)PdCl]_2$ and PPh_3 in butyric acid results in the formation of α-acetoxypropionic acid with a selectivity of 67% for 96% conversion of vinyl acetate.[133]

The carbonylation of alkenyl alkyl carbonates in the presence of palladium complexes leads to the formation of the alkyl esters of βγ-unsaturated carboxylic acids.[134] The reaction takes place in accordance with the equation

$$R^1R^2C{=}CR^3CR^4R^5OC(O)OR \xrightarrow[-CO_2]{CO} R^1R^2C{=}CR^3CR^4R^5COOR\ .$$

The catalysts employed are $Pd(PPh_3)_2(OAc)_2$ and $Pd(PPh_3)_2Cl_2$ in an inert solvent (alcohol, THF) or in its absence. The interaction of methyl 2-propenyl carbonate with carbon monoxide (100 °C, 70 atm CO) in the presence of $Pd(OAc)_2$ and PPh_3 affords a quantitative yield of methyl but-3-enoate.[134]

An analogous procedure is used to obtain methyl pent-3-enoate from but-2-enyl methyl carbonate, ethyl hept-3-enoate from ethyl hex-2-enyl carbonate and methyl 4,8-dimethylnona-3,7-dienoate from butadiene.[124]

Effective methods have been proposed for the carbonylation and regeneration of cobalt–pyridine catalysts used for the synthesis of polyol esters of carboxylic acids from C_3–C_{30} α-olefins (180–185 °C, 200 atm CO).[135–137]

The $Co_2(CO)_8$–isoquinoline complex in an aromatic hydrocarbon and alcohol is used successfully for the synthesis of methyl pent-3-enoate from butadiene.[138,139] Thus methyl pent-3-enoate has been obtained in a high yield from butadiene and carbon monoxide (containing 3% of H_2) in a mixture of benzene, isoquinoline, and methanol (123 °C, 300 atm CO) in the presence of $Co_2(CO)_8$. The catalyst is regenerated by the stepwise distillation of benzene, isoquinoline, methanol, and methyl pent-3-enoate from the reaction mixture. After treating the residue with aqueous solutions of inorganic acids (HCl, HNO_3, H_2SO_4—5% excess relative to cobalt), cobalt carbonate is precipitated with an aqueous Na_2CO_3 solution.

A method has been proposed for the synthesis of dicarboxylic acid esters, including adipic acid ester, by carbonylating unsaturated acid esters[140,141] under conditions analogous to those described in patents.[138,139] The carbonylation of methyl but-2-enoate in methanol and isoquinoline in the presence of $Co_2(CO)_8$ (160 °C, 200 atm, CO containing 0.7% of H_2) gives rise to a 77.9% yield of unsaturated acid esters consisting of 77% of $(CH_2)_3(COOMe)_2$, 18% of the $MeOCOCH_2CH(Me)COOMe$–$MeOCOCH(Et)COOMe$ mixture and 5% of $C_7H_{17}COOMe$. The esters of other dicarboxylic acids, mainly with a linear structure, are obtained similarly in a high yield.[141] Dimethyl adipate has been obtained in 81.8% yield from methyl pent-3-enoate, CO, and methanol, the content of the pentanoic acid ester in mixture not exceeding 3.8%.[142]

The carbonylation of methyl pent-3-enoate in aromatic hydrocarbons under conditions such that the ratio of the tertiary nitrogen-containing base and the cobalt compound is between 2 and 25 leads to the formation of dimethyl adipate in 96.3% yield.[143] Dimethyl adipate has been synthesised in 70.5% yield from methyl pent-3-enoate by the method involving carbonylation in the presence of CoS and tertiary amines (185 °C, 200 atm CO). CoS is then readily isolated and can be reused.[144]

A method has been proposed for the synthesis of succinic acid esters from C_2H_4, CO, and alcohol in the presence of platinum group metal complexes with added iron, copper, and cobalt salts and aminoacids such as glycine, alanine, valine, phenylalanine, etc.[145] For example, dimethyl succinate is formed from a 1 : 1 mixture of C_2H_4 and CO at an overall pressure of 80 atm ($PdCl_2$, glycine, 100 °C) in methanol. Double carbonylation of ethylene takes place during the reaction:[146]

$$CH_2{=}CH_2 + 2CO + 2CH_3OH \rightarrow \begin{matrix} CH_2COOCH_3 \\ | \\ CH_2COOCH_3 \end{matrix}.$$

(b) Carbonylation of olefins in the presence of acid catalysts. The use of organic or inorganic acids or acid complexes as catalysts makes it possible to obtain products branched in the α-position relative to the functional group by carbonylating unsaturated compounds (olefins, dienes).[1,3] The carbonylation is usually carried out at temperatures in the range 20–125 °C and CO pressures up to 200 atm. The catalysts are H_2SO_4, HF, H_3PO_4, $AlCl_3$, SbF_5, HSO_2Cl, FSO_2Cl, BF_3, $BF_3.n\,ROH$, $BF_3.n\,H_2O$, $BF_3.n\,RCOOH$ (n = 1 or 2), etc.[147–153]

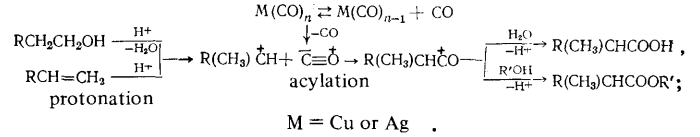
C_{20}–C_{24} α-olefins or their mixtures are carbonylated in concentrated H_2SO_4 at 10–35 °C and a CO pressure of 35–140 atm.[147] Before being supplied to the reactor, the olefins are fused, but the temperature in the reactor is maintained below the melting point of the olefin, which makes it possible to increase the contact time between the olefin and the catalyst and to raise the process selectivity. Thus, when eicos-1-ene heated to 45 °C under a CO pressure of 94 atm is added gradually to vigorously stirred concentrated H_2SO_4, a C_{21} acid is formed in 82.1% yield.

For the molar ratios of H_2SO_4, ethyl formate, and 1-hexanol of 10 : 4 : 1, the overall yields of the ethyl esters and acids in the synthesis products are influenced by the temperature, reactant ratio, and the H_2SO_4 concentration. Mainly ethyl esters of 1-methylcyclopentanecarboxylic and cyclohexanecarboxylic acids are formed from cyclohexanol.[150] The overall yield of the esters and acids obtained in proportions of 2–3 : 1 was 65–75%.

The carbonylation of branched and linear olefins (2-methylbut-2-ene, 2-methyl-pent-2-ene, mixtures of di- and tri-isobutenes, and also hex-1-ene and hept-1-ene) in the presence of BF_3–H_2O and ethyl formate at atmospheric pressure and a temperature of 20–90 °C results in the formation of the ethyl esters of the corresponding acids and directly the acids themselves in an overall yield ranging from 50 to 90%. At the optimum carbonylation temperature of 50 °C, the maximum yields of the ethyl esters of the acids and of the acids themselves obtained from hex-1-ene and hept-1-ene were 51 and 50% respectively.[151]

The corresponding carboxylic acids have been obtained in yields of 45–85% by the carbonylation of C_6–C_{12} iso- and n-olefins with carbon monoxide at 30 °C and atmospheric pressure in the presence of the 97% H_2SO_4 + Ag_2O (or Cu_2O) and $(BF_3.H_2O)(BF_3.H_3PO_4)$ + Cu_2O catalytic systems.[152]

The mechanism of the carbonylation of olefins and alcohols in the presence of the above catalysts has been investigated.[153] The activity of the catalysts increases with increase in their Hammett acidity (H_0): $BF_3.H_2O$ (−11.40) > H_2SO_4 (−10.65) > $(BF_3.H_2O)$. $(BF_3.H_3PO_4)$ (−10.00) > H_3PO_4 (−5.18). The reactivity of olefins with the normal structure is lower than that of branched olefins and the selectivity in the formation of carboxylic acids or their esters is higher for linear α-olefins. The reactivity of alcohols increases on passing from primary to secondary and then to tertiary alcohols. The yields of carboxylic acids are maximum at the optimum rates of the stages involving the protonation of the substrates and the addition of CO to the carbonium ions formed (the acylation stage). This conclusion is valid also when the carbonylation of olefins and alcohols is carried out in the presence of the H_2SO_4, $BF_3.H_2O$, and $(BF_3.H_2O)(BF_3.H_3PO_4)$ catalysts with added Cu_2O and Ag_2O. The carbonylation proceeds in accordance with the scheme:



The protonation of the substrates is ensured by the presence of the acid component and CO is activated by the intermediate formation of Cu(I) or Ag(I) carbonyls during the process. When

ethyl formate is used as the carbonylating agent, carbon monoxide is activated in the stage involving the decomposition of ethyl formate with formation of CO *in situ*.

The carbonylation of propene in the presence of $BF_3.CH_3OH$ (50 °C, 60 atm) results in the formation of mainly methyl isobutyrate with a small amount of methyl dimethylvalerate and methyl neodecanoate.[154] The complex $BF_3.CH_3OH$ with added Cu_2O or Ag_2O is an effective catalyst of this process. When diisobutene is carbonylated by carbon monoxide under pressure, the esters of C_6–C_{11} acids are formed in high yields.[155] Methyl isobutyrate is formed analogously from C_3H_6, CO, and H_2O in the presence of $BF_3.(CH_3)_2CHCOOCH_3$, $BF_3.CH_3OH$, and $BF_3.H_2O$.[156]

One of the most important target products of the carbonylation of olefins in the presence of acid catalysts is isobutyric acid or its esters—the intermediates in the synthesis of acrylic acid or methyl methacrylate.

When a mixture of methanol, methyl isobutyrate, and Cu_2O is used in molar proportions of 31.2 : 97.5 : 1 in the presence of BF_3 (50 °C, 49 atm CO) with subsequent supply of propene into the reactor, methyl isobutyrate is obtained in 99% yield.[157]

Propene is carbonylated in the presence of a 15-fold excess of HF (30 °C, 340 atm CO, 30 min), after which HF is distilled off and directed to the carbonylation stage.[158,159] The isobutyric acid fluoride obtained is hydrolysed (with an acid fluoride : water molar ratio of 1 : 0.2–0.4) at −40 °C in the presence of NaF as the HF acceptor. $NaHF_2$ is separated by centrifugation from the resulting equilibrium mixture of the isobutyric acid anhydride, its fluoride, and $NaHF_2$. The acid fluoride is returned to the hydrolysis stage and $NaHF_2$ is decomposed into NaF and HF, which are directed respectively to the hydrolysis and carbonylation stages. The selectivity in the formation of isobutyric acid anhydride is close to 100%.

Isobutyric acid fluoride is obtained by carbonylating isopropyl chloride in the presence of an excess of HF (20–80 °C, 50 atm CO), after which the product is hydrolysed with water to form isobutyric acid:[160]

$$(CH_3)_2CHCl + CO \rightarrow (CH_3)_2CHCOF \xrightarrow{H_2O} (CH_3)_2CHCOOH + HF.$$

A continuous method has been developed for the synthesis of acid fluorides, in particular isobutyryl fluoride, from C_3H_6, CO, and HF via their effective mixing in a turbulent mixer (30–80 °C, 196 atm CO).[161] The degree of conversion of C_3H_6 reaches 100% and the selectivity in the formation of isobutyryl fluoride is about 90%.

Isobutyric acid can be obtained in 98% yield by the isomerisation of isopropyl formate in the presence of HF:[162]

$$HCOOCH(CH_3)_2 \xrightarrow{CO,\ HF} (CH_3)_2CHCOOH.$$

A method has been proposed for the synthesis of isobutyric acid and its esters by carbonylating propene in an autoclave with a high-speed stirrer in the presence of not more than 2 mol % of alcohol or water in the reaction mixture.[163] The molar ratios H_2O (alcohol) : C_3H_6 : HF : CO = 0.96 : 1 : 10 : 1.5. The process is carried out under continuous conditions at 100–140 °C and a pressure of 80–140 atm. It takes place in the liquid phase and the reaction products (isobutyric acid fluoride and isopropyl isobutyrate) are readily isolated and the mixture is expanded to give a pressure of 1–4 atm. HF, isopropyl fluoride, isopropyl alcohol, and diisopropyl ether are then transferred to the gas phase and are returned to the process. Isobutyric acid fluoride and isopropyl isobutyrate are hydrolysed, HF and isopropyl alcohol are returned to the cycle, and isobutyric acid is purified further by double fractionation. The overall yield of the acid exceeds 90% and the selectivity in its formation is 93%.

An improved version of this process has also been proposed.[164] The reaction is carried out at 70 °C and 120 atm CO, the residence time of propene in the reactor amounting to 5 min. For a molar ratio C_3H_6 : HF = 1 : 20, the yield and selectivity in the formation of isobutyric acid fluoride reach respectively 95 and 96.5%. A characteristic feature of this process is that the carbonylation of C_3H_6 or iso-BrF are carried out in a polyhalogenoalkane (it is best to use 1,1,2,2-tetrachloroethane) with formation of a two-phase system with HF. A method has been proposed for the preparation of isobutyric acid fluoride by passing a mixture of HF, CO, and C_3H_6 (in molar proportions of 40 : 13 : 1) through a tubular reactor (35.7 atm, 20 °C) with a contact time of 1–2 min.[165–167] The yield of isobutyric acid fluoride is then 90%.

Carboxylic acids can be obtained by carbonylating olefins in the presence of the $HF : BF_3 : H_2O$ = 5.1 : 1 : 1.1 catalytic system at 60 °C and a pressure of 7.5 atm.[168]

Contact between the reactants is achieved by means of a stirrer rotating at 1000 rev min^{-1}. This method is suitable for the carbonylation of alcohols. Under the conditions indicated, trimethylacetic acid is formed in 88% yield from isobutyl alcohol after 45 min.

The reaction of C_3H_6, CO_2, and CH_3OH in the presence of $RuCl_2(PPh_3)_2$ (CO_2 pressure 45 atm at 20 °C, reaction temperature 215 °C, 20 h) in acetone results in the formation of a 1 : 1 mixture of methyl isobutyrate and methyl butyrate in 32% yield:[169]

$$C_3H_6 + CO_2 + CH_3OH \rightarrow \begin{cases} (CH_3)_2CHCOOCH_3, \\ CH_3CH_2CH_2COOCH_3. \end{cases}$$

Aromatic hydrocarbons have been carbonylated on the HF–BF_3 catalyst with formation of aldehydes.[170] Ethylbenzene, cumene, xylene, mesitylene, diisopropylbenzene, biphenyl, naphthalene, bibenzyl, isobutylbenzene, tetralin, and toluene can be carbonylated by this method. Under mild conditions (20 °C, 10–15 atm), *p*-toluic aldehyde was obtained selectively in 98% yield from toluene and CO in the presence of the HF–BF_3 catalytic system in apparatus made of copper alloys. A non-specific method of carrying out the process has been developed.

Carboxylic acids branched in the αα-positions, obtained by the method described above, have found extensive applications in the preparation of synthetic lubricants distinguished by high chemical and thermal stabilities,[171] as detergents, corrosion inhibitors,[172] insecticides, perfumes, preservatives, and antifungal preparations.[173]

III. Carbonylation of alcohols

Many valuable chemical products, which have found extensive applications in industry, agriculture, and medicine, can be obtained by carbonylating alcohols. A wide variety of compounds have been obtained from the simplest alcohol (methanol) depending on the process conditions and the catalyst used:

$$CH_3OH \rightarrow \begin{cases} \xrightarrow{CO,H_2} CH_3CHO,\ CH_3CH_2OH,\ HO(CH_2)_nCH_3,\ HO(CH_2)_nOH, \\ \xrightarrow{CO} CH_3COOH,\ CH_3COOCH_3,\ (CH_3)_2O, \\ \xrightarrow{CO} HCOOCH_3 \rightarrow HCOOH. \end{cases}$$

The likely usefulness of the processes involving the carbonylation of alcohols is confirmed by the widespread industrial use of the method of synthesis of acetic acids from methanol in the presence of a rhodium catalyst developed by the Monsanto Company:[1,3]

$$CH_3OH + CO \rightarrow CH_3COOH .$$

In the future, it will be possible to synthesise glycols (ethylene glycol) from CO and H_2, to prepare ethanol by introducing an extra CH_2 group into methanol, etc. The number of publications concerned with the study of the reactions involving the conversion of alcohols, acids, esters, and olefins into higher homologues by the interaction of the latter with CO and H_2 has been increasing. The prospects for the employment of alcohol carbonylation reactions can be inferred from the relevant publications.[174-180]

The available information about the carbonylation of methanol and some of its homologues and derivatives under the conditions of homogeneous and heterogeneous catalysis will be examine below.

In recent year, much attention has been devoted not only to the creation of catalysts but also to the elucidation of the mechanisms of the alcohol carbonylation reactions.[179,180] The most effective catalysts of the carbonylation of methanol with formation of acetic acid are rhodium complexes. Cobalt compounds are less selective and less active. Rhodium complexes with monodentate ligands are less active than those with bidentate ligands. The bidentate complexes exhibit a reduced activity in the initial stage of the process. The identical rates of carbonylation attained when $RhCl_3$ and phosphine complexes of Rh^+ are used indicate the similarity of the nature of the catalytically active species formed from the above compounds during the process.[180]

It has been suggested that rhodium complexes are more selective than catalytic systems based on iridium.[181] Selectivity in the formation of acetic acid on carbonylation of methanol in the presence of rhodium systems approaches 99%. When iridium catalysts are used, the selectivity does not exceed 90%, which is associated with the occurrence of side reactions involving the formation of methane:

$$CH_3OH + CO \rightarrow CH_4 + CO_2 ,$$
$$CH_3OH + H_2 \rightarrow CH_4 + H_2O .$$

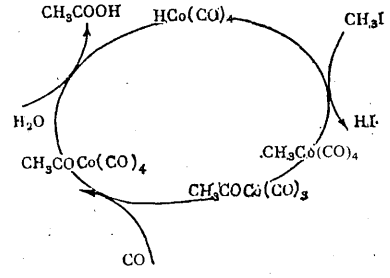
Their contribution increases at high carbon monoxide pressures and for a low water content in the system. An increase in the I^- and H_2O concentrations promotes the water gas conversion reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 .$$

In the presence of a rhodium catalyst, the degree of conversion of CO via this reaction hardly exceeds 10%.

When rhodium and iridium catalysts are used, the CH_3I promoting agent plays an especially important role. The rate of carbonylation of methanol is proportional to the CH_3I and rhodium concentrations and is independent of the concentrations of methanol, carbon monoxide, and acetic acid. For the iridium complexes, the rate of reaction is described by a more complex relation and is determined to a large extent by the composition of the catalytic system and the process conditions. The rate-limiting stage of the process in the presence of the rhodium and iridium catalysts is the oxidative addition of CH_3I to the catalytically active species $[Rh(CO)_2I_2]^-$ and $[Ir(CO)_2I_2]^-$ respectively.[181]

Cobalt catalysts are less selective in the carbonylation of methanol because the cobalt carbonyl hydride $HCo(CO)_4$, responsible for catalysis, catalyses in addition also side reactions: the conversion of methanol into ethanol by the addition of the CH_2 group, the water gas reaction, esterification, etc., which reduces sharply the process selectivity.[181] The catalytic cycle in the methanol carbonylation process in the presence of a cobalt catalyst is presented schematically below:[182]



In the carbonylation reactions of alcohols and esters, Ru, Ni, Pd, Pt, Fe, and Cu compounds also exhibit activity.[182]

The use of CH_3Br instead of CH_3I as the agent promoting the rhodium catalyst reduces the rate of carbonylation of methanol with formation of acetic acids by a factor of ~ 10.[181]

A coupled process involving the carbonylation of mixtures of methanol and ethylene with formation of a mixture of acetic and propionic acids has been patented.[183] The process is carried out in the presence of an industrial catalytic system which inlcudes $RhCl_3$, HI, and CH_3I. The reaction takes place at 185 °C and a CO pressure of 2 atm. The rate of formation of acetic acid is described by the equation

$$r = 5 \cdot 10^{10} e^{-7630/T} [Rh] [I^-] \text{ mol AcOH litre}^{-1} \text{ h}^{-1},$$

where [RH] and $[I^-]$ are the concentrations of rhodium and I^- in solution.

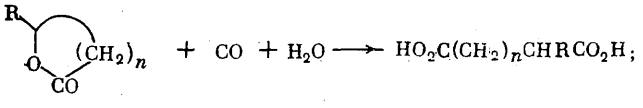
Cobalt and iron clusters having the general formulae $M[FeCo_3.(CO)_{12}]$ or $M[CoFe_3(CO)_{13}]$, where M is a hydrogen atom, an alkali or alkaline earth metal cation, the residue of a nitrogen-containing C_3–C_9 heterocyclic compound, $[(Ph_3P)_2N]^+$, or the cation of a quaternary nitrogen-, phosphorus-, or arsenic-containing base, are used as catalysts of the carbonylation of methanol with formation of methyl acetate.[184] The process takes place in the presence of an iodine-containing promoting agent. The catalyst can also be formed *in situ* from cobalt and iron carbonyls in the presence of M^+. The method makes it possible to obtain acetaldehyde with a high degree of selectivity for the ratio $H_2:CO = 1:1$ at 140–200 °C. For the molar ratio $H_2:CO = 1.5$–3 and a temperature of 200–220 °C, ethanol is formed. The carbonylation of methanol in the presence of $Bu_4N.[FeCo_3(CO)_{12}]$ and CH_3I [molar ratio MeI/(Fe + CO) = 4], at a pressure of 270 atm of the 1:1 CO + H_2 mixture, and at a temperature of 180 °C leads to the formation of acetaldehyde and the aldehyde acetal in 62 and 18% yields respectively.[184]

The complexes $R_2Mg[Fe(CO)_{12}C_5H_5]_2$ and $R_4Mg[Co(CO)_3PBu_3]_2$ are effective carbonylation and hydroformylation catalysts, in the presence of which methanol is converted into methyl acetate in 37% yield (120 °C, 56 atm CO).[185]

In order to lower the alkyl halide concentration (to 0.3 M) and thus weaken the corrosive properties of the medium, it is recommended that the carbonylation of methanol to form acetic acid or methyl acetate be carried out with the addition of phosphonium salts of the type $(CH_3)(C_6H_5)_3P^+I^-$ to the system.[186]

Acetic acid is obtained in 88.2% yield by carbonylating methanol with carbon monoxide at a pressure of 10 atm and a temperature of 200 °C in the presence of the catalyst prepared from five parts (by weight) of graphite, one part of $RhCl_3$, and one part of $IrCl_3$.[187] Acetic acid is also formed from the 1 : 1 CO + H_2 mixture in the presence of cobalt and ruthenium carbonyls and amines, phosphines, arsines, stibines, bismuthines, and halogen-containing compounds used as promoting agents. Thus the interaction of CO with H_2 in an autoclave (280 atm, 220 °C) in the presence of $Ru_3(CO)_{12}$, $Co_2(CO)_8$, PPh_3, and $[CH_3(CH_2)_6]Ph_3P^+Br^-$ in an acid medium leads to the formation of a mixture of acetic acid, methyl acetate, ethyl acetate, and C_1–C_3 alcohols (74.5, 1.5, 15.5, and 8.5 wt.% respectively). In aprotic dipolar solvents (ethers, esters, polyesters, sulphones, or amides), mainly acetic acid with an admixture of propionic acid is formed from CO and H_2 in the presence of a soluble hafnium compound.[189]

Dicarboxylic acids are readily formed on carbonylation of lactones under mild conditions (40 atm CO, 180 °C):[190,191]



$n = 2$–4.

The carbonylation of γ-valerolactone in the presence of $RhCl_3.3H_2O$, CH_3I, and water in caproic acid afforded a mixture of 2-methylglutaric and adipic acids in 65.2 and 20.3% yields respectively.[190]

Dicarboxylic acids are formed with a high selectivity on carbonylation of glycols whose OH groups are not at neighbouring carbon atoms. Thus the interaction of butane-1,4-diol in acetic acid in the presence of $[Rh(PPh_3)(CO)Cl]_2$ and CH_3I (175 °C, 49 atm CO) results in the formation of adipic acid in 74.0% yield. An aromatic glycol (recorcinol) and *p*-phenylene diiodide gave rise to isphthalic and terephthalic acids in an overall yield of 15.0%.[192]

The Rh–Fe, Rh–Mn, Rh–Mn–Cl, Rh–Ru, and Rh–Cr bimetallic catalysts exhibit an appreciable activity in the synthesis of acetic acid from CO and H_2.[193] Acetic acid is also formed selectively in the carbonylation of methanol in the presence of the Rh–RM(Z).$[(O)_nR^1].(O)_mR^2$ complexes (where M = P, As, or Sb, Z = O, S, or Se, and R = H or alkyl; for $n = m = 0.1$, we have $R^1 = R^2 = OH$ and, when $n = m = 0$, MR^1R^2 represents a heterocycle), $RhCl_3$, CH_3I, and Ph_3PO.[194] The carbonylation of a mixture of methyl acetate and methanol, whose composition ranges from 1 : 1 to 3 : 1, with a mixture of CO and H_2 (from 1 to 40% H_2) in the liquid phase in the presence of rhodium compounds, alkyl iodides, phosphines, and also chromium or zirconium compounds results in the formation of acetic anhydride and acetic acid.[195] Under pressure (31.5 atm of CO, 1.5 atm of H_2, 180 °C) and in the presence of $RhCl_3.3H_2O$, CH_3I, $Bu_3P^+(Me).I^-$, and $Cr(CO)_6$, the above reaction takes place significantly less effectively.

Carboxylic acids having the general formula RCOOH (where R = C_1–C_{17} alkyl, Ph, or $PhCH_2$) are obtained by carbonylating the corresponding alcohols in the presence of a homogeneous catalyst containing molybdenum (or tungsten) compounds of an alkali metal as well as a promoting agent—inorganic or organic Br^- or I^- compounds.[196] The process can be carried out also under heterogeneous conditions on catalysts containing the above components (up to 10 wt.%) deposited on Al_2O_3, SiO_2, ZrO_2, clays, etc. In the carbonylation of methanol in acetic acid in the presence of NiI_2, $Mo(CO)_6$, LiI, and CH_3I (200 °C, 4.9 atm H_2, 37 atm CO), acetic acid is formed with a selectivity of 100%. The rate of its formation is 12.3 mol litre^{-1} h^{-1}.

Acetic and pripionic acids are formed jointly on γ-irradiation of methane mixed with CO and CO_2.[197,198] A mixture of acetic acid and methyl acetate is formed from methanol and a mixture of CO and H_2 (160 °C, 250 atm CO) in the presence of $Co_2(CO)_8$, NaI, and EtI.[199]

Ruthenium promoted with halogen-containing compounds is an effective catalyst of the carbonylation of alcohols. Thus the carbonylation of methanol in the presence of Ru/C and CH_3I affords a mixture of acetic acid and methyl acetate in 92.2 and 4.6% yields respectively.[200] The same products are obtained by carbonylating methanol with a mixture of CO and H_2 (80–98% CO) in the presence of a cobalt catalyst, a compound capable of generating I^-, and covalently bound iodine (1–30% of the amount of I^-).[201] Ammonium salts, alkali and alkaline earth metal salts, and phosphonium compounds are used as sources of I^-. Other promoting agents are X_2, HX, RX (where X = Cl, Br, or I), $CoBr_2$, CoI_2, CH_3I, I_2, HI, or $Co_2(CO)_8$. Thus a mixture of 10.5% of acetic acid and 80.5% of methyl acetate is formed in an overall yield of 91% from methanol and a mixture of CO and H_2 (95 and 5 atm respectively) at a pressure of 140 atm and a temperature of 160 °C in the presence of $Co_2(CO)_8$, NaI, and EtI.

Molybdenum deposited in an amount of 2.5 wt.% on activated carbon (gas carbon black) catalyses the carbonylation of methanol and dimethyl ether with formation of methyl acetate and the carbonylation of methyl acetate to form acetic anhydride.[101] Catalysts containing nickel on carbon, SiO_2, and Al_2O_3 as well as molybdenum on SiO_2 and Al_2O_3 are less active. Acetic anhydride is formed in 15% yield and a selectivity of 83% in the carbonylation of methyl acetate (250 °C, 46 atm CO) in the presence of 2.5 wt.% Mo/C and CH_3I.

Catalysts containing between 0.001 and 15 parts by weight of B_2O_3, P_2O_5 or $x B_2O_3.y P_2O_5$ (where $x = 0.05$–0.95 and $y = 0.05$ to 0.95), deposited on activated carbon, exhibit activity in the carbonylation of methanol with formation of methyl acetate.[203]

The study of the kinetics of the carbonylation of methanol[204] in acetic acid showed that the reaction is of first order with respect to methanol. In an aqueous medium, the order with respect to methanol is 0.75. The reaction mechanism involves the formation of CH_3I on interaction of CH_3OH with HI and its subsequent oxidative addition to the complex $[Rh(CO)_2I_2]^-$. This results in the appearance of the complex $[CH_3Rh(CO)_2I_3]^-$, subsequently converted into $[(CH_3CO)Rh(CO)_2I_3]^-$, which decomposes into CH_3COI and $[Rh(CO)_2I_2]^-$. The effectiveness of the solvents is determined by the solubility of CH_3I in them. Thus, an increase in the concentration of methanol in water increases the solubility of CH_3I, which leads to an increase in the rate of carbonylation. In acetic acid, an increase in the concentration of methanol does not affect the solubility of CH_3I.[204]

Acetaldehyde is formed in the vapour-phase carbonylation of methanol in the presence of CH_3I and the Co/C catalyst promoted with palladium salts and alkali metals (after their reduction). The process is carried out in a flow apparatus (180–240 °C, 10–65 atm, $CO/H_2 = 1$). The promoting effect of palladium salts and alkali metals is associated with the intensification of the hydrogenating function of the cobalt catalysts.[205]

Modification of the nickel catalysts with palladium or copper chlorides or nitrates increases the effectiveness of the synthesis of acetic acid and methyl acetate via the vapour-phase carbonylation of methanol. Cl_2, Br_2, or I_2 or their volatile compounds are used as

promoting agents in an amount of 0.05–0.4 of a mole per mole of methanol. The vapour-phase carbonylation of methanol (300 °C, 1 atm, a mixture of CO and CH_3I in molar proportions of 30.1 : 8.6 : 1) in the presence of a catalyst containing 8.7% Ni and 0.03% Pd on activated carbon produces a mixture of acetic acid and methyl acetate in an overall yield of 80%. The degree of conversion of methanol is 65% and the productivity reaches 0.3 kg (AcOH + AcOMe) (litre cat.)$^{-1}$ h^{-1}. The catalysts retain their stability for two weeks of continuous operation.[206] Methanol can be converted into methyl acetate on a palladium catalyst (0.1–1% Pd) deposited on a dealuminated and decationated mordenite in a flow system. The degree of conversion of methanol at 250 °C, a pressure of 1 atm, and a space velocity of 0.4 h^{-1} in the presence of added 10% CH_3I in methanol is 49.1%.[207]

Methanol can be carbonylated to acetic acid and methyl acetate in the presence of effective homogeneous systems containing Group VIII metal compounds. The compounds RX (where R = H or C_1–C_3 alkyls and X = Cl, Br, or I) as well as Group IA and IIA metals, transition metal iodides (or carboxylates), and nitrogen-containing bases are used as promoting agents. Such a reaction takes place, for example, in an autoclave in the presence of $Pd(OAc)_2$, 2,2′-bipyridyl, MeOAc, H_2O, MeI, and NaI (178 °C, 1110 atm), a mixture of acetic acid and methyl acetate being formed at a rate of 0.14 kg litre^{-1} h^{-1}.[208]

Heterogeneous rhodium catalysts on carriers, including faujasites, exhibit a higher activity when they are obtained from $RhCl_3$ than the catalysts obtained from the complex $[Rh(NH_3)_5Cl]Cl_2$. In more active catalysts, the metal is distributed on the surface of the carrier more uniformly and the rhodium particle size is about 9 Å.[209]

Among the catalysts based on Ni, Co, and Fe which have been investigated,[210] the highest activity in the carbonylation of methanol was shown by nickel catalysts on activated carbon. The use of other carriers (γ-Al_2O_3, SiO_2, carbon blacks, and graphite) yielded worse results. In the presence of the iron and cobalt catalysts on activated carbon, the main carbonylation product was dimethyl ether and the yield of acetic acid and methyl acetate did not exceed 11%. At 300 °C, a pressure of 11 atm, and for the molar ratios CO : MeOH : MeI = 20 : 19 : 1, acetic acid and methyl acetate were obtained from methanol in 69.1 and 21.6% yields respectively in the presence of 2.5% Ni/C. The degree of conversion of methanol was 69.1%. The primary reaction products are Me_2O and AcOMe, acetic acid being formed on their subsequent carbonylation.

The selective synthesis of methyl acetate is carried out by the liquid-phase carbonylation of methanol in the presence of the Ru–Co - onium salt (0.25 : 1 : 10–50) catalyst in 1,4- or 1,3-dioxans. The interaction of methanol with CO in the presence of $Rh(OH)_4$, $Co_2(CO)_8$, and Bu_4PBr^- in 1,4-dioxan (180 °C, 245 atm) affords methyl acetate in 83% yield. Ethyl acetate is formed as a side product in 9% yield. The degree of conversion of methanol reaches 95%.[211]

The selective synthesis of methyl acetate from methanol also takes place in the presence of Group VIII metal compounds mixed with pentachlorobenzenethiol or its salts. Thus the carbonylation of methanol in the presence of the $RhCl_3$–C_6Cl_5SH system (175 °C, 50 atm CO) gives rise preferentially to the formation of methyl acetate.[212] When nickel compounds, a phosphine promoting agent, and methyl iodide are used, a mixture of acetic acid and methyl acetate is obtained from methanol. For example, the carbonylation of methanol in the presence of NiI_2, PPh_3, and MeI (28 atm, 150 °C) makes it possible to obtain a mixture of acetic acid and methyl acetate in 73.0 and 25.3% yields respectively.[213]

The selectivity in the formation of methyl acetate in the vapour-phase carbonylation of methanol on the Rh/NaX catalyst falls when the concentration of the rhodium introduced by the method involving the ion exchange of the $[Rh(NH_3)_5Cl]^{2+}$ cations, increases from 0.4 to 4%.[214] The reaction selectivity also falls (approximately by a factor of 4) if the rhodium catalyst is subjected to a preliminary heat treatment in air at 200 °C but remains unchanged if the heat treatment is performed at a higher temperature, up to 422 °C. Heat treatment in H_2 or CO at 320–350 °C deactivates the catalyst to a lesser extent than heat treatment in air. The treatment in CO does not affect the yield of dimethyl ether, while the treatment in H_2 increases it by approximately a factor of 1.5 compared with the heat treatment in air.

Catalysts for the homogeneous carbonylation of methanol having the general formula $R_pM[M'(CO)_mL_n]_2$ (where R is a nitrogen-containing base capable of being coordinated to Group IIA metals, M is a Group IIA metal, M′ is a Group VIB, VIIB, or VIII transition metal, L is a polyfunctional ligand capable of being coordinted to the transition metal, p = 1–4, m = 1–5, n = 0–4, and n + m = 5) have been prepared. The carbonylation of methanol in the presence of $(THF)_4.Mg[Co(CO)_3PBu_3]_2$ and CH_3I in benzene (120 °C, 56 atm CO) affords methyl acetate in 37% yield. Dimethyl ether is hardly formed.[215]

The carbonylation of dimethyl ether with formation of methyl acetate is carried out in the presence of palladium compounds, an iodine-containing promoting agent, and a tertiary amide or alkali or alkaline earth metal salts of a carboxylic acid.[216] The process, which is performed at a CO partial pressure of 30–150 atm and 180–220 °C, is distinguished by high selectivity.

The kinetics of the carbonylation of isopropyl alcohol with formation of isobutyric or n-butyric acid in the presence of the $RhCl_3$–HI catalytic system have been investigated.[217] The rate of carbonylation at 170 °C in an acetic acid–water mixture falls with increase in pressure. The reaction is of first order with respect to Rh, while the order with respect to HI is less than unity. Only the anionic species $[Rh(CO)_2I_2]^-$ have been detected spectroscopically. With increase in pressure from 14.6 to 205 atm, the isobutyric acid/n-butyric acid ratio increases from 0.7 to 1.6. The ratio is independent of the concentrations [Rh] and [HI]. The addition of propene to the mixture tends to increase the content of the n-isomer while the addition of an iodide slightly accelerates the reaction but does not affect the isobutyric acid/n-butyric acid ratio.

On treatment with the synthesis gas in the presence of a rhodium compound, a Group II metal iodide, and a Group VIII metal iodide (or bromide), ethers and esters are converted into mixtures of carboxylic acids or their esters, in which the alkyl group contains one CH_2 group more. Thus the interaction of methyl acetate with the synthesis gas in the presence of $RhCl_3$, $RuCl_3$, and ZnI_2 in 15-crown-5-(or 18-crown-6-) ethers results in the formation of ethyl acetate and acetic acid among other products.[218]

The reductive carbonylation of methanol in the presence of salts containing the anion $[FeCo_3(CO)_{12}]^-$ at 220 °C leads to the formation of ethanol in 73% yield. The reaction proceeds via stages involving the formation of acetaldehyde and methyl acetate. Under optimum conditions, the yield of acetaldehyde reaches 80–82%.[219]

Active nickel catalysts have been proposed for the synthesis of acetic acid by the isomerisation of methyl formate in the presence of iodine-containing promoting agents as well as compounds having the formula VR^1R^2, where V = N, P, Sb, As, or Bi and R, R^1, and R^2 = H, C_1–C_{10} alkyl, cycloalkyl, or aryl.[220] The reaction is carried out at 170–190 °C at normal or elevated pressures.

An effective method has been developed for the synthesis of esters from polyhydric alcohols, hex-1-ene and carbon monoxide in the presence of a cobalt catalyst and γ-picoline as the promoting agent. The catalyst is prepared from cobalt octanoate, γ-picoline, H_2O and CO in a separate apparatus (170 °C, 200 atm). The synthesis is carried out in apparatus of the bubbler type and the CO can contain up to 5 vol.% H_2. The esters obtained, for example, pentaerythritol tetraheptanoate, are used as components of a lubricating oil, plasticisers, and surfactants.[221-224] The initial polyhydric alcohols may be di- and tri-pentaerythritols, pentaerythritol, tris- or tetrakis-(hydroxymethyl)propanes, etc. and the olefins may be, apart from hex-1-ene, also but-1-ene, pent-1-ene, dec-1-ene, dodec-1-ene, etc. A method has been developed for the purification of the final product involving the removal of the cobalt impurities by treatment with aqueous solutions of alkali or alkaline earth metal oxides, carbonates, or bicarbonates at 120–140 °C.[221]

In the synthesis of aliphatic esters from alcohols and CO on an industrial scale, it is essential to use lower temperatures and pressures than is provided for in the majority of the patented processes. By carrying out the process in the presence of traces of H_2 and by using a complex of pyridine with cobalt carbonyl in proportions of 2:1 as the catalyst, it is possible to reduce the reaction temperature from 160–180 °C to 80–100 °C and the pressure from 150–200 to 20 atm.[225]

It has been established[226] that, in order to obtain active and stable deposited rhodium catalysts, the carriers must have definite acid–base properties. The use of oxide carriers with pronounced acid–base properties, such as Al_2O_3 or Al_2O_3–SiO_2, promotes the formation of rhodium complexes of the anionic type $[O \rightarrow Rh(CO)_2Cl]^-$ on the surface. When neutral carriers (SiO_2) are used, rhodium complexes of the type $O \rightarrow Rh(CO)_2Cl$, which are inactive in catalysis, are formed.

A catalyst for the carbonylation of methanol, exhibiting an activity higher by a factor of 50–100 than the usual rhodium catalysts, has been obtained by ion exchange between the NaX zeolite and $[Rh(NH_3)_5Cl]Cl_2$ and subsequent heating to 400 °C in a stream of N_2.[227] It works effectively at temperatures in the range 130–150 °C.

The chlororhodium-phthalocyanine catalyst for the carbonylation of methanol, used together with CH_3I and the sulphonic acids $CH_3C_6H_4SO_3H$, CH_3SO_3H, $PhCH_2SO_3H$, etc., is prepared by treating phthalocyanine or its carboxysulpho-derivatives with rhodium, cobalt, and iridium halides and also phosphorus-, sulphur-, arsenic-, or nitrogen-containing anions.[228] Before use, the catalyst is activated in an atmosphere of CO and H_2 at temperatures in the range 50–100 °C. The carbonylation of methanol in an autoclave (200 °C, 80 atm CO, 80 atm H_2) in the presence of a complex prepared from sodium phthalocyaninetetrasulphonate and $RhCl_3$ afforded a mixture of methyl acetate and acetic acid in 11 and 9% yields respectively.

The addition of lanthanide oxides to the nickel or cobalt catalysts makes it possible to carbonylate methanol with formation of acetic acid and methyl acetate without using halogen-containing promoting agents. The products are formed in high yields at temperatures in the range 130–200 °C and CO pressures from 1 to 50 atm.[229] The catalyst is first reduced in a stream of H_2 at 300–400 °C for 1 h and is then treated with CO (10–80 vol.%) containing N_2, CH_4, or C_2H_6 at 250–300 °C for 1–3 h. A mixture of methyl acetate, acetic acid, and methyl formate has been obtained in yields of 87.0, 8.7, and 0.87% respectively from methanol and carbon monoxide (in proportions by volume of 1:9) at 190 °C and a pressure of 5 atm on a catalyst containing 0.5% Rh and 15% of lanthanum oxide on SiO_2. Catalysts containing platinum (0.8–2.0 wt.%), cerium (15–20%), or lanthanum (10–20%) deposited on Al_2O_3 and TiO_2 are also active in this reaction.[230]

The rhodium ions in the Rh/NaX catalyst obtained by ion exchange are in a state close to their state in a homogeneous catalyst, but the activation energy for the heterogeneous carbonylation of methanol is nevertheless twice as high as for the homogeneous carbonylation.[231] The Rh/NaX catalysts are stable only at temperatures not exceeding 220 °C. The reaction is of zero order with respect to rhodium.

Oxidative carbonylation of fluorinated alcohols with carbon monoxide in the presence of Group IIB elements in the ionic form can result in the formation of the corresponding carbonates. Fluorine-containing carbonates and polycarbonates based on them have found extensive application in the pressing and moulding of plastics. The reaction takes place under mild conditions. Thus the interaction of CF_3CH_2OH with CO bubbling through it at atmospheric pressure and 20 °C in the presence of $Hg(OAc)_2$, 1,2,2,6,6-pentamethylpiperidine, and the sodium salt of dimethyl sulphoxide afforded $(CF_3CH_2O)_2O$ in 90% yield.[232]

But-3-enoic acid is obtained by the liquid-phase carbonylation of allyl alcohol in the presence of the palladium complex $LnPdCl_2$ (where L = nitrile, phosphine, or amine and n = 0 or 2) at 75 to 200 °C and a pressure of 35–140 atm.[233] Thus the carbonylation of allyl alcohol in acetic acid ($PdCl_2$, 80 °C, 90 atm CO) produces but-3-enoic acid in 64% yield. In acetonitrile, the yield falls to 40%. But-3-enoic acid is a valuable intermediate in the synthesis of γ-butyrolactone and 2-pyrrolidinone.

Nickel and cobalt catalysts promoted with compounds of Group IV elements (Si, Ge, and Sn), Group IA and IIA elements (Li, Ca, and Sr), as well as nitrogen-containing bases showed a high effectiveness in the synthesis of acetic acid from methanol. The promoting agents are iodine-containing compounds and aluminium, zinc, copper, lanthanum, and cerium iodides or bromides. Thus the carbonylation of methanol in acetic acid in the presence of nickel powder, SnI_4, 2,4-dimethylpyridine, CH_3I, and LiOAc (195 °C, 20 atm CO, and 3 atm H_2) gave rise to acetic acid in 97.6% yield.[234] The use of compounds (cobalt and nickel) with added alkyl- or arylphosphines and iodine-containing promoting agents as catalysts makes it possible to carry out the liquid-phase carbonylation of methanol. Thus the carbonylation of methanol (350 atm CO, 200 °C) in the presence of $Co(AcO)_2.4H_2O$, HI, and Bu_3P in an aqueous medium results in the formation of a mixture of methyl acetate and acetic acid in an overall yield of 91.0%.[235] Methyl acetate is formed selectively in the carbonylation of methanol (125 atm, 120 °C) in the presence of $Mn_2(CO)_{10}$ and CH_3I.[236]

The treatment of esters of mono- or di-carboxylic acids with the synthesis gas in the presence of homogeneous cobalt and rhodium compounds as well as LiI or LiBr results in the formation of aldehydes, carboxylic acids and their esters. Thus the interaction of methyl acetate with the synthesis gas (CO/H_2 = 1, 180 °C, 210 atm) in the presence of $Co(AcO)_2.4H_2O$, $Rh(acac)(CO)_2$, and LiI produced a mixture of MeCHO, HOAc, and AcOEt, the selectivity in the formation of acetaldehyde amounting to 86%.[237]

Lower carboxylic acids are obtained by the carbonylation of alcohols in the presence of nickel complexes and iodine-containing promoting agents. Acetic acid has been formed in a high yield in the interaction of methanol with CO (150 °C, 21 atm CO) in the presence of $(Ph_3P)_2Ni(CO)_2$, PPh_3, and CH_3I.[239] In order to reduce the corrosion of the apparatus by iodine-containing compounds, it is

recommended that alcohols be carbonylated with formation of acids and their esters in solution in aryl acetates.[240]

A method has been developed for the transesterification and carbonylation of the esters of lower aliphatic C_1–C_5 carboxylic acids and C_1–C_4 alcohols by carbon monoxide and phenols in the presence of Group VIII metal compounds with added iodine compounds as promoting agents.[241] The reaction is accelerated by tertiary amines NRR^1R_2 or the compounds $N(COR)R^1R^2$, where R, R^1, and R^2 = H, alkyl, or aryl. Thus the interaction of methyl acetate with CO and phenol (30 atm CO, 180 °C) in acetic acid in the presence of $RhCl_3$ and CH_3I converted half of the initial methyl acetate into acetic acid and phenyl acetate (the degrees of conversion were 97.5 and 96.8% respectively).

The $RhCl_3$–graphite and $RhCl_3$–graphite–I_2 systems, prepared by depositing $RhCl_3$ and I_2 on petroleum or coal coke in a high vacuum or in an inert gas atmosphere at 300 °C, are effective catalysts of the carbonylation of methanol to acetic acid.[242] Thus, by passing an MeOH : CO = 1 : 4 mixture at a space velocity of 45 cm^3 min^{-1} through a glass tube charged with the catalyst (2% $RhCl_3$ + 0.4% I_2)/C (with a specific surface of 10 m^2 g^{-1}) at 200 °C, methyl acetate and acetic acid have been obtained in 35.5 and 8.5% yields.

Carboxylic acids and esters are obtained together on interaction of compounds having the general formula RCO_2R' with the synthesis gas:

$$RCO_2R' + CO + H_2 \begin{cases} \longrightarrow RCOOH + R'COOH, \\ \longrightarrow RCH_2COOR', \\ \longrightarrow R'COOR. \end{cases}$$

The reaction is catalysed by rhodium compounds as well as compounds of other Group VIII metals, phosphines, and alkyl iodides or bromides. Thus treatment of methyl acetate with a 1 : 1 mixture of CO and H_2 in the presence of $RuCl_3$, $RhCl_3$, MeI, and PPh_3 (160 °C) leads to the formation of a mixture of acetic acid and ethyl acetate.[243]

Carboxylic acids and their anhydrides are obtained by carbonylating ethers or esters in the presence of metals or Group VIII metal compounds, Br^-, I^-, or their compounds. Thus a mixture of acetic acid and acetic anhydride can be obtained in a high yield by treating methyl acetate with carbon monoxide in the presence of the rhodium acetate dimer, 1-methylimidazole, and CH_3I at 175 °C.[244]

The interaction of carboxylic acids with the synthesis gas in the presence of rhenium and ruthenium compounds leads to the formation of acid esters. Thus treatment of acetic acid with a 1 : 1 mixture of CO and H_2 in the presence of $Ru_3(CO)_{12}$ and $NaRe(CO)_2$ (240 °C, 245 atm) affords a mixture of methyl and ethyl acetates.[245]

A method has been proposed for the preparation of methyl formate by carbonylating methanol in the presence of sodium methoxide. The introduction of $H_2N(CH_2)_6NH_2$ into the reaction zone increases the degree of conversion of methanol, while the addition of water poisons the catalysts.[246–249] The formation of methyl formate is facilitated in the presence of 0.1–30 wt.% of pyridine and 0.1–28 wt.% of the hydroxylated epoxide oligomer $HO(CH_2CHRO)_nH$ (where n = 2–600 and R = H or Me).[247] The reaction is carried out in the temperature range 60–100 °C. Conditions have been found for the hydrolysis of methyl formate with formation of formic acid in the presence of a strongly acid sulphonic acid cation exchanger based on styrene and divinylbenzene.[248,249] The hydrolysis is carried out at 60–100 °C and the resulting reaction mixture is transferred to a second vat-reactor where the hydrolysis is completed at 100–105 °C.

The interaction of methanol with the synthesis gas (CO/H_2 = 1) in the presence of $Al(acac)_3$ (250 °C, 200 atm) results in the formation of methyl acetate and methyl formate with selectivities of 62.5 and 35.1% respectively. The degree of conversion of methanol is 21%.[250]

Treatment of C_1–C_{20} alkyl, aryl, arylalkyl, and alkylaryl formates with the synthesis gas in the presence of a catalytic system containing rhodium compounds and LiI leads to the formation of the corresponding carboxylic acids. Thus the interaction of methyl formate with a 1 : 1 mixture of CO and H_2 in the presence of the $Rh(CO)_2(acac)_2$–LiI system results in the formation of acetic acid with a selectivity of 95% for a formate conversion of 65%.[251]

The technology of the synthesis of formic acid via methyl formate has been investigated on a scaled-up experimental apparatus. A procedure for the isolation of pure formic acid after the stage involving the hydrolysis of methyl formate and its concentration to 96% has been developed.[252]

The carbonylation of alcohols with formation of branched carboxylic acids proceeds under mild conditions on effective acid catalytic systems.[253–256] Thus trimethylacetic acid has been obtained with a high selectivity in the interaction of isobutyl alcohol with carbon monoxide (7.5 atm) in a liquid-phase reactor with vigorous stirring (1000 rev min^{-1}) at 60 °C in the presence of the $HF : BF_3 : H_2O$ = 5.1 : 1 : 1 catalytic system.[253]

The esters of αα-branched carboxylic acids are obtained in the presence of BF_3 with added copper(I), silver(I), or gold(I) carbonyls, formed in a strongly acid medium under mild conditions (temperature from −20° to +20 °C, 1 atm).[254]

Trimethylacetic acid is obtained selectively by carbonylating isobutyl alcohol in the presence of H_2SO_4 as the catalyst and ethyl formate as the carbonylating agent.[256] The reaction takes place at atmospheric pressure, 40–60 °C, and with molar ratios H_2SO_4 : 1-hexanol : $HCOOC_2H_5$ = 8–10 : 1 : 4. The mild process conditions are due to the formation of activated carbon monoxide on decomposition of ethyl formate in an acid medium and the evolution of ethanol as the esterifying agent.

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In conclusion, we shall identify certain problems associated with the catalytic syntheses based on carbon monoxide. Despite the promising nature of many methods and the availability of large resources of carbon monoxode derivatives, there are as yet few industrial processes using this gas. The main causes of this situation are as follows: (1) the complexity and high cost of the majority of catalytic systems known at present; (2) the necessity to used special apparatus resistant to the corrosive action of the catalytic systems; (3) the insufficient number of highly selective and very stable catalysts which can be readily removed from the reaction products.

The introduction into industrial practice in recent years of the synthesis of acetic acid by the carbonylation of methanol can be regarded as one of the greatest advances in the field of carbonylation. Despite major successes achieved in their theoretical study, other processes have not so far found much practical application. Analysis of the extensive literature data presented in the present review shows that in most cases the proposed catalytic systems,

ensuring a high selectivity, are extremely complex and are frequently insufficiently stable. The questions of the repeated use of such systems have not been resolved.

Since virtually all carbonylation processes take place only at elevated pressures, a far-reaching study of their mechanism is difficult. Therefore in most cases the role of each component of the catalytic system is not entirely clear and so far the catalysts are selected empirically.

The present review naturally cannot embrace the entire literature devoted to the catalytic syntheses based on carbon monoxide. It includes only the main studies demonstrating the principal trends in the development of this important branch of science and technology.

The concentration of the research effort on the most promising and most thoroughly developed aspects of the field will apparently permit in the immediate future a significant expansion of the range of processes based on the use of carbon monoxide.

One should note that, among all types of the catalysts of the carbonylation reactions which have been investigated, the homogeneous catalysts exhibit the highest activity and selectivity. However, their separation from the reaction mixture presents certain difficulties. One way of solving this problem is the development of a method for the immobilisation of the soluble catalyst on an insoluble carrier. Such hybrid catalysts, which combine the high activity and selectivity of homogeneous systems with the ease of separation characteristic of heterogeneous catalysts, will probably find extensive application in industry. Another possible solution of the problem of the catalyst involves the carrying out of the reaction in a two-phase liquid–liquid system in which the catalyst and reaction products are dissolved in different phases.

References

1. A L Lapidus, S D Pirozhkov *Itogi Nauki i Tekhniki. Ser. Kinetika i Kataliz* (Advance in Science and Engineering. The Kinetics and Catalysis Series), Izd.VINITI, Moscow, 1980, Vol. 7, p. 58
2. A Storch, N Golumbic, R Anderson *The Fischer-Tropsch and Related Syntheses* (Translated into Russian), Inostr. Lit., Moscow, 1954, 516 pp
3. R A Sheldon *Chemical Products Based on the Synthesis Gas* (Russian Translation from English edited by S M Loktev), Izd. Khimiya, Moscow, 1987, 248 pp
4. D V Sokol'skii, R N Khasanova, USSR P. 335 934; *Byul. Izobret.*, 1976(7) 199
5. D V Sokol'skii, L V Levchenko, Yu A Pridanova, et al., USSR P. 447 028; *Byul. Izobret.*, 1976(2) 180
6. G M Brailovskii, V S Shestakova, G L Luk'yanova, et al., USSR P. 577 203; *Byul. Izobret.*, 1977(39) 56
7. G M Shulyakovskii, N F Alekseeva, USSR P. 573 184; *Byul. Izobret.*, 1977(35) 14
8. L G Bruk, O N Temkin, Z V Goncharova, et al., *React. Kinet. Catal. Lett.*, 1978, **9** 303
9. N G Mekhryakova, L G Bruk, O L Kaliya, et al. *Kinet. Katal.*, 1979, **20** 629
10. I A Orlova, N F Alekseeva, A D Troitskaya, et al. *Zhur. Obshch. Khim.*, 1979, **49** 1601
11. I A Orlova, O N Temkin, A T Troitskaya, et al. *XIII Vsesoyuznoe Chugaevskoe Soveshchanie po Khimii Kompleksnykh Soedinenii* (The XIIIth All-Union Chugaev Conference on the Chemistry of Complex Compounds), Moscow, 1978, p. 298
12. French P. 2 376 116; *Chem. Abs.*, 1979, **91** 4962
13. Japanese P. 53-1410; *Ref. Zhur. Khim.*, 1979, 23N47P
14. US P. 4 055 721
15. French P. 1 532 089
16. Japanese P. 73-11088; *Chem. Abs.*, 1973, **79** 18132
17. Japanese P. 75-25524; *Chem. Abs.*, 1975, **83** 58155
18. B P Gusev, E A El'perina, V F Kucherova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 603
19. L P Bruk, G M Shulyakovskii, N F Alekseeva, et al., USSR P. 798 092; *Byul. Izobret.*, 1981(3) 79
20. G M Shulyakovskii, O N Temkin, G V Pavlyuk, et al. *Nukleofil'nye Reaktsii Karbonil'nykh Soedinenii* (Nucleophilic Reactions of Carbonyl Compounds) (Edited by V G Kharchenko), Izd. Saratov. Univ., Saratov, 1982, p. 103
21. W Keim (Editor) *Catalysis in C_1 Chemistry* (Russian Translation from English edited by I I Moiseev), Izd. Khimiya, Leningrad, 1987, 296 pp
22. Japanese Appl. 81-133242; *Chem. Abs.*, 1982, **96** 68373
23. BRD Appl. 2 933 581; *Ref. Zhur. Khim.*, 1981, 2N79P
24. B. P. 2 014 136; *Chem. Abs.*, 1980, **92** 180 679
25. Japanese Appl. 56-86133; *Ref. Zhur. Khim.*, 1982, 9N60P
26. BRD Appl. 3 246 149; *Ref. Zhur. Khim.*, 1985, 7N148P
27. US P. 4 246 183
28. F J Fanans, H Hoberg *J. Organomet. Chem.*, 1984, **275** 249
29. Japanese Appl. 59-67423; *Ref. Zhur. Khim.*, 1985, 10N80P
30. BRD Appl. 2 951 950; *Ref. Zhur. Khim.*, 1982, 12N37P
31. French Appl. 2 512 813; *Ref. Zhur. Khim.*, 1984, 9N57P
32. US P. 4 471 067
33. Japanese P. 80-51039; *Chem. Abs.*, 1980, **93** 185 780
34. B.P. 2 029 820; *Chem. Abs.*, 1980, **93** 185 786
35. Belgian P. 877 770; *Chem. Abs.*, 1980, **92** 214907
36. US P. 4 259 519
37. BRD Appl. 3 146 313; *Chem Abs.*, 1982, **97** 109 565
38. BRD Appl. 2 836 518; *Ref. Zhur. Khim.*, 1980, 1N52P
39. BRD Appl. 2 837 815; *Chem Abs.*, 1980, **92** 214 910
40. BRD Appl. 2 924 785; *Ref. Zhur. Khim.*, 1981, 21N51P
41. Europ. P. 21 010; Chem Abs., 1981, **94** 174 373
42. J F Knifton *Fundamental Research into Homogeneous Catalysis. Proceedings of I International Conference, Corpus Christi, Texas, 1978*, New York–London, 1979, Vol. 3, p. 199
43. US P. 4 491 546
44. US P. 4 404 394
45. L I Zakharkin, V V Guseva, USSR P. 1 092 150; *Byul. Izobret.*, 1984(18) 58
46. L I Zakharkin, V V Guseva, USSR P. 763 319; *Byul. Izobret.*, 1980(34) 117
47. B. P. 1 340 873
48. Japanese Appl. 59-170086; *Ref. Zhur. Khim.*, 1985, 19N109P
49. Japanese Appl. 56-154440; *Ref. Zhur. Khim.*, 1981, 24N136P
50. Japanese Appl. 55-55137; *Ref. Zhur. Khim.*, 1981, 22N97P
51. Japanese Appl. 58-74640; *Chem. Abs.*, 1983, **99** 87707
52. Europ. P. 74 912; *Chem. Abs.*, 1983, **99** 70 227
53. Europ. P. 75 524; *Chem. Abs.*, 1983, **99** 70 228
54. French Appl. 2 512 812; *Ref. Zhur. Khim.*, 1984, 8L203P
55. Japanese Appl. 81 134 526; *Chem. Abs.*, 1982, **96** 142 280
56. Japanese P. 5 859 942; *Chem. Abs.*, 1983, **99** 157 840

57. BRD P. 2 133 349
58. BRD P. 2 134 684
59. Dutch P. 8 202 190; *Chem. Abs.*, 1983, **98** 106 816
60. US P. 4 372 889
61. A L Lapidus, S D Pirozhkov, A Vellekov, et al. *Primenenie Tseolitov v Katalize. II. Vsesoyuznaya Konferentsiya* (Applications of Zeolites in Catalysis. II. All-Union Conference), Izd. UDN im. Patrisa Lumumby, Moscow, 1981, p. 285
62. A L Lapidus, E Z Gil'denberg, S D Pirozhkov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 2532
63. A L Lapidus, S D Pirozhkov, A Vellekov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 2304
64. A L Lapidus, S D Pirozhkov, A Vellekov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 142
65. A L Lapidus, S D Piroshkov, A V Dolidze, et al. *Izv. Akad. Nauk Gruz. SSR, Ser. Khim.*, 1984, **10** 269
66. US P. 4 209 643 *Chem. Abs.*, 1980, **103** 185 768
67. BRD Appl. 3 121 573; *Ref. Zhur. Khim.*, 1983, 21N62P
68. BRD Appl. 3 046 651; *Ref. Zhur. Khim.*, 1983, 14N36P
69. US P. 4 301 090
70. US P. 4 257 973
71. US P. 4 22 977; *Chem. Abs.*, 1984, **100** 102 773
72. M G Katsnel'son, V V Kashina *Zhur. Prikl. Khim.*, 1981, **54** 1201
73. BRD Appl. 2 912 489; *Chem. Abs.*, 1981, **94** 102 845
74. Japanese Appl. 55-22647; *Ref. Zhur. Khim.*, 1981, 3N36P
75. BRD Appl. 3 119 594; *Ref. Zhur. Khim.*, 1983, 22N69P
76. Dutch P. 6 902 651; *Ref. Zhur. Khim.*, 1981, 24N52P
77. US P. 4 354 036; *Chem. Abs.*, 1982, **97** 215 588
78. International P. 84 013 776; *Chem. Abs.*, 1984, **101** 110 369
79. Japanese Appl. 59-10545; *Ref. Zhur. Khim.*, 1985, 5N58P
80. E Z Gil'denberg, L L Krasnova, S D Pirozhkov, et al. *Kinet. Katal.*, 1980, **21** 810
81. L Ya Startseva, V A Semikolenov, A S Lisitsyn, et al. *Kinet. Katal*, 1984, **25** 506
82. French Appl. 2 545 821; *Chem. Abs.*, 1985, **103** 22 172
83. Japanese P. 8 149 333; *Chem. Abs.*, 1981, **95** 97 066
84. US P. 4 258 206; *Chem. Abs.*, 1981, **94** 208 332
85. A L Lapidus, S D Pirozhkov, N A Buiya, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 1454
86. A L Lapidus, S D Pirozhkov, N A Buiya, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2816
87. G k-I Magomedov, L V Morozov, A V Medvedeva, et al., USSR P. 721 409; *Byul. Izobret.*, 1980(10) 94
88. S Baller, B Lucke, S Nowak, DDR P. 216 003
89. US P. 4 469 886
90. Europ. P. 33 422; *Chem. Abs.*, 1981, **95** 203 338
91. G k-I Magomedov, G V Druzhkova, O V Shkol'nikov, et al. *Novye Oblasti Primeneniya Metalloorganicheskikh Soedinenii* (New Applications of Organometallic Compounds), Moscow, 1983, p. 29
92. US P. 4 414 409; *Chem. Abs.*, 1984, **100** 34 125
93. BRD Appl. 3 034 420; *Chem. Abs.*, 1982, **96** 217 260
94. US P. 4 158 668
95. A D Karpyuk, A V Protchenko, E S Petrov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 2155
96. A D Karpyuk, N D Kolosova, M I Terekhova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 2291
97. A D Karpyuk, M I Terekhova, N D Kolosova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 639
98. A V Protchenko, T E Kron, A D Karpyuk, et al. *Zhur. Obshch. Khim.*, 1986, **56** 90
99. M G Katsnel'son, V B Del'nik, USSR P. 952 838; *Byul. Izobret.*, 1982(31) 125
100. V A Rybakov, A M Nalimov, S K Ogorodnikov, USSR P. 559 548; *Byul. Izobret.*, 1983(16) 230
101. Japanese Appl. 60 237 046; *Chem. Abs.*, 1986, **104** 129 648
102. Japanese Appl. 60 231 630; *Chem. Abs.*, 1986, **104** 109 252
103. Japanese Appl. 56-22750; *Ref. Zhur. Khim.*, 1982, 11N126P
104. Japanese Appl. 81-22749; *Chem. Abs., 1981*, **94** 191970
105. Japanese Appl. 81-15242; *Chem. Abs.*, 1981, **94** 208566
106. Japanese Appl. 55-94689; *Ref. Zhur. Khim.*, 1983, 3N118P
107. A D Karpyuk, L F Starosel'skaya, E S Petrov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 218
108. US P. 4 414 409
109. P Hoffmann, K Kossing, F Schaefer *Ind. Eng. Chem. Prod. Res. Develop.*, 1980, **19** 330
110. B Desplyroux, H Alper *Ann. N.Y. Acad. Sci.*, **415** (Catal. Transition Met. Hydrides) p. 148
111. BRD App. 2 912 489; *Ref. Zhur. Khim.*, 1981, 16N52P
112. P Hoffmann *Chem. -Ind. Techn.*, 1982, **54**(7) 694
113. Europ. P. 47 834; *Chem. Abs.*, 1982, **96** 217 267
114. Europ. P. 47 831; *Chem. Abs.*, 1982, **96** 217266
115. Europ. P. 46674; *Chem. Abs.*, 1982, **97** 55 321
116. V N Zudin, G N Il'inich, V A Licholobov, et al *J.Chem. Soc., Chem. Commun.*, 1984, 545
117. Japanese Appl. 55-85534; *Ref. Zhur. Khim.*, 1981, 18N34P
118. US P. 4 332 966
119. *Chem. Eng. News*, 1984, **62**(18) 28
120. Japanese Appl. 5 872 539; *Chem. Abs.*, 1983, **99** 121 829
121. H Alper, D Leonard *J. Chem. Soc., Chem. Commun.*, 1985, 511
122. BRD Appl. 3 332 018; *Ref. Zhur. Khim.*, 1985, 24N64P
123. A Mazuda *J. Nat. Chem. Lab. Ind.*, 1980, **75**(10) 445
124. US P. 4 235 744; *Chem. Abs.*, 1981, **94** 139 247
125. US P. 4 238 357; *Chem. Abs.*, 1981, **94** 139 252
126. US P. 4 331 612; *Chem. Abs.*, 1982, **97** 181 742
127. US P. 4 344 866
128. Europ. P. 41 587; *Chem. Abs.*, 1982, **96** 122 239
129. US P. 4 536 597
130. BRD Appl. 2 648 004; *Chem. Abs.*, 1978, **89** 42 485
131. M G Katsnel'son, L S Kuz'mina, S S Misnik, et al. *Sbornik Gosudarstvennogo Instituta Prikladnoi Khimii. Razrabotka Khimicheskikh Sposobov Polucheniya Aminokislot* (Collected Reports from the State Institute of Applied Chemistry. Development of Chemical Methods for the Synthesis of Aminoacids) (Edited by I Ya Tyuryaev), Izd. GIPKha, Leningrad, 1984, p. 31
132. US P. 4 508 660; *Chem. Abs.*, 1985, **102** 220 468
133. US P. 4 377 708
134. US P. 4 450 285
135. BRD P. 4 322 314
136. BRD Appl. 3 016 653; *Ref. Zhur. Khim.*, 1983, 4N203P
137. Japanese Appl. 57-12810; *Ref. Zhur. Khim.*, 1984, 24L194P
138. Japanese Appl. 57-88146; *Ref. Zhur. Khim.*, 1983, 13N54P
139. US P. 4 350 668
140. Europ. P. 92 491; *Chem. Abs.*, 1984, **85** 85 271
141. French Appl. 2 517 298; *Ref. Zhur. Khim.*, 1984, 19N49P
142. French Appl. 2 524 876; *Ref. Zhur. Khim.*, 1984, 19N48P
143. French Appl. 2 526 421; *Ref. Zhur. Khim.*, 1984, 20N52P
144. Japanese Appl. 82 881 146; *Ref. Zhur. Khim.*, 1983, 13N54P
145. US P. 3 759 984

146. US P. 4 224 232
147. Japanese P. 8 014 235; *Chem. Abs.*, 1981, **94** 102 854
148. Europ. P. 31 205; *Chem. Abs.*, 1981, **95** 186 654
149. M B Ordyan, A S Stepanyan, S D Pirozhkov, et al. *Zhur. Org. Khim.*, 1982, **18** 1634
150. M B Ordyan, A S Stepanyan, S D Pirozhkov, et al. *Zhur. Org. Khim.*, 1981, **17** 2564
151. S D Pirozhkov, A S Stepanyan, M B Ordyan, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 2292
152. S D Pirozhkov, A S Stepanyan, M B Ordyan, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 629
153. S D Pirozhkov, A S Stepanyan, T N Myshenkova, et al. *Materialy III Vsesoyuznoi Konferentsii po Mekhanizmu Kataliticheskikh Reaktsii* (Proceedings of the IIIrd All-Union Conference on the Mechanisms of Catalytic Reactions), Izd. Inst. Katal. Sibir. Otd. Akad. Nauk SSSR, Novosibirsk, 1982, Part 2, p. 152
154. Europ. P. 31 205; *Chem. Abs.*, 1981, **95** 186 654
155. Japanese P. 58 201 748; *Chem. Abs.*, 1984, **100** 138 609
156. Europ. P. 105 699; *Chem. Abs.*, 1984, **101** 191 157
157. US P. 4 518 798
158. Swiss P. 649 757
159. Australian P. 372 071
160. Europ. P. 161 322; *Chem. Abs.*, 1986, **104** 167 997
161. Swedish Appl. 439 301; *Ref. Zhur. Khim.*, 1986, 5N54P
162. BRD Appl. 2 551 289; *Ref. Zhur. Khim.*, 1982, 12N22P
163. BRD Appl. 3 033 655; *Ref. Zhur. Khim.*, 1983, 4N52P
164. BRD Appl. 3 213 395; *Chem. Abs.*, 1984, **100** 34 163
165. US P. 4 499 029
166. British Appl. 2 106 893; *Ref. Zhur. Khim.*, 1984, 4N59P
167. French Appl. 2 514 345; *Ref. Zhur. Khim.*, 1984, 9N31P
168. Japanese Appl. 56-97245; *Ref. Zhur. Khim.*, 1982, 19N25P
169. BRD Appl. 2 948 888; *Ref. Zhur. Khim.*, 1982, 13N52P
170. S Fudziusa *Japan. Chem. Ind. Assoc. Mon.*, 1983, **36**(2) 11
171. T S Chao, Kyohaas, J de Jovine *Ind. Eng. Chem. Prod. Res. Dev.*, 1983, **33** 357
172. Z G Ragulev, N B Davydenko, M I Abdullin, et al. *I Vsesoyuznoe Soveshchanie po Khimicheskim Reaktivam* (The Ist All-Union Conference on Chemical Reagents), Ufa, 1985, p. 203
173. Japanese P. 8 291 948; *Chem. Abs.*, 1982, **97** 181739
174. S Nadziri *Petrotech.*, 1982, **5** 321
175. *Chem. Eng. News*, 1980, **58**(14) 37
176. M E Fakley, R A Head *Appl. Catal.*, 1983, **5**(1) 3
177. O Kadeyama *Kagaku Kogou.*, 1981, **45**(12) 112
178. *Petrotech*, 1981, **4** 710
179. H Staege *Verfahrenstechnik*, 1981, **15** 347
180. D Forster, T C Singleton *J. Mol. Catal.*, 1982, **17** 299
181. D Forster *Adv. Organometal. Chem.*, 1979, **17** 255
182. A Mullen *React. Struct. Concepts. Org. Chem.*, 1980, **11** 243
183. US P. 4 111 981
184. Us P. 4 408 069
185. US P. 4 318 826
186. BRD Appl. 3 432 170; *Chem. Abs.*, 1985, **103** 104 550
187. Japanese P. 7 318 217; *Chem. Abs.*, 1973, **78** 158 953
188. Japanese Appl. 5 867 641; *Chem. Abs.*, 1983, **99** 70 222
189. BRD Appl. 5 931 730; *Ref. Zhur. Khim.*, 1985, 6N55P
190. Japanese P. 8 051 637; *Chem. Abs.*, 1980, **93** 149 816
191. Y Sado, K Tajima *Ann. Rept. Noguchi Inst.*, 1980(23) 52
192. US P. 4 060 547
193. K Ishii, T Yokoyama *Shokubai* (Catalyst), 1981, **23** 15
194. Europ. P. 114 703; *Chem. Abs.*, 1984, **101** 19 152
195. Japanese Appl. 59 53440; *Chem. Abs.*, 1984, **101** 54 582
196. US P. 4 482 497
197. Japanese Appl. 80 113 737; *Chem. Abs.*, 1981, **94** 46 789
198. Japanese Appl. 80 145 635; *Chem. Abs.*, 1981, **94** 139 238
199. Europ. P. 11 043; *Chem. Abs.*, 1981, **94** 3753
200. International P. 8 100 856; *Chem. Abs.*, 1981, **95** 97 081
201. French Appl. 2 440 349; *Ref. Zhur. Khim.*, 1981, 21N45P
202. I Shikada, H Yagita, K Fujimoto, et al. *Chem. Lett.*, 1985(4) 547
203. USSR P. 977 002; *Byul. Izobret.*, 1982(4) 22
204. S B Dake, R V Chanduari *J. Mol. Catal.*, 1984, **26** 135
205. K Fujimoto, T Setoyama, H Tominaga *Chem. Lett.*, 1983(12) 1811
206. BRD Appl. 3 323 654.2; *Ref. Zhur. Khim.*, 1985, 20N49P
207. A L Lapidus, S D Pirozhkov, Z K Tyulyushova, et al. *Khimicheskikh Sintez na Osnove Odnouglerodnykh Molekul. Tezisy Dokladov Vsesoyuznogo Soveshchaniya* (Chemical Synthesis on the Basis of One-Carbon Molecules. Abstracts of Reports at the All-Union Conference), Izd. Nauka, Moscow, 1984, p. 42
208. Europ. P. 90 443; *Chem. Abs.*, 1984, **100** 191 388
209. D R Denley, R H Raymond, S C Tang *Springer Ser. Chem. Phys.*, 1983, Vol. 27, *(EXAFS) Near Edge Struct.*, p.325
210. K Fujimoto, T Shikada, K Omata, et al. *Ind. Eng. Chem. Prod. Res. Develop.*, 1982, **21** 429
211. US P. 4 484 002
212. Europ. P. 42 633; *Chem. Abs.*, 1982, 96 122 227
213. US P. 4 356 320
214. M S Scurell, S K Johnson, H Svendsen *Trudy V Mezhdunarodnogo Simpoziuma po Geterogennomu Katalizu v Varne* (Proceedings of the V-th International Symposium on Heterogeneous Catalysis in Varna), Sofia, 1983, Part 2, p. 39
215. US P. 4 321 211
216. Japanese Appl. 55-107 855; *Ref. Zhur. Khim., 1983, 9N78P*
217. T W Dekleva, D Forster *J. Amer. Chem. Soc.*, 1985, **107** 3568
218. *Res. Discl.*, 1981, **208** 327
219. G Doyle *J. Mol. Catal.*, 1981, **13** 237
220. Japanese Appl. 56-73040; *Ref. Zhur. Khim.*, 1982, 13N38P
221. Japanese P. 55-38942; *Ref. Zhur. Khim.*, 1981, 10N65P
222. Japanese Appl. 75 12 9 508; *Chem. Abs.*, 1976, **84** 43 354
223. Japanese P. 55-33380; *Ref. Zhur. Khim.*, 1981, 10N67P
224. US P. 4 244 882
225. *Chem. Age India*, 1976, **27** 729
226. A Krzymici M Marzewski *J. Mol. Catal.*, 1976, **6** 431
227. M S Scurell, R Howe *J. Mol. Catal.*, 1980, **7** 535
228. French Appl. 2 431 481; *Ref. Zhur. Khim.*, 1981, 3N37P
229. Japanese Appl. 56-104 839; *Ref. Zhur. Khim.*, 1982, 17N61P
230. Japanese Appl. 56-104 838; *Ref. Zhur. Khim.*, 1982, 20N21P
231. J Yemains, K C Lien, M Caracotsios, et al. *Eng. Comm.*, 1981, **11** 355
232. US P. 4 234 504
233. US P. 4 189 608
234. Japanese Appl. 57-175 140; *Ref. Zhur. Khim.*, 1980, 24N44P
235. US P. 4 218 340
236. BRD P. 3 043 112; *Chem. Abs.*, 1981, **95** 80 202
237. US P. 4 511 741
238. Japanese Appl. 58-14324; *Ref. Zhur. Khim.*, 1985, 16N53P
239. US P. 4 356 320 *Chem. Abs.*, 1982, **98** 4 312
240. US P. 4 212 989 *Chem. Abs.*, 1981, **93** 238 850
241. US P. 4 234 733

242. Japanese P. 53-12493; *Ref. Zhur. Khim.*, 1979, 12N46P
243. Europ. P. 75 337; *Chem. Abs.*, 1983, **99** 53156
244. Japanese Appl. 87 869; *Chem. Abs.*, 1984, **100** 5874
245. Japanese Appl. 58-144 347; *Chem. Abs.*, 1984, **100** 5877
246. I I Moiseev, E N Mokryi, O A Tagaev, et al. *Vestnik L'vov. Politekh. Inst.*, 1980, **139** 146
247. USSR P. 828 661; *Byul. Izobret.*, 1984(40) 195
248. USSR P. 784 285; *Byul. Izobret.*, 1984(40) 195
249. USSR P. 1 085 972; *Byul. Izobret.*, (14) 80
250. Japanese Appl. 55-160-743; *Ref. Zhur. Khim.*, 1981, 24N66P
251. Europ. P. 146 823; *Chem. Abs.*, 1985, **103** 177 967
252. BRD Appl. 2 914 671; *Ref. Zhur. Khim.*, 1981, 20N39P
253. Japanese Appl. 56-97245; *Ref. Zhur. Khim.*, 1981, 19N25P
254. Japanese Appl. 57-154142; *Ref. Zhur. Khim.*, 1984, 4N74P
255. Japanese Appl. 56-110641; *Ref. Zhur. Khim.*, 1982, 24N57P
256. M B Ordyan, A S Stepanyan, S D Pirozhkov, et al. *Zhur. Org. Khim.*, 1982, **18** 1634

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Activation of oxygen by metalloenzymes and their models

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ABSTRACT. Studies on the activation of molecular oxygen by metalloenzymes and their models are surveyed.
The bibliography includes 105 references.

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I. Introduction

The description of biological oxidation-reduction processes at the elementary step level is virtually impossible owing to the complexity of the protein objects studied, but the various kinds of model systems which reproduce in a simplified form particular functional features of biological systems can help.

In the present review, we shall confine ourselves to the examination of problems of the modelling of the elementary mechanisms of the action of metalloenzymes catalysing processes with participation of O_2.[1] Attention has been traditionally concentrated on these processes as a consequence of the great importance of O_2 for the vital activity of organisms, in connection with the prospect of using O_2 as an ecologically pure oxidant, and also because of the abundance of processes with participation of O_2 in the environment.

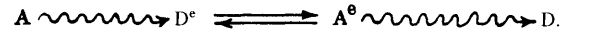
In examining metalloenzyme systems and their models, one must take into account the chemical and biological characteristics of each elementary step. The chemical characteristics are of a general character for many enzyme systems, while the biological characteristics define the specificity of the given system, determined by the structural features of the active centre and of the entire metalloenzyme molecule, and the dynamic properties of macromolecules with their multipoint intermolecular interactions. It would be premature to make any kind of generalisations for complex systems of this kind. On the other hand, the chemical characteristics of the elementary step make it possible to consider from general standpoints the mechanisms of oxidation-reduction reactions in both enzyme and model systems. This postulate constitutes the basis of the review. Its aim is an attempt to represent biological oxidation-reduction processes in terms of the electron transfer step.

The theory of outer-sphere electron transfer has been developed[2] and its quantitative aspect has been applied.[3]

Outer-sphere electron transfer takes place in a collision (unoriented and unstabilised) complex as a consequence of the fluctuations in the dipoles of the medium which equalise the energy levels of the initial and final states:[2,3]

$$A + D^e \rightarrow (A...D^e \longleftrightarrow A^e...D)^{\neq} \rightarrow A + D^e,$$

where A is the electron acceptor and D^e the one-electron donor. The energy of the reorganisation of the solvent in the outer-sphere electron transfer depends quadratically on the number of electrons transferred. By virtue of this, the transfer of two electrons via the outer sphere mechanism is relatively ineffective although it has been detected in many instances. On the other hand, when one speaks of reactions with participation of O_2, in enzyme systems its reduction takes place as a two-electron process with formation of $O_2^{2-}(H_2O_2)$ or effectively as a four-electron process with formation of $O^{2-}(H_2O)$. These reactions occur mostly as a result of the formation of complexes between O_2 and reduced variable valence metal ions—usually copper and iron ions. In general, one may call such reactions inner-sphere electron transfer reactions. Intramolecular electron transfer is sometimes also implied by the inner-sphere transfer:



Such transfer usually takes place either when the molecule contains bridging electron-conducting groups (with a "rigid" molecular structure) or as a result of intramolecular collisions of the donor–acceptor functional groups (flexible dynamic structure).

Consideration of complexes between electron-donating and electron-accepting species led Mulliken to introduce the concept of charge transfer complexes (CTC).[4,5] The studies by one of the authors of the present review have been devoted to the role of such complexes in oxidation-reduction reactions.[6,7] Subsequently oxidation-reduction reactions with participation of O_2 in model and enzyme systems were considered from the standpoint of ideas postulating intramolecular electron transfer as a chemical step in which the products of the final electron transfer are formed on decomposition of the intermediate donor–acceptor complex with *partial* charge transfer (PCTC):

$$A + D^e \rightleftarrows (AD)^e \rightarrow A^e + D,$$

where $(AD)^e$ is a PCTC with one-electron inner-sphere transfer.

The final two-electron process can be represented analogously:

$$A + D^{2e} \rightleftarrows (AD)^{2e} \rightarrow A^{2e} + D.$$

The fundamental difference between the "activated" collision complex and the PCTC consists in the mutual orientation of the donor and acceptor and the distance between them or, more precisely, in the extent of the electron-exchange interaction (V) of the donor–acceptor orbitals. In the outer-sphere case, the reactants approach one another to a distance $\gtrsim 4$ Å and $V < kT$; in the inner-sphere case, the distance between the reacting species is less than the sum of the van der Waals or ionic radii but is greater than the sum of the covalent radii of the atoms in contact, while the energy of the exchange donor–acceptor interaction exceeds the energy of the thermal motion: $kT < V \lesssim 10\ kT$. Evidently, depending on the values of V, the intermolecular transfer can take place either via the "outer-sphere" mechanism or via the "inner-sphere" mechanism [a partial charge transfer (PCT) state is produced]. Intramolecular electron transfer over long distances is the most typical property of biological electron-transport systems.

II. Characteristic features of inner-sphere electron transfer reactions and of intermediate complexes with partial charge transfer

We shall consider the distinctive features of the donor–acceptor PCTC by virtue of which they play an important role in metal complex and especially metalloenzyme catalysis. Their main feature is the existence of a rapidly established (thermal) equilibrium between the ground (N) and electronically excited (E) states. At the present time, complexes of this kind are referred to as examples of redox isomerism. In the ground state, the complex decomposes into the initial reactants, while in the electroncially excited state it decomposes into the electron transfer products:

$$A + D^{e} \rightleftarrows (AD)^{e}_{N} \overset{kT}{\rightleftarrows} (AD)^{e}_{E} \rightarrow A^{e} + D,$$
$$A + D^{2e} \rightleftarrows (AD)^{2e}_{N} \overset{kT}{\rightleftarrows} (AD)^{2e}_{E} \rightarrow A^{2e} + D.$$

As a result, the PCTC can interact with any "third" species and, existing simultaneously in two (ground and electronically excited) states, it can manifest the properties of both the initial reacting species and of the electron transfer products. Such "duality" in the properties of the PCTC has been clearly interpreted in terms of the ideas of Mulliken's resonance theory,[4,5] according to which the PCTC can be represented by a "superposition" of states without charge transfer and with complete charge transfer:

$$(AD)^{e} \equiv (AD^{e} \longleftrightarrow A^{e}D),$$
$$(AD)^{2e} \equiv (AD^{2e} \longleftrightarrow A^{2e}D).$$

Identical contributions of the limiting structures obtain when the energies of the donor–acceptor pair without (i) and with (f) complete charge transfer in the absence of electron-exchange interaction are equal.[6,8] The difference between the energies of these states (ΔH_e) can be estimated from thermodynamic considerations:[5]

$$\Delta H_e \simeq \Delta\sigma^0_{el} + RT \ln (K_{c,i}/K_{c,f}),$$

where $\Delta\sigma_{el}$ is the difference between the redox potentials of the donor and the acceptor and the constants K_c are the stability constants of the hypothetical complexes of the initial and final states. When the values of $K_{c,i}$ and $K_{c,f}$ are similar, the condition $\Delta H_e \simeq \Delta\sigma_{el} \simeq 0$ implies the approximate equality of the redox potentials of the partners involved in the bond:

$$\varphi_0(A/A^{e,2e}) \simeq \varphi_0(D^{e,2e}/D).$$

When the values of $K_{c,i}$ and $K_{c,f}$ or methods for their formation are available, account can be taken also of the contribution by the complex formation effect to ΔH_e.

The thermodynamic factor determines not only the properties of the PCTC (the degree of charge transfer in the ground and electronically excited states depends on ΔH_e) but also the relative probability of the decomposition into the electron transfer products.

The rate of the final electron transfer via the inner-sphere mechanism depends on the nature of the intermediate PCTC and the process thermodynamics. It is possible to differentiate two extreme cases:[8] the rate of the electron transfer is determined either by the rate of formation of the PCTC (as a rule when $\Delta\sigma^0_{el} < 0$) or by the rate of its decomposition into the electron transfer products (usually when $\Delta\sigma^0_{el} > 0$).

Since the properties of the PCTC and the probability of their decomposition into the electron transfer products depend on parameters such as ΔH_e and $\Delta\sigma^0_{el}$, there is a possibility of the operation of several "external" mechanisms whereby these parameters are influenced.

When ionic and highly polar reactants participate in the reactions, the values of $\Delta\sigma^0_{el}$ depend on the polarity of the medium. Solvation effects diminish ΔH_e and correspondingly increase the degree of charge transfer in the donor – acceptor complex. Appreciable changes in the polarity of the medium usually occur at the water–non-polar phase interface, as a result of which effective charge transfer, induced by relatively small movements of the reacting species in a medium with a polarity gradient, are to be expected in precisely such boundary regions.

Another pathway leading to the final electron transfer in PCTC is associated with the effects of the coupling of oxidation-reduction and acid–base reactions. The mechanism whereby a proton is supplied to the acceptor can be various: a proton can be drawn from the aqueous medium or from other proton donors in close proximity. The transition from an ionic to an electrically neutral reaction entails a sharp alteration of $\Delta\sigma^0_{el}$ and ΔH_e. In fact such energy coupling of electron and proton transfer appears as the transfer of a hydrogen atom in a one-electron process or of a hydride ion in a two-electron process. In protein macromolecules, there is an inter-relation between small local changes in the relative disposition of the atoms in the active centre and the change in the structure in the entire macromolecule.[9] As a result of this, there is a possibility of the energy coupling of the structural and electronic-structural characteristics accompanied by a change in V and $\Delta\sigma^0_{el}$. The dynamic conformational properties of the macromolecule thereby determine also its functional possibilities in effecting electron transfer. Any coupling merely "manifests" some property characteristic of the PCTC, while the essential feature of the inner-sphere electron transfer remains unaltered.

The intrinsic concept of an "inner-sphere" process refers usually to electron transfer reactions in the inner coordination spheres of transition metal ions.

In contrast to the intermolecular donor–acceptor (valence) bond, in the case of metal ions the coordinate bond is collective in character. By virtue of this feature, appreciable changes in the geometrical and electronic structures of the complex can occur without appreciable energy expenditure.[11] Two consequences of such collective binding are very important for the occurrence of "true" inner-sphere electron transfer reactions.

The first concerns the dynamic character of the metal–ligand bond: despite the high strength of each bond considered separately, in the absence of steric limitations or chelation the complex ion exists permanently in the state of ligand exchange. This occurs either as a result of conformational instability (the dynamic Jahn–Teller effect)[12] or as a result of transitions between close conformationally excited states of the complex differing in the symmetry of the ligand environment and hence in the electronic-structural characteristics of the central ion.[9] In transition metal ions, there may be three types of conformationally excited states:

(1) For an unchanged coordination number (CN), only the symmetry of the ligand environment changes, which can entail a change in the spin state and population of the *d* orbitals of the central ion.

(2) In conformational excitation, the CN increases by 1 or 2—vacant sites appear in the coordination sphere and are available for the introduction of one or two ligands.

(3) On conformational excitation, the CN diminishes by 1 or 2—the dissociation of the ligands (one or two) takes place.

The second consequence is associated with the possibility of identifying the donor–acceptor bond between the metal ion and the redox ligand as a "valence" bond. Bearing in mind the limitations to the strength of such a bond ($V \lesssim 10\ kT$) and the types of conformationally-excited states of the metal complex ion quoted above, one can infer *a priori* the presence or absence of sites in the coordination sphere of the metal ion potentially vacant and available for the binding of a redox ligand with formation of a coordination PCTC.[9]

Variable-valence metal ions in the oxidised state (M^{2+}) are usually coordinatively unsaturated to the maximum extent. In this case the incorporation of redox ligands—two-electron donors (D^{2-})—in the inner coordination sphere is possible only via the ligand substitution mechanism:

$$LM^{2+} + D^{2+} \overset{-L}{\rightleftarrows} MD \rightleftarrows M^{+} + D^{\cdot-}.$$

On the other hand, in the reduced form, metals frequently have potentially vacant sites for the binding of a redox ligand. The incorporation of the ligand in the inner coordination sphere takes place in this case via a mechanism of the oxidative addition type:

$$LM^{+} + A \rightleftarrows L(MA)^{+} \rightarrow LM^{2+} + A^{\cdot-}.$$

If A is a two-electron acceptor, there is a possibility of an inner-sphere two-electron transfer with formation of the metal ion in the superoxidised state M^{3+}:

$$M^{+} + A \rightleftarrows MA^{+} \rightleftarrows M^{3+} + A^{2-}.$$

An inner-sphere two-electron reaction can take place analogously also in the interaction of the M^{3+} ion with a two-electron donor D^{2-}:

$$M^{3+} + D^{2-} \rightleftarrows MD \rightarrow M^{+} + D.$$

In each of the examples of the one- and two-electron inner-sphere transfer, the intermediate complex exists simultaneously in the ground and electronically excited states, decomposing respectively into the initial reactants or the electron transfer products. In order to have a clear idea about the nature of the PCTC, the initial reactants from which it is formed, and the products into which it decomposes, in describing the PCTC it is convenient to use Mulliken's terminology,[5] defining "limiting structures" as respectively the initial reactants and the products of the final electron transfer. In this case, the intermediate binary PCTC with inner-sphere one- or two-electron transfer can be represented as a "superposition" of structures without and with complete charge transfer:

$$(MA^{+})_{I} = (M^{+}A \leftrightarrow M^{3+}A^{2-}),$$
$$(MA^{+})_{II} = (M^{+}A \leftrightarrow M^{2+}A^{\cdot-}),$$
$$MD = (M^{2+}D^{2-} \leftrightarrow M^{+}D^{\cdot-},$$
$$MD^{+} = (M^{3+}D^{2-} \leftrightarrow M^{+}D).$$

The double arrow between states without charge transfer (initial reactants) and those with full charge transfer (products) reflects here the mixing of these two stages on formation of the PCTC.

Ternary PCTC can include either one or two metal ions. In the former case, inner-sphere electron transfer takes place in the coordination sphere of one metal ion. Such complexes are formed in the interaction of binary PCTC with a redox ligand. Accordingly, four types of ternary complexes can be formed:

$$(DMA^{-})_{I} = (D^{2-}M^{+}A \leftrightarrow D^{\cdot-}M^{2+}A^{2-} \leftrightarrow DM^{+}A^{2-}),$$
$$(DMA^{-})_{II} = (D^{2-}M^{+}A \leftrightarrow D^{\cdot-}M^{+}A^{\cdot-} \leftrightarrow D^{\cdot-}M^{2+}A^{2-} \leftrightarrow DM + A^{2-}),$$
$$(AMD) = (AM^{2+}D^{2-} \leftrightarrow A^{\cdot-}M^{2+}D^{\cdot-} \leftrightarrow A^{\cdot-}MD \leftrightarrow A^{2-}M^{2+}D),$$
$$(AMD^{+}) = (AM^{3+}D^{2-} \leftrightarrow A^{\cdot-}M^{2+}D \leftrightarrow A^{\cdot-}M^{3+}D^{\cdot-} \leftrightarrow A^{2-}M^{3+}D).$$

Their decomposition into particular electron transfer products is determined by the corresponding values of $\Delta\sigma^{0}_{el}$ and can be controlled by the energy coupling effect manifesting particular "limiting" structures.

A second metal ion can also play the role of a redox partner in the binary PCTC with the resulting formation of dinuclear bridged PCTC:

$$M^{+} + (MA^{+})_{II} \rightleftarrows (MAM)^{2+} \rightarrow 2M^{2+} + A^{2-},$$
$$MD + M^{2+} \rightleftarrows (MDM)^{2+} \rightarrow 2M^{+} + D,$$
$$M^{+} + M(A{-}{-}A)^{+}_{I} \rightleftarrows (MA{-}{-}AM)^{2\cdot} \rightarrow 2(MA^{+})_{I} \rightarrow 2M^{3+} + 2A^{2-},$$
$$MD^{+} + MD^{+} \rightleftarrows (MD-DM)^{2+} \rightarrow 2M^{+} + D-D.$$

Dinuclear bridged PCTC can be formed also in the interaction of the initial dinuclear metal complex ion (ion pair) with the corresponding redox ligand:

$$\underset{\text{|———|}}{M^{+}\ldots M^{+}} + A \rightleftarrows \underset{\text{|——|}}{(MAM)^{2+}} \rightarrow \underset{\text{|———|}}{M^{2+}\ldots M^{2+}} + A^{2-},$$
$$\underset{\text{|——|}}{M^{2+}\ldots M^{2+}} + D^{2-} \rightleftarrows \underset{\text{|—|}}{(MDM)^{2+}} \rightarrow \underset{\text{|——|}}{M^{+}\ldots M^{+}} + D.$$

Polynuclear cluster complexes with a strong metal–metal bond can also participate in energy coupling effects:

$$-M^{+}-M^{+} + A \rightleftarrows (-MMA)^{2+} \rightarrow -M^{2+}-M^{2+} + A^{2-},$$
$$-M^{2+}-M^{2+} + D^{2-} \rightleftarrows -M^{+}-M^{+} + D.$$
$$\uparrow$$
$$\rightleftarrows (-MMD)^{2+} \rightleftarrows$$

The above schemes describe in a general form virtually all cases of the formation of molecular and coordination PCTC in oxidation-reduction reactions.

The proposed classification of the PCTC is useful when the nature, properties, and reactivities of the intermediate complexes formed in catalytic redox reactions are considered. In fact, knowing the structural and energy characteristics of the metal ion and the redox ligand, it is possible to predict the possibility of the formation of the PCTC, its reactivity in relation to "third" species, the preferred decomposition channels, and the rate constant for the final electron transfer.[7,10] Ideas about PCTC have proved extremely productive in the analysis of both the general questions and specific examples of the activation of molecular oxygen by variable valence metal ions.[7]

III. The ligand properties of molecular oxygen and the reactivity of metal—oxygen complexes

Molecular oxygen is a redox ligand without unshared electron pairs for the formation of the usual (σ-donor) coordinate bond. By virtue of this factor, the incorporation of O_2 in the coordination sphere of a metal ion is possible only at a potentially vacant site in the conformationally excited complex. A donor-acceptor metal—oxygen bond is formed on partial transfer of one or two electrons from the t_{2g} orbital of a metal ion, which existed initially in the reduced form, to the antibonding orbitals of the O_2 molecule.

This question has been investigated in detail[9,13,14] and we shall consider only the geometrical structure of the metal—oxygen complexes. It follows from symmetry considerations that the combination of the $\pi^*(O_2)$ and $t_{2g}(M^+)$ orbitals can be achieved in two ways—with retention or breakdown of the equivalence of the O atoms. In the former case, the product is only PCTC of the peroxy-type (oxygen acting as a bidentate ligand) with inner-sphere two-electron transfer:

$$(MO_2^+)_I = \left(M^+ \cdots \begin{matrix} O \\ \| \\ O \end{matrix} \longleftrightarrow M^{3+} \begin{matrix} O^- \\ | \\ O^- \end{matrix} \right)$$

The latter case involves a one-electron transfer with formation of a complex of the superoxide type (oxygen acting as a monodentate ligand) with a "linear" structure:

$$(MO_2^+)_{II} = \left(M^+ \cdots \overset{O}{\overset{\|}{O}} \ (^1\Delta) \longleftrightarrow M^{2+} - \overset{O^-}{O} \right).$$

The establishment of singlet oxygen (sp^2-hybridisation of the atomic orbitals) in a complex of the "superoxide" type has been confirmed by the results of quantum-chemical calculations[15] and by direct measurements using IR spectroscopic methods.[16] Together with the singlet oxygen structure, the presence of the superoxide radical has been detected in the complexes with the "linear" structure.[17,18]

Complexes of the "superoxide" type have been isolated in the solid state for Co^{2+} (d^7) and Fe^{2+} (d^6) ions[16] in a planar ligand environment: salicylideneamines, porphyrins, and other macrocyclic ligands. Many such complexes have been characterised in solution by EPR. These are $(OH^-)Ti^{4+}O_2^-$,[19] Mn^{3+}(porphyrin)O_2^-,[20] Co^{3+}(corrin)O_2^{2-}, vitamin B_{12},[21] $Sn^{4+}O_2^-$,[22] etc. Analogous metal—oxygen complexes are formed in the interaction of HO_2 with Ti^{4+} [23] and other d^0 elements (V^{5+}, Zr^{4+}, U^{6+}, Th^{4+}, Mo^{6+}) [23-25] and also in the interaction of vitamin B_{12} in the oxidised form with the O_2^- radical-ion.[26]

The equivalence of the O atoms in the complex with the "linear" structure is attained only on formation of dinuclear μ-peroxo-complexes:

$$(MOM)^{2+} = \left(M^+ \cdots \overset{O \cdots M^+}{\overset{\|}{O}} \longleftrightarrow M^{3+} - \overset{O^- - M^{3+}}{O^-} \right).$$

Complexes of this type are most characterstic of ions with the d^7 electronic configuration (Co^{2+}) [27,28] and also with the d^5 electronic configuration: Mn^{2+}(phthalocyanine) in the presence of pyridine[29] and Ru^{2+} + EDTA in an alkaline medium.[30,31] Analogous complexes are formed in the interaction of Ru^{3+} EDTA with H_2O_2.[31] The formation of dinuclear μ-peroxo-complexes is possible also for M^+ ions with the d^9, d^{10} electronic configuration.

The preferential formation of a particular type of oxygen complex depends on the presence of one or two potentially vacant sites in the coordination sphere of the metal ion and on the value of $\Delta\sigma_{el}^0$ for the corresponding electron transfer reaction.

Although the binding of O_2 in complexes with variable valence metals is of intrinsic interest as regards the study of natural O_2 transferring agents,[14] the question of the activation of O_2 as an oxidant is more significant. The complete or partial reduction of O_2 to reactive products such as HO_2 and OH leads to the activation of O_2. Attention should be drawn to the fact that, the higher the reactivity of the intermediate species, the smaller the chance of its being detected or isolated in the solid state. The "unobserved" oxygen complexes can therefore play a role in the activation of O_2.

From the standpoint of the PCT concept, the reactivity of coordinated oxygen is determined by the nature of the oxygen complex and the possibility of the incorporation of the oxidised substrate in the inner coordination sphere of the metal ion.

In the case of complexes of the "superoxide" type, reactions of three kinds are most characteristic.

1. Outer-sphere electron transfer reactions similar to the reactions of the superoxide radical-ion[32] but occurring much more effectively as a consequence of the increase in the redox potential of the oxygen coordinated to the highly charged central ion:

$$(MO_2^+)_{II} + D^{2-} \rightarrow MO_2 + D^-.$$

(2) Inner-sphere redox reactions for the *cis*-coordination of the oxidised substrate: in this case the incorporation of the substrate in the inner coordination sphere is possible either at a potentially vacant site or via the ligand substitution mechanism in the *cis*-position relative to the coordinated oxygen:

$$(MO_2^+)_{II} + RH \rightleftarrows (MO_2RH)^+ \begin{cases} \longrightarrow M^{3+} + HO_2^- + R' \\ \longrightarrow M^+ + HO_2 + R' \\ \longrightarrow M^+ + H_2O_2 + \text{product}. \end{cases}$$

The latter reaction is of greatest interest, since it entails the two-electron oxidation of the substrate in the inner coordination sphere of the metal ion with formation of hydrogen peroxide as the O_2 reduction product and without the final change in the (reduced) oxidation state of the metal ion. Such a reaction has been discovered in the oxidation of ascorbic acid by copper ions[7,33-36] and in the oxidation of methanol by the complexes $L_2Cu^+O_2$ (L = 2,2'-bipyridyl).[37]

When the substrate has reducing (DH^-) and ligand properties, there is a possibility of the formation of a ternary PCTC and the substrate can be bound to the metal also before the interaction with O_2.

(3) Inner-sphere redox reactions with a second metal ion. These are common in autoxidation processes:

$$(MO_2^+)_{II} + M^+ \xrightarrow{2H^+} 2M^{2+} + H_2O_2.$$

Two M^+ ions may exist also in a "pair":

$$M^+ \ldots M^+ + O_2 \rightleftarrows (M{-}O_2{-}M)^{2+} \begin{cases} \xrightarrow{2H^+} M^{2+}M^{2+} + H_2O_2 \\ \xrightarrow{2H^+} M^{2+}M^{2+} + 2H_2O \end{cases}$$

The reactivity of mononuclear oxygen complexes of the peroxy-type is due to two factors.

(1) The manifestation by such complexes of the reactive properties of metal ions in the superoxidised state as one- and two-electron acceptors. The formation of superoxidised states of the metal ion can be accompanied by the complete or partial oxidation of the coordinated ligands. For example, the autoxidation of the complexes of Fe^{2+} with 1-hydrazinophthalazine,[38] phosphines,[39] and EDTA is accompanied by inner-sphere oxidation of these ligands. The incorporation of a redox ligand in the coordination sphere is possible both in the interaction of M^+ with O_2 and after the binding of O_2 in a complex with the metal. A high reactivity in relation to H^+ and OH^- with the "appearance" of coordinated hydrogen peroxide or the superoxidised metal ion respectively is characteristic of complexes of the peroxy-type.

(2) In complexes with strong two-electron charge transfer, the dissociation of the O—O bond as a result of the stabilisation of O^{2-} with "partial" formation of atomic oxygen may prove to be more favourable than the hydrogen peroxide structure by virtue of the increase in the effective charge on the central metal ion, especially in weakly polar media:[40]

$$(MO_2^+)_I = \left(M^+ \ldots \overset{O}{\underset{O}{\|}} \longleftrightarrow M^{3+}\!\!<\!\!\begin{matrix} O^- \\ | \\ O^- \end{matrix} \longleftrightarrow M^{3+}\!\!:\!\!\begin{matrix} O^{2-} \\ | \\ O \end{matrix} \right).$$

Accordingly, complexes of the peroxy-type with strong charge transfer can exhibit the reactivity characteristic of the superoxidised metal ion and can participate, like atomic oxygen, in substrate hydroxylation and epoxidation reactions.

Among the model hydroxylating systems based on O_2, the Fe^{3+}/Fe^{2+}—EDTA—ascorbic acid (DH_2) system, discovered in 1954 by Udenfriend[41] and catalysing reactions of the type

$$RH + DH_2 + O_2 \rightarrow ROH + D + H_2O$$

has been most widely investigated. The role of the electron donor in this reaction reduces to regenerating the reduced form of the iron ethylenediaminetetra-acetate complex participating in the activation of O_2 with formation of an oxygen complex of the peroxy-type.

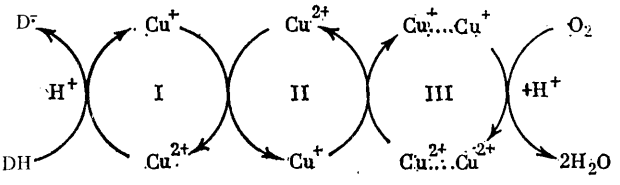
IV. Activation of oxygen by metal-containing enzymes

The biological catalysts and processes involving oxidation by molecular oxygen are widely distributed in nature. Resorting to the ideas and characteristic mechanisms of the activation of O_2 described above, we shall consider metal-containing enzymes—oxidases and oxygenases. The former use oxygen as an electron acceptor and the latter use it as a donor of an O atom.[42]

Oxidases—the catalysts of the four-electron reduction of O_2 to water—have been most thoroughly investigated: laccase, ascorbate oxidase, and cytochrome *c* oxidase. A characteristic feature of all these enzymes is the separation in space of the centres for the transformation of the substrate and reduction of O_2.

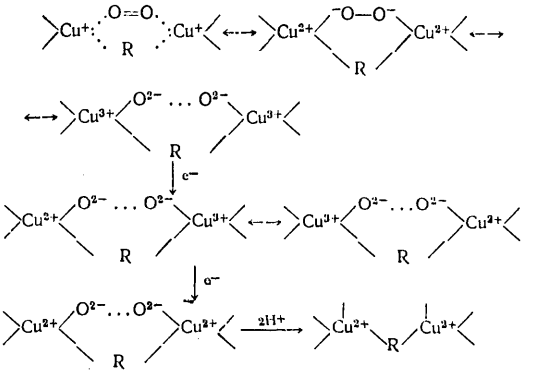
Thue "blue oxidases" (laccase, ascorbate oxidase) contain copper ions of three types: EPR-detectable "blue" [type (I)] and "non-blue" [type (II)] Cu^{2+} ions as well as a pair of Cu^{2+} ions [type (III)] which are not detectable by EPR.[43] In these oxidases, there is direct electron transfer between copper ions of types (I) and (II) and between types (II) and (III).[44] In fact, O_2 is not activated in the substrate oxidation process for this group of enzymes. The role of O_2 consists in the regeneration of the oxidised form of the enzyme. The rate of the enzyme reaction is limited by the interaction of the substrate with the "blue" Cu^{2+} ion, while the rate of regeneration of the oxidised form of the oxidase is limited by the interaction of O_2 with the reduced type (III) ions.

The mechanism of the action of laccase and ascorbate oxidase is of the same type and includes the usual cyclic scheme involving the alternate oxidation of the substrate and reduction of O_2:



The reduced enzyme is oxidised via the intermediate formation of a dinuclear μ-peroxo-complex analogous to the complexes of O_2 with the copper-containing O_2 transferring agent (haemocyanine) and ceruloplasmin.[42] The reduction of the bridging hydrogen peroxide in such a complex to water requires the transfer of two additional electrons from the substrate binding centre. Such electron transport takes place via a "non-blue" copper ion in the case of laccase and ascorbate oxidase.

Within the framework of the concept of the PCTC, the mechanism of the four-electron reduction of O_2 in "blue" oxidases can be represented by a sequence of the following inner-sphere reactions of type (III) ions:



R = bridging ligand.

The inner-sphere two-electron oxidation of each copper ion in the dinuclear complex is called upon to play a stabilising role by virtue of the inertness of Cu^{2+} [Cu^{3+}? (Ed. of Translation)] in ligand substitution reactions. In the binding of O_2, the rate of the intermolecular electron transfer from the centre (I) to the centre (III) increases by two orders of magnitude,[42] which apparently in fact ensures the possibility of the four-electron reduction of O_2 before the complex decomposes to H_2O_2 via the μ-peroxo-complex state.

A copper–polymer complex (Cu^{2+}–polyvinylpyridine) is a functional model of ascorbate oxidase:[44,45] in its presence, ascorbate anions are oxidised via a one-electron process and O_2^- radical-ions do not migrate outside the limits of the macromolecular coil because of the high local concentration of copper ions in the metal–polymer complex.

Cytochrome *c* oxidase is an enzyme which plays an important role in respiratory processes, catalysing the oxidation of cytochrome *c*:

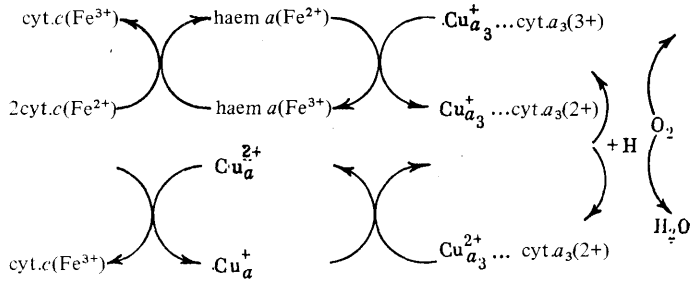
$$4\text{cytochrome } c(2+) + 4H^+ \rightarrow 4\text{cytochrome } c(3+) + H_2O.$$

It has been established by EPR that two magnetically isolated centres enter into the composition of the enzyme—the low-spin cytochrome *a* and Cu_a ($S = 1/2$; $\varphi_0 = 0.25$ V) as well as the $S = 2$ centre due to the antiferromagnetic coupling of cytochrome a_3 ($S = 5/2$) and Cu_{a_3} ($S = 1/2$), separated by a distance of 5 Å ($\varphi_0 = 0.35$ V).[46] These two centres are apparently linked via a bridge comprising a common ligand-oxygen (cytochrome a_3-O-Cu^{2+}), imidazole, or sulphur.[47–52] However, in the study of various synthetic imidazole-bridged dimers, it was demonstrated by measurements of the magnetic susceptibility between 4 and 300 K that the antiferromagnetic coupling does not correspond to that observed in cytochrome *c* oxidase ($-J > 200$ cm^{-1}).[52] It is most likely that in the oxidised enzyme the cytochrome a_3 and Cu_{a_3} centres are linked via oxygen or sulphur atoms.[49] The ligands in Cu_a are cysteine and histidine residues.[53] There is a haem–haem interaction between cytochromes *a* and a_3 accompanied by a change from the high-spin to the low-spin state of iron in cytochrome a_3 as the molecular environment in haem *a* is altered.[54] The study of the partly reduced form of cytochrome *c* oxidase demonstrated the presence of reduced low-spin haem iron, type (I) copper ions in the reduced form, and the high-spin ferrihaem a_3. Both the oxidised and the one-electron reduced enzymes oxidise cytochrome *c* also in the absence of O_2. The two-electron reduction of the oxidised form of cytochrome *c* oxidase converts it into the active form. The subsequent reduction is not significant for the manifestation of catalytic activity.

The activation of the enzyme is apparently associated with the reduction of a dinuclear haem a_3–Cu centre, which results in the possibility of the incorporation of O_2 in the coordination spheres of copper and iron ions as a bridging ligand.

In the functioning of the enzyme, haem *a* and Cu_a are independent electron acceptors on contact with the substrate, while haem a_3 and Cu_{a_3} form jointly a dinuclear O_2 binding centre.[53,55] Experiments with cross-link reactants established that the electron transfer from the haem of ferrocytochrome *c* to the haem *a* of cytochrome *c* oxidase takes place over a long distance and at a constant rate close to the rate of diffusion. The interaction of cytochrome *c* with the Cu_a centre takes place independently but much more slowly than the interaction with haem *a*.[53]

Structural studies have shown that the plane of haem *a* is at right angles to the plane of the phospholipid membrane near the water–non-polar phase interface, i.e. in the region of a dielectric constant gradient in the medium. The "cooperation" with electron transfer as a result of low changes in the polarity of the medium, mentioned previously, is thereby achieved for this enzyme. The "proton cooperation" in the stage involving the reduction of O_2 to water is also significant for the functioning of the enzyme.[55,56] The mechanism of the action of cytochrome *c* oxidase can be represented by a scheme analogous to that presented for ascorbate oxidase:

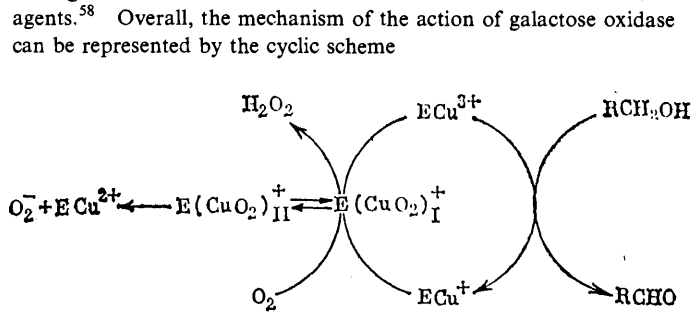


In the reduction of the bridging oxygen molecule to H_2O, three intermediate compounds are distinguished: $[Fe_{a_3}-O-O-Cu_{a_3}]^{3+}$, $[Fe_{a_3}-O-O-Cu_{a_3}]^{2+}$, and $[Fe_{a_3}-O-O-Cu_{a_3}]^{+}$.[57] These forms can be regarded as dinuclear PCTC.

It follows from the mechanisms of the action of oxidases presented that the metal ion in the oxidised form (Cu^{2+} or Fe^{3+}) participates in the oxidation of the substrate–electron donor (cytochrome *c*) or H atom (ascorbate), while a pair of metal ions in the reduced form, forming a relatively stable intermediate μ-peroxo-complex, participates in the reduction of O_2 to H_2O. The proton cooperation by the medium plays an important role in the subsequent reduction of this complex.

The metalloenzymes catalysing the reduction of O_2 to H_2O_2 contain in the active centre as a rule one "non-blue" copper ion [type (II)]. Certain amino-oxidases, galactose oxidase, and uricase are representatives of this group of "colourless" enzymes. The mechanism of the action of enzymes of this group can be various.

In the case of the galactose oxidase, the catalytic cycle includes the Cu(I) and Cu(III) enzyme forms, i.e. Cu(I) interacts with O_2 via the inner-sphere two-electron transfer mechanism. The formation of oxygen complexes of the peroxy-type is characteristic of copper(I) ions, but in the absence of the substrate they are readily transformed into complexes of the superoxide type.[58] The copper(II) formed on dissociation of this form of the enzyme is catalytically inactive. The inactive Cu(II) and the active Cu(III) forms of the enzyme can undergo interconversions under the influence of one-electron redox agents.[58] Overall, the mechanism of the action of galactose oxidase can be represented by the cyclic scheme



E = protein ligand

The copper ion in the superoxidised state functions as the oxidant species.

Reactions of this type have been modelled for the oxidation of ascorbic and dihydroxyfumaric acids and methanol using aquocopper ions and copper complexes of 2,2′-bipyridyl.[9]

In the case of the enzyme uricase, O_2 is activated as a result of the formation of a metal–oxygen complex of the superoxide type:

$$Cu\,(I) + O_2 \rightarrow CuO_2^{\cdot}(II),$$

$$CuO_2\,(II) + \text{substrate} \rightarrow Cu\,(I) + H_2O + \text{product}.$$

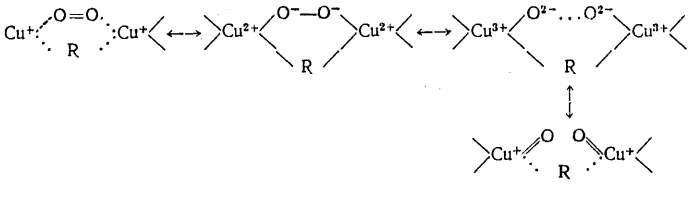
Here the oxidant species is a metal–oxygen complex of the "superoxide" type.[59]

Xanthine oxidase is the enzyme which catalyses the oxidation of hypoxanthine to xanthine and of xanthine to uric acid.[60] Xanthine oxidase is frequently used to generate O_2 radicals. The active centre incorporates a molybdenum ion, iron sulphur clusters (eight paired Fe atoms), and two FAD molecules. When FAD is removed, the enzyme loses its ability to reduce O_2 but retains its ability to oxidise xanthine. The function of molybdenum thus reduces to oxidising the substrate and the function of the iron–sulphur clusters is to transfer an electron from the reduced molybdenum to FAD, which in fact participates in the reduction of O_2. As for other FAD-dependent oxidases, O_2 is reduced without the formation of a metal–oxygen complex.

Oxygenases can be divided into copper- and iron-containing enzymes. The most typical representatives of the copper-containing oxygenases are tyrosinases, characterised by a multiplicity of forms. The coordination environment of the copper ions in the active centre is similar for enzymes of different origin and is made up of four histidine residues. The inhibition of the enzyme activity of tyrosinases by carbon monoxide indicates the involvement of the reduced form of copper in the process mechanism.[61] The mechanism of the activation of O_2 by tyrosinases has not been established.

Tyrosinase exhibits both hydroxylating and oxidase activities.[62] In the reduced state, the enzyme is capable of reversible binding of O_2, the spectrum of oxytyrosinase resembling that of oxyhaemocyanine. Like the latter, oxytyrosinase decomposes reversibly to a Cu^{2+}-enzyme and H_2O_2.[63] It has been suggested[64,65] that the structure of oxytyrosinase resembles that of oxyhaemocyanine, i.e. the active centre of this enzyme contains two copper ions. This makes it necessary to postulate distinct oxidative properties in the dinuclear copper–oxygen complex. The detection of electrophilic intermediates in the mechanism of the action of tyrosinase[66–68] indicates the possible dissociation of the O–O bond in this complex with formation of species of the type $ECuO^+$.

Within the framework of the concept of PCTC, one can postulate the coexistence of the following states of oxytyrosinase:



R = bridging ligand.

In the presence of the corresponding substrates (mono- and di-phenols), oxytyrosinase exhibits either the properties of Cu^{3+} as an electron acceptor, similarly to the dinuclear centre of the "blue" oxidases, or the properties of an O donor as a hydroxylating species.

Another representative of copper-containing monoxygenases is dopamine β-hydroxylase containing one or two Cu^{2+} ions in the active centre.[64] The activation of the apoenzyme requires two copper ions.[65] Whereas tyrosinase does not require an extraneous electron donor, dopamine β-hydroxylase functions only in the presence of a donor (ascorbate),[42] which reduces the Cu^{2+}-enzyme to the Cu^+-form.

Among iron-containing oxygenases, one may distinguish aromatic aminoacid monoxygenases (phenylalanine 4-monoxygenase, tyrosinase monoxygenase, tryptophan 5-monoxygenase) and hydroxylating enzymes containing cytochrome P-450.

Pterin-dependent aromatic acid monoxygenases contain one non-haem iron ion (Fe^{2+}) in the active centre.

As for the copper-containing oxygenases, the mechanism of the activation of O_2 has not been established. There is only evidence for the formation of a multicomponent charge transfer complex[70] (enzyme, substrate, and a coenzyme as the electron donor), which can decompose in different ways on interaction with O_2. In particular, the oxidation of the coenzyme can lead to the formation of hydrogen peroxide. The influence of the addition of peroxidase and catalase on the process stoichiometry[70] shows that the mechanism of the action of the iron-containing monoxygenases O_2 may be activated both as a result of the formation of the peroxy-type oxygen complex FeO_2 and as a result of the interaction of the reduced enzyme–substrate complex with H_2O_2.

During the last twenty years, the attention of investigators was concentrated on the study of non-specific hydroxylating enzyme systems containing cytochrome P-450.[69,71–77] These enzymes are widely distributed in nature and participate not only in processes involving the hydroxylation of endogenic substrates but also in detoxication reactions of various xenobiotics.[78,79] O_2 and two reduced equivalents, usually NADPH, participate in the substrate hydroxylation processes:

$$SH + NADP\cdot H + H^+ \rightarrow SOH + H_2O + NADP^+.$$

The haem of cytochrome P-450 participates in the activation of O_2, its reduction occurring with the aid of the electron-transport (reductase) enzyme system.[42]

Bacterial cytochrome P-450 has been isolated in a crystalline form and characterised by X-ray diffraction with a resolution of 5.5 Å.[75] The haem iron ion in the active centres of cytochrome P-450 is coordinated to cysteine residues in the 5-position and histidine residues or water in the 6-positions, undergoing comparatively readily a change in the valence spin states. In the reduced form, the enzyme forms a complex with CO, which has an intense absorption band at 447 nm and this has in fact given rise to the name of this group of haemoproteins. Oxidised cytochrome P-450 exists in a low-spin state and, on binding the substrate, it is fully or partly (depending on the temperature, pH, the polarity of the medium, and the nature of the substrate) converted into a high-spin (pentacoordinate) form. The structural aspects of cytochrome P-450 have been examined in reviews[80–83] and also in other communications.[84–90] In the reduced form, cytochrome P-450 exists predominantly in a high-spin state and readily interacts with O_2.[91]

The microsomal hydroxylating system in the liver contains, apart from cytochrome P-450, also NADPH-cytochrome P-450 reductase and phospholipids. The role of NADPH-cytochrome P-450 reductase consists in electron transport from NADPH to cytochrome P-450. The role of phospholipids in the hydroxylation process has not been ultimately elucidated. The phase transition in microsomal phospholipids at 16–25 °C alters sharply the activation characteristics of the oxidation substrates and in many instances leads to a change in the rate-limiting stage of the hydroxylation process. One cannot rule out the possibility that the effect of phospholipids on microsomal oxidation processes is associated with the manifestation of the influence of the local changes in the polarity of the medium, noted above, and the probability of electron transfer. The influence of certain lipids on the conformational states and the equilibrium involving the spin forms of cytochrome P-450 has been recorded.[92–97]

The mechanism of the enzyme reaction involves the formation of an enzyme-substrate complex with the oxidised form of cytochrome P-450 as a result of the binding of the substrate to a site adjoining haem. As a result of local structural changes, the cysteine ligand – iron ion distance changes and there is a corresponding alteration in the symmetry of the ligand environment, the spin state, and the redox characteristics of the iron ion.[98–100] After the one-electron reduction of the enzyme – substrate complex, Fe^{2+} – haem interacts with O_2 to form an oxygenated complex, which in many instances may be isolated and characterised spectroscopically.[101] The substrate is hydroxylated in the subsequent one-electron reduction of the oxygenated complex, which apparently takes place as a result of the formation of a peroxy-type iron – oxygen complex (with strong charge transfer) as the hydroxylating species.

In contrast to copper ions, whose oxidation state changes only within the limits $Cu^{+}-Cu^{3+}$, in the case of haem the range of the possible formal valence state extends from Fe^{+} to Fe^{6+}. Admittedly, the Fe^{3+} state is hardly realisable and in the $Fe^{5+,6+}$ state there is charge transfer from the porphyrin ligand to the central ion. The structural characteristics of iron-porphyrins (PFe) suggest the formation of a peroxy-type oxygen complex in the interaction of PFe^{2+} with O_2:[6]

$$(PFeO_2)^{2+}=P\left(Fe^{2+}\begin{matrix}O\\ \|\\ O\end{matrix}\longleftrightarrow Fe^{4+}\begin{matrix}O^{-}\\ |\\ O^{-}\end{matrix}\right)$$

The transfer of an additional charge to this complex leads formally either to the formation of the oxygen complex PFe^{+} or to the dissociation of the O – O bond in the limiting peroxy-structure:

$$P(FeO_2)^{+}=P\left(Fe^{+}\begin{matrix}O\\ \|\\ O\end{matrix}\longleftrightarrow Fe^{3+}\begin{matrix}O^{-}\\ |\\ O^{-}\end{matrix}\longleftrightarrow Fe^{3+}\begin{matrix}O^{2-}\\ \vdots\\ O\end{matrix}\longleftrightarrow Fe^{4+}\begin{matrix}O^{2-}\\ \vdots\\ O^{-}\end{matrix}\right)$$

On protonation of O^{2-}, the last two states are found to be stoichiometrically equivalent to the structure of compound (I) of peroxidase.[102]

The proportions of the "limiting" structures are determined by the structural-energetic characteristics of the enzyme – substrate complex and the polarity of the medium. The $PFe^{3+}O$ and $PFe^{4+}O^{-}$ states, which may be formed on protonation of a coordinated oxygen dianion, for example, via the transfer of H^{+} from an aminoacid in close proximity, are characterised by a high hydroxylating capacity. An oxenoid mechanism of the insertion of the O atom in a C – H bond is to be expected for the $PFe^{3+}O^{-}$ species and intramolecular oxidation of substrates by a radical mechanism is to be expected for species of the type $PFe^{4+}O^{-}$.[103] The ambiguity of the evidence concerning the radical or oxenoid mechanism of the hydroxylation of various substrates is apparently also associated with the "dual" reactivity of species of the type $PFeO^{3+}$.[42,104,105]

It is of interest to note that the oxidation of many substrates in the microsomal hydroxylating system takes place in the same way also in the presence of hydroperoxides instead of O_2. This indicates the presence of the same type of intermediate species in both systems. Thus the question of the activation of O_2 is indissolubly linked with the question of the activation of hydrogen peroxide in the case of cytochrome P-450 as well as other oxygenases.

References

1. B G Malmström *Ann. Rev. Biochem.*, 1982, **51** 21
2. R A Marcus *J. Chem. Phys.*, 1956, **24** 966
3. V M Berdnikov, G A Bogdanchikov *Zhur. Fiz. Khim.*, 1979, **53** 273 [*Russ. J. Phys. Chem.*, 1979(2)]
4. R S Mulliken *J. Amer. Chem. Soc.*, 1952, **74** 811
5. R S Mulliken, W B Person *Molecular Complexes*, Wiley Intersci., New York, 1969
6. Yu I Skurlatov *Uspekhi Khimii Kompleksov s Perenosom Zaryada i Ion Radikal'nykh Solei* (Advances in the Chemistry of Charge-Transfer Complexes and Radical-Ion Salts) (Edited by M L Khidekel' et al.), Chernogolovka, 1986, p. 164
7. Yu I Skurlatov, Doctoral Thesis in Chemical Sciences, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1980
8. R R Dogonadze, A M Kuznetsov *Kinetika Khimicheskikh Reaktsii v Polyarnykh Rastvoritelyakh. Fizicheskaya Khimiya, Kinetika* (Kinetics of Chemical Reactions in Polar Solvents. Physical Chemistry and Kinetics), Izd. VINITI, Moscow, 1973.
9. A Ya Sychev, S O Train, G G Duka, Yu I Skurlatov *Kataliticheskie Reaktsii i Okhrana Okruzhayushchei Sredy* (Catalytic Reactions and Protection of the Environment), Izd. Shtiintsa, Kishinev, 1983
10. M MacKinen *Methods and Advances in Bioinorganic Chemistry* (Translated into Russian), Izd. Mir, Moscow, 1978, p. 11
11. K I Zamaraev *Kinet. Katal.*, 1980, **21** 36
12. I B Bersuker *Stroenie i Svoistva Koordinatsionnykh Soedinenii* (The Structure and Properties of Coordination Compounds), Izd. Khimiya, Leningrad, 1975
13. V A Starodub, I V Krivoshei *Uspekhi Khimii Kompleksov s Perenosom Zaryada i Ion-Radikal'nykh Soelei* (Advances in the Chemistry of Charge-Transfer Complexes and Radical-Ion Salts) (Edited by M L Khidekel' et al.), Chernogolovka, 1986, p. 132
14. E Bayer, P Schretzman *Structure and Bonding* (Translated into Russian), Izd. Mir, Moscow, 1969, p. 273
15. K Fukui, S Inagaki *J. Amer. Chem. Soc.*, 1975, **97** 4445
16. J P Collman, R R Gange, C A Reed, et al. *J. Amer. Chem. Soc.*, 1975, **97** 1427
17. J H Bayston, N K King, F D Looney *J. Amer. Chem. Soc.*, 1969, **91** 2775
18. R J Wilkins *Adv. Chem. Ser.*, 1971, **100** 111

19. V M Berdnikov, P V Schastnev *Kinet. Katal.*, 1975, **16** 83
20. K O Ohkubo *Tetrahedron Lett.*, 1971, **39** 2899
21. J H Bayston, N K King, F D Looney, M E Winfield *J. Amer. Chem. Soc.*, 1969, **91** 2775
22. A P Moravskii, Candidate's Thesis in Chemical Sciences, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1975
23. W T Dixon, R C Norman *Nature*, 1962, **196** 891
24. V F Shuvalov, N M Bazhin *Zhur. Strukt. Khim.*, 1969, **10** 548
25. A Samuni, G Czapski *J. Phys. Chem.*, 1970, **74** 4592
26. J Ellis, J M Pratt, M Green *J. Chem. Soc., Chem. Commun.*, 1973, **70** 781
27. L Vaska, L S Chen, C V Senoff *Science*, 1971, **174** 587
28. Yu I Bratushko, K B Yatsimirskii *Uspekhi Khimii Koordinatsionnykh Soedinenii* (Advances in the Chemistry of Coordination Compounds), Izd. Naukova Dumka, Kiev, 1975, p. 7
29. J A Elvige, A B P Lever *Proc. Chem. Soc.*, 1959, 195
30. N A Ezerskaya, T P Solovykh *Zhur. Neorg. Khim.*, 1966, **11** 1462 [*Russ. J. Inorg. Chem.*, 1966(6)]
31. N A Ezerskaya, T P Solovykh *Zhur. Neorg. Khim.*, 1967, **12** 2922 [*Russ. J. Inorg. Chem.*, 1967(11)]
32. V M Berdnikov, L L Makarshin, L S Ryikina *React. Kinet. Catal. Lett.*, 1978, **3** 275
33. N V Gorbunova, A P Purmal', Yu I Skurlatov *Zhur. Fiz. Khim.*, 1975, **49** [*Russ. J. Phys. Chem.*, 1975( )]
34. N V Gorbunova, Yu I Skurlatov *Zhur. Fiz. Khim.*, 1977, **51**(4) 875 [*Russ. J. Phys. Chem.*, 1977(4)]
35. N V Gorbunova, Yu I Skurlatov *Khimicheskaya Kinetika i Kataliz* (Chemical Kinetics and Catalysis), Izd. Nauka, Moscow, 1979, p. 89
36. S O Travin, N V Gorbunova, Yu I Skurlatov *Zhur. Fiz. Khim.*, 1979, **53** 213 [*Russ. J. Phys. Chem.*, 1979(1)]
37. S O Travin, Yu I Skurlatov, N V Gorbunova, A P Purmal' *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, (7) 1480
38. D Walk, S Fallab *Helv. Chim. Acta*, 1970, **44**(1) 13
39. R P Hanzlik, D Williamson *J. Amer. Chem. Soc.*, 1976, **98** 6570
40. H S Mason *Adv. Enzymol.*, 1957, **19** 79
41. S Udenfriend, C T Clark, J Axelrood, B B Brodie *J. Biol. Chem.*, 1954, **208** 731
42. D I Matelitsa *Modelirovanie Okislitel'no-Vosstanovitel'nykh Fermentov* (Modelling of Oxidation-Reduction Enzymes), Izd. Nauka i Tekhnika, Minsk, 1984
43. H P Molitoris, B Reinhammar *Biochim. Biophys. Acta*, 1975, **386** 493
44. R Malkin, in *Inorganic Biochemistry* (Edited by G L Eichron), Izd. Mir, Moscow, 1978, Vol. 2
45. Yu I Skurlatov, Ya Kovner, S O Travin *Europ. Polym. J.*, 1979, **15** 811
46. A E Cass, P F Knowles *Inorganic Biochemistry*, The Royal Soc. Chem., London, 1981, Vol. 2, p. 151
47. C M Elliott, A Kozo *J Amer. Chem. Soc.*, 1982, **100** 2671
48. G Palmer, C T Babcock, L E Vicker *Proc. Nat. Acad. Sci.*, 1976, **73** 2206
49. K S Cynthia, A Kozo, C M Elliott, P A Oren *J. Amer. Chem. Soc.*, 1984, **106**
50. J G Maxwell, J B Kevin, S M Keith *J. Amer. Chem. Soc.*, 1984, **106** 4227
51. S E Dessens, C L Merrill, R J Saxton, et al. *J. Amer. Chem. Soc.*, 1982, **104** 4357
52. J T Landrum, C A Reed *J. Amer. Chem. Soc.*, 1978, **100** 3232
53. R A Capaldi, F Malatesta, U Darley *Biochim. Biophys. Acta*, 1983, **726** 135
54. J A Freedman, S H P Chan *J. Bioenerg. Biomembr.*, 1984, **16** 75
55. B G Malmströem *Biochim. Biophys. Acta*, 1985, **811** 1
56. B G Malmströem *Biochim. Biophys. Acta*, 1979, **549** 281
57. D F Blair, S N Witt, S J Chan *J. Amer. Chem. Soc.*, 1985, **107** 7389
58. G R Dyzkacz, R D Libby, G A Hamilton *J. Amer. Chem. Soc.*, 1976, **98** 626
59. O M Pitts, D G Priest, W W Fish *Biochemistry*, 1974, **13 888**
60. E Hodgson, T Fridovich *Arch. Biochem. Biophys.*, 1976, **172** 202
61. D Kertsz, R Zito *Biochim. Biophys. Acta*, 1965, **96** 447
62. V G Hearing, T M Ekel, P A Montague, J M Nicholson *Biochim. Biophys. Acta*, 1980, **611**
63. R L Jolley, L H Evans, H Makino, U S Mason *J. Biol. Chem.*, 1974, **249**
64. J J Villafrance *Copper Proteins* (Edited by T G Spiro), Wiley, New York, 1981, p. 265
65. N Y Blackburn, H S Mason, P F Knowles *Biochem. Biophys. Res. Commun.*, 1980, **95** 1275
66. W H Vanneste, A Zuberbuhler *Molecular Mechanism of Oxygen Activation* (Edited by O Hayaishi), Acad. Press, New York–London, 1974, p. 371
67. L L Ingraham *Biochemical Mechanisms* (Translated into Russian), Izd. Mir, Moscow, 1964, p. 100
68. D I Metelitsa, Doctoral Thesis in Chemical Sciences, Institute of Chemical Physics, USSR Academy of Sciences, Chernogolovka, 1975
69. D Dolphin, B R James *ACS Symp. Ser.*, 1983, 371
70. S Kaufman, D B Fisher *Molecular Mechanism of Oxygen Activation* (Edited by O Hayaishi), Acad. Press, New York–London, 1974, p. 205
71. J H Dawson, K S Eble *Advances in Inorganic and Bioinorganic Mechanisms* (Edited by A G Sykes), Acad. Press, New York, 1986, p. 1
72. E Hiefanen, M Laitinen, O Hanninen *Cytochrome P-450, Biochemistry, Biophysics and Environmental Implications*, Elsevier, Amsterdam, 1982
73. L S Alexander, H M Golf *J. Chem. Educ.*, 1982, **59** 179
74. R W Estabrook *Oxygenases and Oxygen Metabolism* (Edited by N Mitsuhiro), Acad. Press, New York, 1982, p. 37
75. I C Gunsalus *Fifth International Symposium on Microsomes and Drug Oxidation Abstracts*, Tokyo, 1981, p. 2
76. D Mansay *The Coordination Chemistry of Metalloenzymes* (Edited by J Bertini, et al.), Reidel, Dordrecht, Holland, 1983, p. 343
77. M J Coon *Trans. N. Y. Acad. Sci.*, 1983, **41** 1
78. K Ishihare, I Yamakawa, E Kusinose *J. Biochem.*, 1979, **86** 139
79. F P Guengerich, T L McDonald *Acc. Chem. Res.*, 1984, **17** 9
80. W R Scheidt, C A Reed *Chem. Rev.*, 1981, **81** 543
81. J E Hahn, K O Hodgson, L A Andersson, J H Dawson *J. Biol. Chem.*, 1982, **257** 10934
82. L A Andersson, M N Sono, J H Dawson *Biochim. Biophys. Acta*, 1983, **746**
83. D M Dooley, J H Dawson *Coord. Chem. Rev.*, 1984, **60** 1
84. P M Champson, B R Stallard, G C Wagner, J C Gunsalus *J. Amer. Chem. Soc.*, 1982, **104** 5469

85. J H Dawson, L A Andersson, M Sano *J. Biol. Chem.*, 1982, **257** 3606
86. J Peisach, W B Mims, J L Davis *J. Biol. Chem.*, 1979, **254** 12379
87. S E Groh, A Nagahisa, S L Tan, W H Orme-Johnson *J. Amer. Chem. Soc.*, 1983, **105** 7445
88. G R Janig, R Dettmer, S A Usanov, K Ruckpane *FEBS Lett.*, 1983, **159** 58
89. G R Janig, A Makower, H Rabe *Biochim. Biophys. Acta*, 1984, **784** 8
90. O Dippelt, J Fiscer, R Weiss *J. Amer. Chem. Soc.*, 1984, **106** 5188
91. P P Tamburini, G G Gibson, W L Backes *Biochemistry*, 1984, **23** 4526
92. Y L Chiang, M J Coon *Arch. Biochem. Biophys.*, 1979, **195** 178
93. T Y Tsong, C S Yang *Proc. Natl. Acad. Sci. USA*, 1978, **75** 5955
94. C S Yang, T Y Tsong *IV International Symposium on Microsomes and Drug Oxidations. Abstracts*, University of Michigan, Ann Arbor, USA, 1979, p. 79
95. A A Akhrem, P A Kiselev, M A Kisel', et al. *Dokl. Akad. Nauk SSSR*, 1979, **254**
96. G G Gibson, D L Cinti, S D Sligar, J B Schenkman *Biochem. Soc. Trans.*, 1979, **7** 1289
97. G G Gibson, D L Cinti, S D Sligar, J B Schenkman *J. Biol. Chem.*, 1980, **255**
98. S D Sligar, J C Gunsalus *Biochemistry*, 1979, **18** 2290
99. G G Gibson, P P Tamburini *Xenobiotica*, 1984, **14** 27
100. S D Sligar, D L Cinto, G Gibson, J B Schenkman *Biochem. Biophys. Res. Commun.*, 1979, **9** 925
101. J H Dawson, S P Cramer *FEBS Lett.*, 1979, **88** 127
102. M B McCarthy, R E White *J. Biol. Chem.*, 1983, **258** 9153
103. J T Groves, D V Subramanian *J. Amer. Chem. Soc.*, 1984, **106** 2177
104. R A Sheldon *J. Mol. Catal.*, 1983, **20** 1
105. E C Heinbrook, S D Sligar *Biochem. Biophys. Res. Commun.*, 1981, **9** 530

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Synthesis and properties of α-aminonitriles

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ABSTRACT. The information about the synthesis, chemical, physicochemical, and biological properties, and also the stereochemistry of α-aminonitriles has been classified. The bibliography includes 283 references.

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I. Introduction

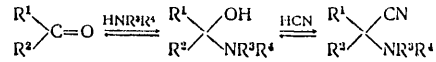
Throughout the period of over 130 years since their discovery, α-aminonitriles have been the subject of study for research scientists in different countries. There is continuous interest in this class of compounds mainly because they are intermediates in convenient preparative methods for obtaining α-amino acids [1] and nitrogen-containing heterocycles,[2] which are biologically important compounds. There has recently been a report about the possibility of the prebiological synthesis of the simplest example of an α-amino-nitrile—aminoacetonitrile—in an interstellar medium[3] as well as under conditions simulating the original atmosphere of the Earth.[4] There is theoretical interest in the mechanisms of the reactions used in the synthesis of α-aminonitriles and also the characteristics of the reactivity of the amino and cyano groups related to their close proximity in α-aminonitriles.

A brief review of methods for synthesising α-aminonitriles is given in one book.[5] The use of the Strecker reaction for obtaining α-aminonitriles has been examined.[6] A further review on α-amino-nitriles has been published in Danish[7] and is difficult to access as a literature source. Classification of the reactions involving α-amino-nitriles and examples of them have been reported in one study,[8] which, however, falls far short of including all known types of reactions of α-aminonitriles. The use of α-aminonitriles in organic synthesis is the topic of another review,[9] which appeared in Japanese in a journal that is difficult to obtain in the USSR.

II. Synthetic methods

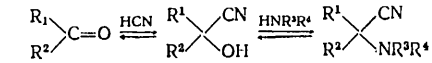
1. The Strecker reaction

In 1850 Strecker[10] carried out the synthesis of glycine and alanine by treatment of formaldehyde and acetaldehyde with aqueous solutions of ammonia and hydrocyanic acid followed by hydrolysis of the α-aminoacetonitrile and α-aminopropionitrile formed. This reaction was subsequently extended to ketones and amines and became known as the Strecker reaction.[11]



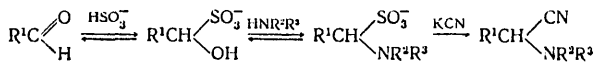
The replacement of volatile hydrocyanic acid and ammonia by a mixture of potassium or sodium cyanide and ammonium salts was proposed by Zelinskii and Stadnikov.[11] In this case ammonium chlorides or sulphates are reacted directly or are prepared *in situ*.

A modification of the Strecker reaction proposed by Tiemann[11] involves changing the order of mixing the reagents. It is suggested that the increase in yield of α-aminonitriles that often occurs in this case is due to participation of α-hydroxynitriles (cyanohydrins) (I) in the reaction.



(I)

When the aldehydes have low reactivity, their bisulphite adducts (II) are subjected to the Strecker reaction. When primary and secondary α-aminonitriles are prepared, the reaction is carried out in water with ammonium or alkylammonium salts in the presence of an excess of free base. This form of the Strecker reaction has become known as the Knoevenagel–Bucherer method.[6] The closest parallel with it in the Soviet literature[11] is given by the first two stages of the Bucherer–Bergs reaction,[12] in which adducts (II) are also frequently used.



(II)

In recent years the Strecker reaction itself[13–29] as well as the Zelinskii–Stadnikov,[6,16,30–48] Tiemann,[12,52–55] and Knoevenagel–Bucherer[6,55–58] modifications have been repeated many times on other substrates. Furthermore, the Strecker reaction in a broad sense has been considerably extended by the use of other solvents and sources of amino and cyano groups.

A number of syntheses of α-aminonitriles have been carried out under non-aqueous conditions—in alcohols,[29,59–64] tetrahydrofuran,[65] benzene,[66] in excess amine,[67] and also without any solvent.[68] When

the synthesis is carried out in liquid ammonia, it is necessary to use a low temperature and high pressure,[12,52,69] which makes it difficult to obtain primary α-aminonitriles by this method.[68] By using DMSO–H_2O (9 : 1, 19 : 1, and 20 : 1) systems as the solvent together with water and a water–methanol (1 : 1) mixture, it was possible to increase the yield of a number of α-aminonitriles by improving the solubility of the initial aldehydes.[70]

The role of water in the Strecker reaction is not simply that of a solvent. It was shown[67] that water, including that formed during the reaction, accelerates the epimerisation of a kinetically controlled α-aminonitrile and is therefore a catalyst for the process.

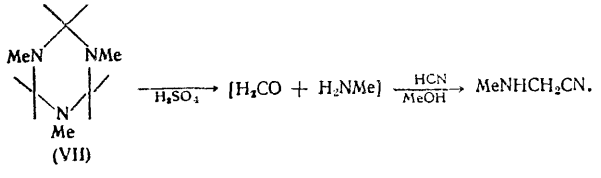
The nature of the products in the Strecker reaction is considerably affected by the pH of the medium, the ratio of reagents, and the reaction temperature. The primary or secondary α-aminonitriles formed initially are capable of undergoing a further *N*-α-cyanoalkylation reaction.[22–25,33–48,71,72] Thus in diamine (III) the hydrogen atoms of the primary amino groups are replaced first of all and then those of the secondary groups are replaced.[71] A high pH value of the medium helps to remove the primary α-aminonitrile (IV) from the reaction as an azomethine (V).[25,73] It is also possible to stop the process at the first or second stages by selecting the ratio of reagents[23,36,39,41,72] or the reaction temperature.[34,41] The exhaustive cyanomethylation of ammonia to give nitrilotriacetonitrile (VI) has been reported in a large number of patents.[22,23,33–48]

$$H_2NC_2H_4NH_2 \xrightarrow{H_2CO,HCN} NCCH_2NHC_2H_4CH_2CN \xrightarrow{H_2CO,HCN}$$
(III)
$$\rightarrow (NCCH_2)_2NC_2H_4N(CH_2CN)_2,$$

$$NH_3 + H_2CO + HCN \rightarrow H_2NCH_2CN \underset{H^+}{\overset{H_2CO}{\rightleftharpoons}} H_2C{=}NCH_2CN$$
(IV) (V)
$$\downarrow H_2CO, HCN$$
$$N(CH_2CN)_3 \xrightarrow{H_2CO,HCN} HN(CH_2CN)_2 \xrightarrow{H_2CO} H_4C(N(CH_2CN)_2)_2.$$
(VI)

N-α-polycyanoalkylation reactions are catalysed by alkali metal cyanides.[71]

It is possible to use paraformaldehyde instead of formaldehyde in the synthesis of α-aminonitriles (VI). Urotropine [37,41–43,45,74] and 1,3,5-trimethylhexahydro-*sym*-triazine (VII) [49] can serve at the same time as sources of both formaldehyde and ammonia or methylamine. The thermolysis of formamide is a convenient method in the preparative sense for generating a mixture of hydrogen cyanide and ammonia.[75]

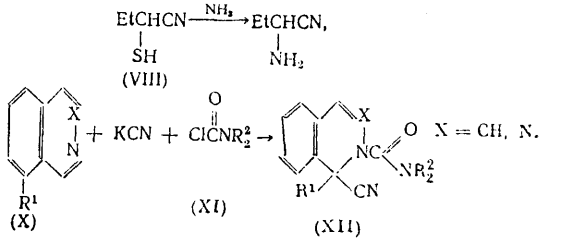


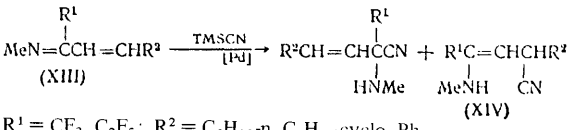
The most significant development of the Strecker reaction has been the introduction of new sources of cyano groups into synthetic use. Acetone cyanohydrin,[67,76,77] isobutyral cyanohydrin,[78] benzoyl cyanide,[79] diethylphosphonocyanide,[65] and trimethylsilyl cyanide (TMSCN) [59,60,68,80] have been used for this. The addition of TMSCN to aldehydes is catalysed by Lewis acids, in particular by zinc iodide,[59] and previously unobtainable α-aminonitriles can be prepared. However, this reagent is susceptible to hydrolysis, and therefore it is necessary to work under absolutely anhydrous conditions. The most acceptable methods for synthesising TMSCN are reported in two studies.[83,84]

A scheme for the extended Strecker reaction has been drawn up to take account of these changes (see Scheme 1 below).

All the reactions positioned on the scheme above the continuous line are reversible. Moreover, the synthesis of α-aminonitriles is also carried out from individual compounds shown on the scheme between the horizontal dotted line and the continuous line. Thus, for example, the amination of cyanohydrins (I) with ammonia or amines[12,25,30,52,53,60,62,64,69,85–96] and even the reaction of α-mercaptobutyronitrile (VIII) with ammonia[30] can be regarded as specific examples of the Tiemann reaction.

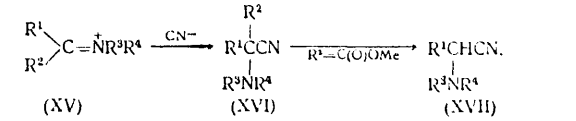
The use of Schiff bases such as (IX) [3,19,21,77,79,80,97–100] and hydrazones[101–103] as substrates of CN^- ions has been reported. Aromatic nitrogen-containing heterocycles (X) can be regarded as Schiff bases with an endocyclic C=N bond; when they are treated with potassium cyanide and *N*,*N*-disubstituted carbamoyl chlorides (XI), analogues of Reissert compounds (XII) are obtained.[104] When they are reacted with TMSCN in the presence of palladium compounds, azomethines (XIII) also exhibit properties of 1-aza-1,3-dienes, leading to the formation of by-products (XIV) from 1,4-addition.[100]





$R^1 = CF_3, C_2F_5$; $R^2 = C_6H_{13}$-n, C_6H_{11}-cyclo, Ph,
HC = CHMe-*trans*.

According to the modified method of Polonovskii–Potier[105] iminium salts of the type (XV) obtained *in situ* are treated with KCN. When a methoxycarbonyl group is present on the reaction centre it can be eliminated, and as a result demethoxycarbonylation products (XVII) are formed together with α-aminonitriles.[106,107]



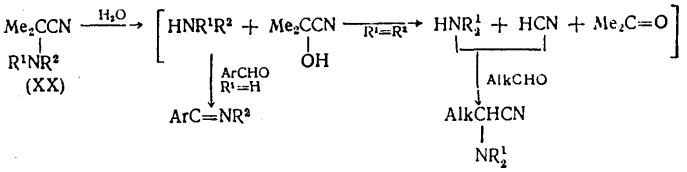
The addition of hydrocyanic acid to enamines such as (XVIII) in a basic medium also gives α-aminonitriles.[108] All this naturally raises the question about the mechanism of the expanded Strecker reaction.

This problem was examined in the greatest detail in two studies.[67,96] However, the results obtained in them are ambiguous. Thus, for example, in one article,[96] α-aminonitriles obtained by the Strecker and Tiemann reactions have the same optical purity. On the basis of this experiment the authors rejected a mechanism involving stereochemical control of the reaction due to steric hindrance in attack on cyanohydrins (I) and considered the stereoselective addition of HCN to geometric isomers of Schiff bases of the type (IX) more likely. In the other study[67] it was concluded that cyanide ions most probably add on to ketiminium cations of

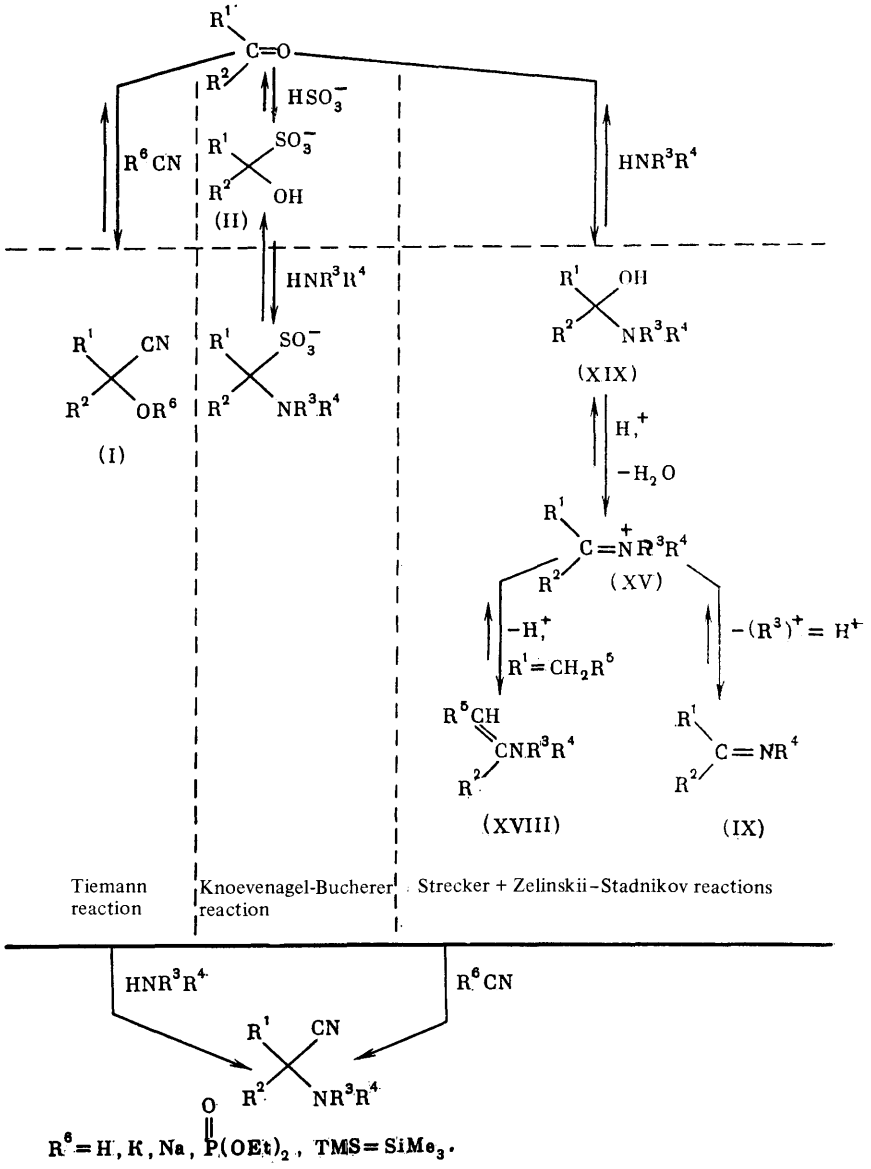
the type (XV), the presence of which in the reaction mixture was reliably detected. Moreover, the authors did not rule out the possibility of α-aminonitriles being formed by S_N2 attack of CN^- on aminoalcohols such as (XIX).

Valuable information about the mechanism of this reaction was obtained when the "retro-Strecker" decomposition of α-aminonitriles was analysed. This process occurred in water at different pH values,[109,110] during mass spectrometry,[111] during vacuum flash thermolysis, gas-phase pyrolysis, and thermolysis.[112] It was shown that the decomposition of *N*, *N*-dialkyl-α-aminonitriles occurs via ketiminium ions such as (XV).[109] In the case of primary and secondary α-aminonitriles, intermediates of the type (XV) are also formed, but they are much more difficult to identify because of their rapid conversion to Schiff bases.

The molecular ions generated from primary and secondary α-aminonitriles eliminate HCN to give Schiff bases, and only in the case of tertiary α-aminonitriles does the elimination of an amino group predominate, corresponding to a "retro-Tiemann" reaction.[111] The latter type of decomposition was also demonstrated for aqueous solutions of isobutyronitriles (XX) from the chemical reaction of its products.[113]



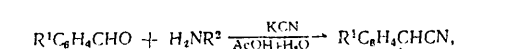
Scheme 1



A reliable determination of the mechanism of the Tiemann reaction is made possible by comparing the yield of α-aminonitriles obtained by this and other methods. In one study[63] it was shown that the yield of a number of α-aminonitriles from cyanohydrins such as (I) is invariably higher than from azomethines such as (XVIII). The difference between the Tiemann reaction and the "classical" Strecker reaction is also exhibited when TMSCN is used as the cyano group donor. In this case, however, the Strecker variant is more favourable because of the low thermal stability of cyanohydrins of the type (I) (where R^6 = TMS).[68]

The data given indicate that in some cases cyanohydrins of the type (I) lie within the sphere of the Tiemann reaction. By and large the mechanism of the Strecker reaction is not universal and depends on the nature of the solvent and the reagents and also on the order in which they are mixed.

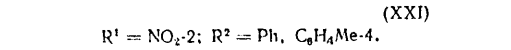
The various forms of the Strecker reaction differ slightly with respect to their synthetic possibilities. Thus, out of the very large number of α-aminonitriles obtained by the Strecker reaction only compound (XXI) contains a substituent with distinct electron-withdrawing properties on the α-carbon atom.[17] When TMSCN was it was possible to add to this a number of compounds such as 2-amino-(4-cyano- and 4-carboxymethyl-phenyl)acetonitriles (XXII).[59] It should be noted that the yield of α-aminonitriles (XXII) is considerably lower than for the analogous compounds not containing strong electron-withdrawing groups at the α-position (15%, 17%, and 90–99% respectively).[59] α-Aminonitriles with strong electron-withdrawing groups at the 2-position, synthesised from cyanohydrins, also constitute a small proportion of the total number of compounds obtained by such methods, but nevertheless ten 2-amino-2-fluorocarbonitriles (XXIII) [86] and six 2-carbonyl-amino-2-(2-, 3-, and 4-nitrophenyl)acetonitriles (XXIV) [66] are among them.



$R^1C_6H_4CHO + H_2NR^2 \xrightarrow[AcOH+H_2O]{KCN} R^1C_6H_4CHCN,$ with HNR^2

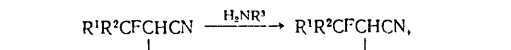
(XXI)

$R^1 = NO_2\text{-}2;\ R^2 = Ph,\ C_6H_4Me\text{-}4.$



$4\text{-}R^1C_6H_4CHO + TMSCN + NH_3 \xrightarrow{MeOH} 4\text{-}R^1C_6H_4CHCN,$ with NH_2

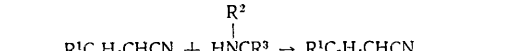
$R^1 = CN,\ COMe.$ (XXII)



$R^1R^2CFCHCN \xrightarrow{H_2NR^3} R^1R^2CFCHCN,$ with OH and HNR^3

(XXIII)

$R^1 = Alk^1,\ R^2 = Alk^2,\ R^1 + R^2 = (CH_2)_n,\ n = 4.5.$



$R^1C_6H_4CHCN + HNCR^3 \rightarrow R^1C_6H_4CHCN,$ with OH, O, R^2, NCR^3, O

(XXIV)

$R^1 = NO_2\text{-}4,\ NO_2\text{-}3,\ NO_2\text{-}2;\ R^2 = H,\ Et;\ R^3 = OEt,\ NH_2.$

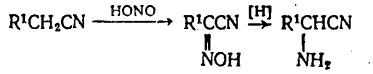
It should be noted that in the latter reaction weakly basic compounds such as urethane and urea are used as the amino components. Apart from urea and urethanes,[62,65] benzamide[54] and formamide[91,92] also react with cyanohydrins.

A comparison of two other modifications of the Strecker reaction (the Zelinskii–Stadnikov and Knoevenagel–Bucherer methods) on eight substrates has been carried out.[6] It showed that the first method is suitable for preparing *N*-adamantyl and *N*-benzyl derivatives of α-aminonitriles, while catalysis with sodium metabisulphite is advisable for the synthesis of primary α-aminonitriles. In this case it was only possible to obtain 2-methylamino-2-(4-benzyloxyphenyl)acetonitrile using the Knoevenagel–Bucherer method. These results indicate that the choice of a specific modification of the Strecker reaction can also be determined by the nature of the substituent in the amino group of the target compounds.

Thus, by using the Strecker reaction and its modifications with various sources of the cyano group, catalysts, and solvents it is possible to obtain a variety of α-aminonitriles in a relatively simple manner, but α-aminonitriles with strong electron-withdrawing groups at the 2-position are not very amenable to synthesis.

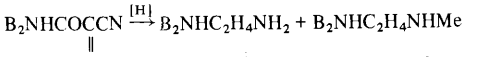
2. Other methods

A further limitation of the Strecker reaction is the difficulty in obtaining α-oxo- and α-cyano-aldehydes, so that 2-amino-3-oxopropionitrile and 2-aminomalonitrile cannot be prepared by it. In this case the synthesis of primary α-aminonitriles is carried out by reduction of accessible 2-hydroxyiminoacetonitriles (XXV) with sodium dithionite,[114,115] aluminium amalgam,[116–120] and bis(2-methoxyethoxy)aluminium hydride.[121] Reduction of *N*-benzyl-2-cyano-2-hydroxyimino acetamide is complicated by rearrangement of the intermediate α-aminonitriles to ethylenediamines (XXVII) and (XXVIII).[121]



$R^1CH_2CN \xrightarrow{HONO} R^1CCN \xrightarrow{[H]} R^1CHCN$, with NOH and NH_2

(XXV) (XXVI)



$B_2NHCOCCN \xrightarrow{[H]} B_2NHC_2H_4NH_2 + B_2NHC_2H_4NHMe$, with NOH

(XXVII) (XXVIII)

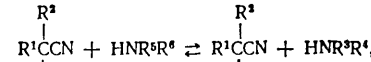


$R^1 = CN,\ CR^2.$

The reduction of derivatives of 2-hydroxyimino-2-cyanoacetic acid with alkali metal dithionites,[122] hydrogen on platinum,[123] and zinc dust[124,125] in simple organic acids or their anhydrides results in the formation of *N*-acylated α-aminonitriles. When these reactions are carried out it is necessary to bear in mind that the cyano group in the α-aminonitrile formed is also susceptible to reduction.

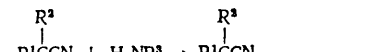
Direct introduction of an amino group into the 2-position of malonodinitrile is achieved by treating it with *O*-(2,4,6-trimethoxyphenylsulphonyl)hydroxylamine.[126]

It is possible to increase the number of α-aminonitriles by transaminating them; the yield of the secondary compounds (XXIX) in this case amounts to 13–82%.[127] Introduction of an amino group also takes place by treatment of 2-haloacetonitriles with a twofold excess of ammonia or primary amine.[128]



$R^1CCN + HNR^5R^6 \rightleftarrows R^1CCN + HNR^3R^4,$ with R^3NR^4 and R^5NR^6

(XXIX)



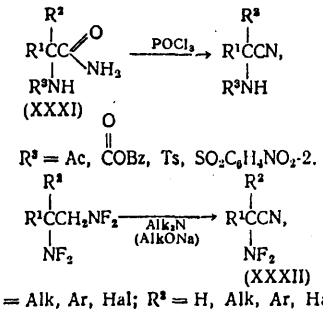
$R^1CCN + H_2NR^3 \rightarrow R^1CCN,$ with Hal and HNR^3

(XXX)

$R^1 = C_nH_{2n+1},\ n = 1 - 11,\ Ph;\ R^2 = H,\ Me;\ R^3 = H,\ C_6H_4Cl\text{-}4,$ CH (Me) Ph; Hal = Cl, Br.

The other group of methods for synthesising α-aminonitriles is made up by reactions that form a cyano group in amines. One of these, for example, is the dehydration of *N*-substituted α-amino-amides (XXXI) with phosphorus oxychloride.[129] However, this method has no synthetic value since the initial amides (XXXI) are, in turn, usually obtained from α-aminonitriles. A process which is

formally the reverse of reduction of α-aminonitriles forms the basis for obtaining *N*,*N*-difluoro-α-aminonitriles (XXXII).[130]



(XXXI)

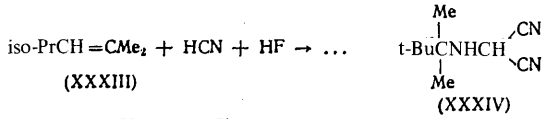
R^3 = Ac, COBz, Ts, $SO_2C_6H_4NO_2$-2.

(XXXII)

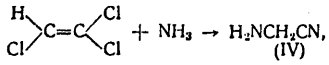
R^1 = Alk, Ar, Hal; R^2 = H, Alk, Ar, Hal.

The simultaneous introduction of amino and cyano groups is achieved when the olefin (XXXIII) is reacted with hydrocyanic and hydrofluoric acids. 2-*N*-Alkylaminomalononitrile (XXXIV) has been identified among the products of this reaction.[131] Treatment of 1,2,2-trichloroethylene with ammonia at high pressure is the most effective method for synthesising aminoacetonitrile.[132,133]

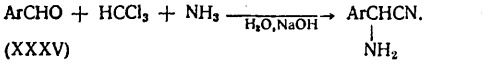
The synthesis of primary α-aminonitriles from aromatic aldehydes (XXXV), chloroform, ammonia, and water in the presence of alkali at a raised temperature and pressure[134] should be noted in particular. A study of the mechanism of this reaction could show whether its resemblance to the Strecker reaction is purely superficial. The scope for applying this method,[134] however, is limited to aldehydes (XXXV) that are readily soluble in chloroform.



(XXXIII) (XXXIV)



(IV)

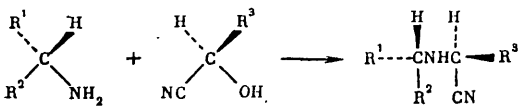


(XXXV)

III. Stereochemistry

α-Aminonitriles are widely used for the synthesis of α-amino acids, whose biological activity depends fundamentally on their configuration.[1] Therefore, a considerable amount of attention has been given by synthetic chemists to stereoselective methods for obtaining α-aminonitriles.

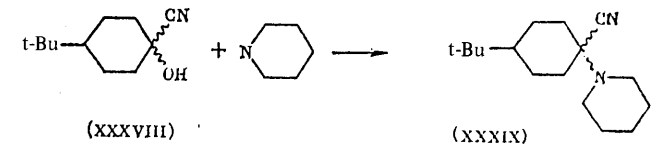
It was possible to obtain optically active products from the Tiemann reaction by introducing just one optically pure reagent into it. Thus, for example, the reaction of optically active cyanohydrins with ammonia or amines occurs with a considerable degree of inversion of the chiral centre.[86] From a racemic mixture of cyanohydrins (XXXVII), the (*R*)-form predominantly reacts with (*S*)-amines (XXXVI).[96] When the latter reaction was carried out according to the Strecker method this also gave an optically active product, which had an optical purity that differed slightly from that achieved in the first method (36–51% and 44–48% respectively).[96]



(XXXVI) (XXXVII)

R^1 = Me, COOH; R^2 = Ph; $C_{10}H_7$; R^3 = Me, Et, Pr-iso, CH_2Pr-iso.

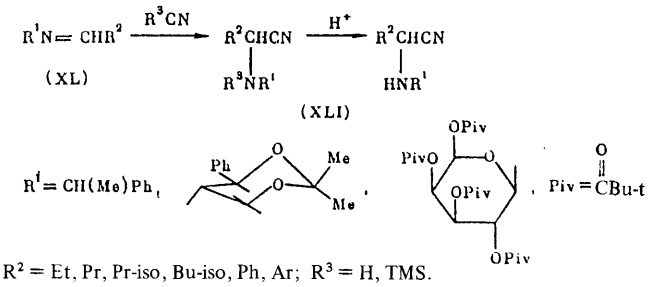
Under quasi-kinetic conditions, piperidine mainly attacks axially the conformer of 4-t-butylcyclohexanone cyanohydrin (XXXVIII) with an equatorial configuration of the cyano group.[67] In the presence of water the kinetically controlled α-aminonitrile (XXXIX) rapidly epimerises.



(XXXVIII) (XXXIX)

The correspondence between the thermodynamic properties of the racemisation of optically active secondary α-aminonitriles and those for their decomposition to Schiff bases and hydrocyanic acid indicates that there is a common mechanism for these two processes.[135]

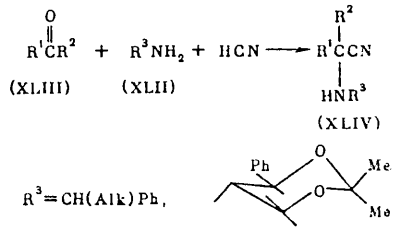
The addition of HCN and TMSCN to the C=N bond of Schiff bases (XL) also takes place stereoselectively; the optical purity of α-aminonitriles (XLI) is improved when a bulky R^1 substituent is introduced into compounds (XL) and when the addition of TMSCN is carried out in the presence of Lewis acids.[4,20,61,97,98,136–139]



(XL) (XLI)

R^2 = Et, Pr, Pr-iso, Bu-iso, Ph, Ar; R^3 = H, TMS.

An asymmetric Strecker synthesis has also been used widely to obtain optically active α-amino acids.[20,61,96,136–140] The amino components used in it are amines that are readily separated into enantiomers and containing those substituents which are readily eliminated from the required α-amino acids. Among such substituents are *N*-phenylalkyl, removed by hydrogenation of palladium, and *N*-(2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl), which is eliminated on oxidation. The presence of the latter substituent in amine (XLII) gives better results.[20,61,136–140] Thus, the (*S*)-(−)-α-amino acid is obtained from amine (XLII) with a (4*S*,5*S*)-(+)-configuration, while the (*R*)-(+)-α-amino acid is obtained from the (4*R*,5*R*)-(−)-amine. It should be noted that only ketones (XLIII) (R^1 and $R^2 \neq$ H) are suitable for conducting the asymmetric synthesis; otherwise asymmetric transformation of the chiral centre formed in α-aminonitriles (XLIV) will occur during the reaction.[136]



(XLIII) (XLII) (XLIV)

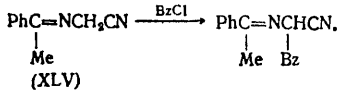
R^3 = CH(Alk)Ph,

In contrast to the Tiemann reaction, dehydration of α-aminoamides occurs with retention of configuration.[128]

In the remaining cases a racemic mixture of enantiomeric α-aminonitriles is formed. In order to resolve this, either fractional crystallisation[135] or salt formation with optically pure organic acids such as tartaric acid[57,141-143] and its derivatives[143] and brucine[89] are used. In one study[141] it was possible to obtain pure isomers only when this reaction was carried out in the presence of ketones.

IV. Chemical properties

α-Aminonitriles can contain a different number of reaction centres. Thus, for example, *C*-benzylation of compound (XLV) occurs on its methylene group.[144]



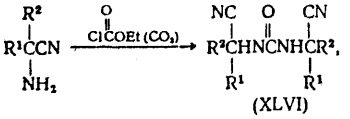
C-Alkylation,[145] *C*-bromination,[146] and intramolecular interaction between the cyano and methylene groups[147] have also been reported. Ammonia[148] and hydrazine[149] replace the ethoxyl group in ethyl 2-amino-2-cyanoacetate.

However, the overwhelming majority of reactions of α-aminonitriles involve their amino and cyano groups. In making a convenient presentation of the material, these two classes of reactions are described in the respective sections. The syntheses that involve both amino and cyano groups also shed light on the reactivity of these functional groups in α-aminonitriles. Moreover, intermediates have been isolated in some of them. However, in view of the importance of α-aminonitriles for heterocyclic chemistry, reactions of the latter type have been grouped in a separate section of this review.

1. Reactions of the amino group

The amino group in α-aminonitriles is quite basic and therefore readily undergoes characteristic reactions. Primary and secondary α-aminonitriles undergo *N*-acylation,[26,58,77,84,90,120,123,124,135,142,150-155] which is a reason for their use in peptide synthesis.[156,157] Removal of the protecting group causes certain difficulties since the cyano group in α-aminonitriles is sensitive to both acids and bases. In this respect it is convenient to use a 2-nitrophenylsulphenyl protecting group, which is readily removed on treatment with hydrochloric acid.[128]

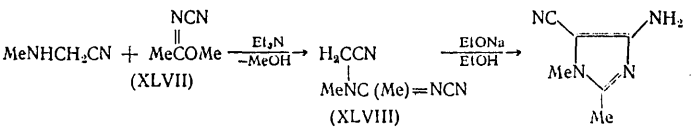
When primary α-aminonitriles are treated with half the quantity of ethyl chloroformate or an equimolar quantity of carbon dioxide[12,159] it is possible to obtain symmetrical ureas (XLVI).



(XLVI)

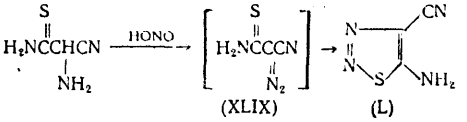
$R^1 = H$, Me; $R^2 = H$, Me, Et.

The synthesis of asymmetric ureas and thioureas starting from α-aminonitriles can be achieved with the use of isocyanates[160] and isothiocyanates[149,161] respectively. The reaction of primary α-aminonitriles with aldehydes[70,73,162] and ketones[163-165] gives azomethines. When primary α-aminonitriles were treated with ortho esters and imidates under mild conditions, the corresponding *N*-substituted imidates were obtained.[166-172] On the other hand, the base-catalysed addition of *N*-cyanoimidate (XLVII) to *N*-methylaminoacetonitrile results in elimination of the methoxyl group and formation of amidine (XLVIII), which cyclises under these conditions without participation of the cyano group from the initial α-aminonitrile.[173]



(XLVII) (XLVIII)

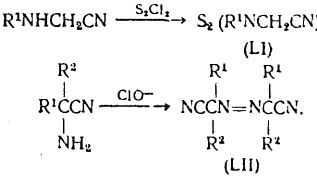
N-Alkylation of primary and secondary α-aminonitriles was carried out using derivatives of acrylic acid;[174-176] tertiary α-aminonitriles were quaternised with alkyl halides in propanol and acetone.[177] 9-Chloroacridine derivatives arylate the amino group of primary α-aminonitriles.[178,179] Diazotisation of primary α-aminonitriles gives 2-diazonitriles;[117,150,180-183] the diazothioamide (XLIX) generated in this way cyclises to 5-amino-1,2,3-thiadiazole (L) during the reaction.[184,185]



(XLIX) (L)

Primary α-aminonitriles undergo an azo–amino interaction with diazonium salts to form triazenes, which then cyclise to heterocycles containing three nitrogen atoms.[186,187]

N-Chlorination of primary and secondary α-aminonitriles is carried out with chlorine[188] and isopropyloxonium chloride.[189] Replacement of the hydrogen atoms of the amino group in α-aminonitriles by a cyano group is carried out using cyanogen chloride.[190] The reaction of secondary α-aminonitriles with 98% nitric acid results in the formation of *N*-nitro derivatives.[191] The synthesis of diaminodisulphides (LI) from secondary α-aminonitriles and sulphur monochloride has been reported in a patent.[192] Oxidation of primary α-aminonitriles with alkali metal hypochlorites in an organic solvent gives azobisnitriles (LII).[193]



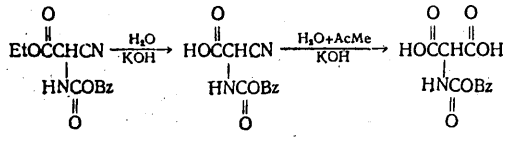
(LI)

(LII)

2. Reactions of the cyano group

Historically the first and most important use of α-aminonitriles has been their hydrolysis to the corresponding α-amino acids,[1] which are widely used in organic synthesis, medicine, agriculture, and other areas of the economy. The hydrolysis is carried out in aqueous and water–ethanol solutions[99] of mineral acids (hydrogen halide[50,51,71,80,86,88,96-99,141] or sulphuric acids[71] and also bases.[10,47,71,72,133,142,194-199] In one patent[200] the hydration of α-aminonitriles on polymer-bonded *N*-acyl-4-piperidones is reported.

When there are other groups that are susceptible to hydrolysis in the α-aminonitrile molecule, the reaction can be caried out selectively by choosing a suitable solvent.[201]

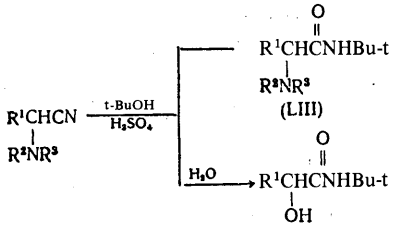


The reaction of α-aminonitriles with water is catalysed by compounds and alloys of zinc, cadmium, and boron,[64,87] and also by iron(III) chloride.[90]

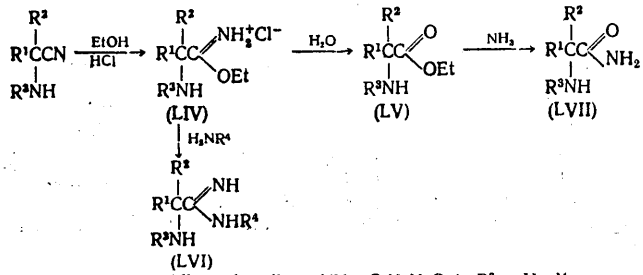
When suitable conditions (concentrated sulphuric acid at room temperature[202] or aqueous alkali in the presence of ketones[197,203]) are chosen, it is possible to discontinue the hydrolysis of α-aminonitriles at the stage when α-aminoamides are formed. On the other hand, dilution of the sulphuric acid and raising the reaction temperature[202] or increasing the time of contact with alkali[197] results in the conversion of aminoamides to amino acids.

The directed synthesis of α-aminoamides is carried out by treating α-aminonitriles with aqueous hydrogen peroxide.[204] It is possible to hydrate selectively one cyano group in polycyanomethylamines using this method.[204]

N-t-Butyl α-aminoamides (LIII) were obtained by the Ritter reaction, which was complicated in a number of cases by hydrolysis of the tertiary amino group.[205]

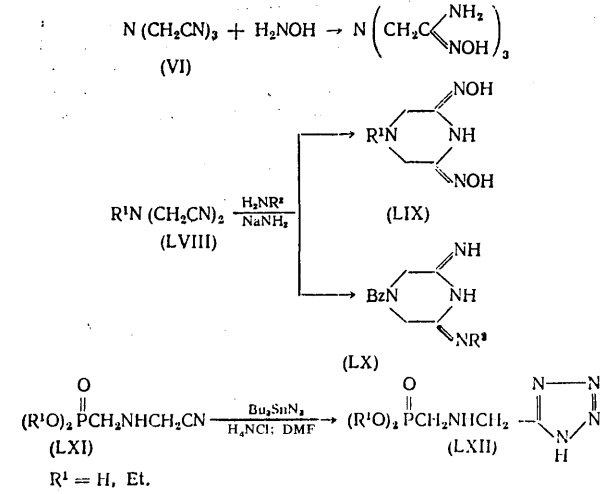


The reaction of α-aminonitriles with alcohols in the presence of hydrogen halides under anhydrous conditions gives the corresponding imidates (LIV),[86,206,207] which can then be converted to esters (LV) [128] or amidines (LVI).[206] In aqueous ethanol in the presence of hydrogen chloride the initially formed imidates (LIV) are spontaneously hydrolysed to esters (LV),[27] which can be converted to the corresponding amides (LVII).[207]



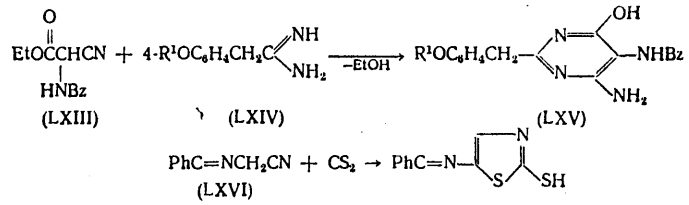
R^1 = H, Alk, Alk-cyclo, alkenyl,Ph, C_6H_4MeO-4; R^2 = H, Me; R^3 = H, Me, Ph, Ar, C(O)C_5H_{11}; R^4 = H, Bz.

Nitrilotriacetonitrile (VI) can add on 3 moles of hydroxylamine directly.[208] In the presence of sodamide, dicyanomethylamines (LVIII) add on primary amines to give 2,5-diiminopiperazines (LIX) and (LX).[208] The α-aminonitriles (LXI) add on azide ions to give tetrazoles (LXII).[209]

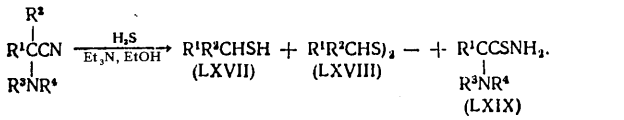


R^1 = H, Et.

The *N*-benzyl protecting group excludes the amino group of compound (LXIII) from the reaction with amidines (LXIV), which results in the formation of pyrimidines (LXV).[210] In a similar manner carbon disulphide does not affect the benzylidenamino group in the aminoacetonitrile derivative (LXVI).[164]

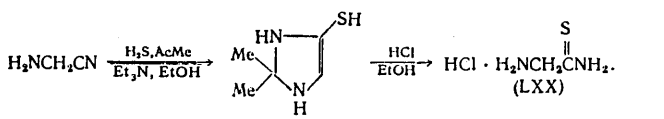


In the examples given α-aminonitriles undergo reactions that are typical for nitriles in general.[211,212] On the other hand, addition of carbon disulphide to α-aminonitriles usually gives a mixture of thiols (LXVII), disulphides (LXVIII), and α-aminothioamides (LXIX).[26,56,120] In this case the latter component is only stabilised when R^1 = H; R^2, R^3, R^4 = Ph, H, iso-Pr; $C_6H_3(MeO)_2$-3, 4, H, Me; $C_6H_3(MeO)_2$-3, 4, Me, Me; Ph, Me, Me; $C_6H_3(MeO)_2$-3, 4, H, Ph; Ph, H, H; t-Bu(O)C, R^3 + R^4 = Phth



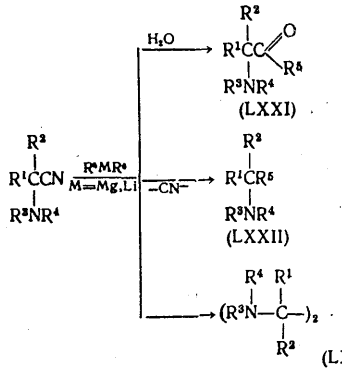
The reaction of α-aminonitriles with hydrogen sulphide followed by oxidation of the initially formed thiols so that disulphides (LXVIII) can be obtained deliberately is reported in a patent.[213]

The synthesis of 2-aminothioacetamide hydrochloride (LXX) was successfully carried out in two stages.[214]



The reactions of α-aminonitriles with organometallic compounds also occur in a unique manner. Thus, for example, in the reaction of α-aminonitriles with Grignard reagents and lithium alkyls, products

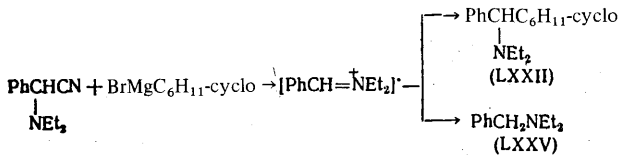
with a "normal" structure—α-aminoketones (LXXI)—have been detected.[77,215] However, a more typical course for the reaction of α-aminonitriles with organometallic compounds is replacement of the cyano group by the radical R^5, resulting in the formation of amines (LXXII).[77,216,217] In two studies[218,219] the formation of diamines (LXXIII) has been recorded in the reaction between α-aminonitriles and Grignard reagents.



(LXXIII)

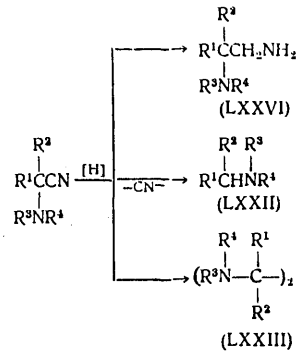
The general mechanisms of the reaction between α-aminonitriles and organometallic compounds has been discussed in a review.[220] They are determined by the nature of the α-aminonitriles themselves and the reagents. Thus, for example, it was observed that an increase in the degree of substitution of α-aminonitriles and the size of the substituents R^3 and R^4 leads to a change in the ratio of aminoketones (LXXI) to amines (LXXII) in favour of the former;[219] the sole products of the reaction between *N*-acetyl-α-aminonitriles and Grignard reagents and alkyllithium are compounds (LXXI).[77] Derivatives of aminoacetonitrile that are not substituted on the carbon atom react with alkylmagnesium halides to give mainly substitution products (LXXII).[77] In general, replacement of the Grignard reagent by alkyllithium [77] and dialkylmagnesium[215] assists in the formation of products (LXXI) derived from addition on the cyano group.

In one study[218] using a deuterium label it was possible to determine the mechanism of the reaction of α-aminonitriles (LXXIV) with cyclohexylmagnesium bromide, which gave a compound of the type (LXXII) and a reduction product (LXXV)



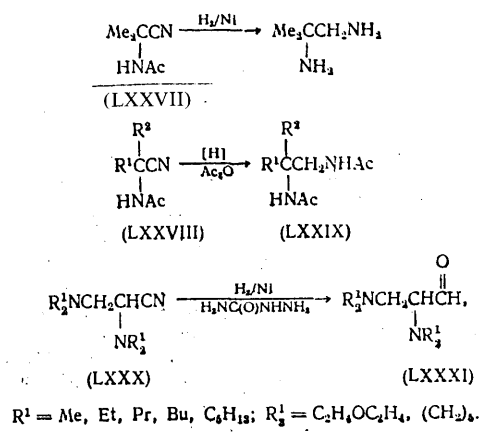
The other group of reactions of the cyano group that is closely related to that just considered is made up by the reactions of α-aminonitriles with reducing agents. Thus, for example, when α-aminonitriles are reduced with sodium in a water–ether emulsion[221,222] and boiling toluene,[223] with hydrogen on Raney nickel, platinum, and palladium,[224] and also with lithium aluminium hydride,[225] the same by-products (LXXII) and (LXXIII) are formed as in the reaction with organometallic compounds. In general, these reducing agents can in principle be regarded as a special case of "organometallic" compounds in which hydrogen or aluminium plays the role of the metal and H· represents the "organic" radical.

At the same time there have been reports about the reduction of α-aminonitriles with hydrogen on Raney nickel,[58,224] platinum, and palladium,[224] lithium aluminium hydride,[70,142] and also diborane and diisopropylbutylaluminium [70] giving exclusively "normal" products—ethylenediamines (LXXVI). As hydrogen is evolved it reduces α-aminonitriles to compounds of the type (LXXVI) only when R^1 and R^2 = Ar.[221] Otherwise the formation of products (LXXII) from the reductive elimination of the cyano group (LXXII) [221–223] and their dimers (LXXIII) occurs. Hydrogenation of α-aminonitriles on Raney nickel, platinum, and palladium [224] also generally gives a mixture of compounds such as (LXXVI) and (LXXIII). When the reaction is carried out in an alcoholic solution of ammonia, the formation of dimers of the type (LXXIII) is inhibited.[226] When treated with sodium borohydride [227,228] and hydrogen on palladium oxide in 0.5 *N* hydrochloric acid,[54] α-aminonitriles are selectively converted to products of the type (LXXII) derived from the reductive elimination of the cyano group.



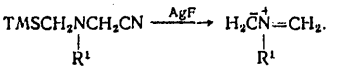
In the reaction of α-aminonitriles with lithium aluminium hydride, an excess of reducing agent[218] assists the formation of diamines of the type (LXXVI), the presence of aluminium chloride [229] favours the formation of amines (LXXII), and the formation of dimers such as (LXXIII) is assisted by an excess of initial α-aminonitrile [225] and a high reaction temperature.[230] The course of the reaction is also related to steric factors.[231]

Reduction of the cyano group in α-aminonitriles may be accompanied by side reactions. Thus, for example, the hydrogenation of *N*-acetyl-α-aminonitriles (LXXVII) on Raney nickel takes place concurrently with removal of the protecting group.[232] Reduction of the acetyl derivative (LXXVIII) in acetic anhydride, on the other hand, gives the diacylated product (LXXIX).[233] An exception to the general pattern of reactions of α-aminonitriles with reducing agents is the hydrogenation of compounds (LXXX) on Raney nickel in the presence of semicarbazide to give α-aminoaldehydes (LXXXI).[234]



R^1 = Me, Et, Pr, Bu, C_6H_{13}; R^1_2 = $C_2H_4OC_2H_4$, $(CH_2)_5$.

Treatment of *N*-trimethylsilyl-α-aminonitriles with silver fluoride results in elimination of the trimethylsilyl and cyano groups with formation of azomethine ylides (LXXXIII).[235,236]



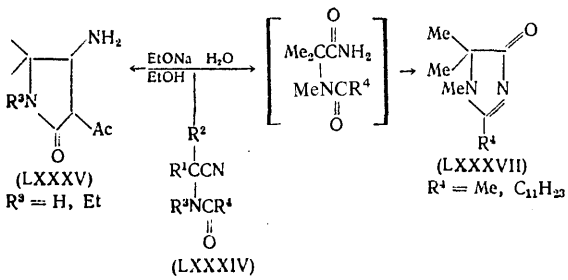
(LXXXII) (LXXXIII)

3. Reactions of the amino and cyano groups

(a) α-Aminonitriles in the synthesis of heterocycles

Usually both nitrogen atoms of the initial molecule are retained when α-aminonitriles undergo heterocyclisation, while one of them can be converted to an exocyclic amino functional group. This nitrogen atom always originates from the cyano group in α-aminonitriles.

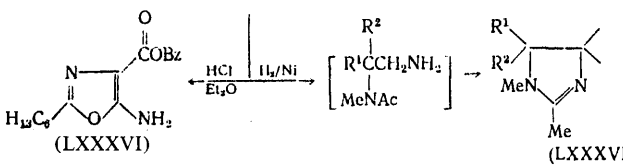
α-Aminonitriles that contain not less than one double bond in the amino functional group will undergo heterocyclisation. Thus, for example, *N*-acylated α-aminonitriles (LXXXIV) can, depending on the conditions, cyclise to pyrrolidones (LXXXV),[237] the oxazole (LXXXVI),[238] imidazolinones (LXXXVII),[38,238] or imidazolines (LXXXVIII).[58]



(LXXXV) R^3 = H, Et

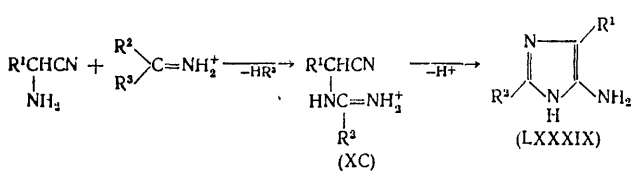
(LXXXIV)

(LXXXVII) R^4 = Me, $C_{11}H_{23}$



(LXXXVI) (LXXXVIII)

The reactions of primary α-aminonitriles with immonium salts are widely used for the synthesis of 5(4)-aminoimidazoles (LXXXIX). The reaction of α-aminonitriles with amidines,[90,149,239] imidates,[240–244] and thioimidates [242,245,246] is accompanied by elimination of ammonia, alcohols, and mercaptans respectively. In one study[242] an intermediate of the type (XC) was isolated in a pure state

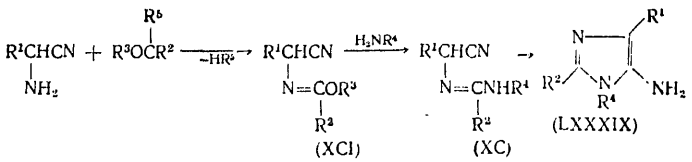


(XC) (LXXXIX)

R^1 = H, Ph, C_6H_3OMe-4, COEt, COPr-iso, COBz, COPh, COC_6H_4Cl-4, CNH_2, CONHMe, CNHEt, CNHPh, CN; R^2 = H, Alk, C(=O)C_6H_{11}-cyclo, Bz, glycosyl, CH_2OPh, C_2H_4Ph, COEt, Ar, Het, OMe, SH, SMe, SBz, SPh; R^3 = NH_2, OAlk, SMe, SBz.

However, it should be noted that only condensation of α-aminonitriles with thioimidates achieved a satisfactory yield of imidazoles (LXXXIX).

"Linear imidates" (XCI), obtained from primary α-aminonitriles and imidates under mild conditions or from α-aminonitriles and ortho esters, when treated with primary amines are also converted to amidines of the type (XC) and then cyclise to aminoimidazoles such as (LXXXIX).[93,168,169,247,248]



(XCI) (XC) (LXXXIX)

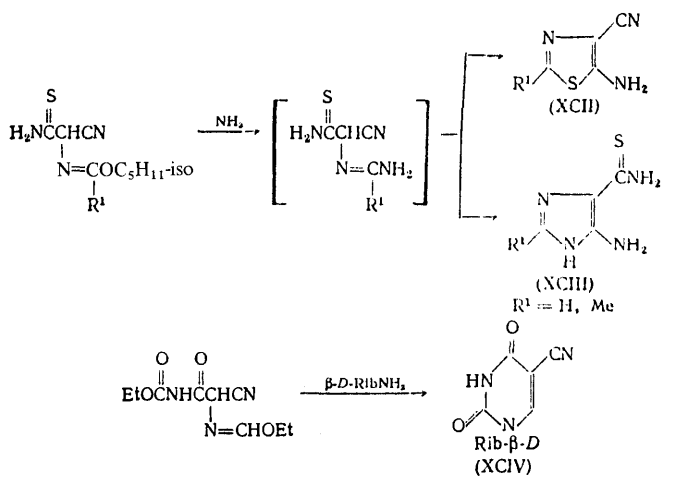
R^1 = CPh, COEt, CNH_2, CNHMe, C(=NH)NH_2, CN; R^2 = H, Me, $CH_2CH(OH)CH_2OH$, Bz; R^3 = Me, Et, Bu-iso C_5H_{11}; R^4 = H, Alk, C(=O)C_6H_{11}-cyclo, CHCOEt, *D*-ribofuranosyl, galactosyl, xylopyranosyl, phosphoribosyl

CN

NH_2, NHMe, NMe_2;

R^5 = NH_2; OR^3.

When there are other reactive groups in addition to the cyano group in the "linear imidate" molecule, alternative pathways of cyclisation are possible, leading, for example, to thiazoles (XCII) or imidazoles (XCIII) [249] and pyrimidinediones (XCIV).[250]



(XCII)

(XCIII)

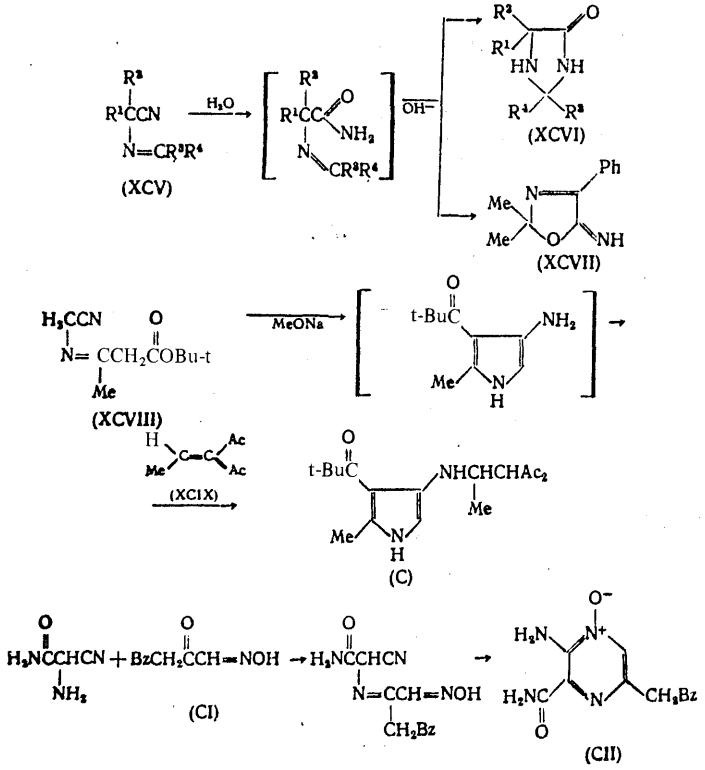
R^1 = H, Me

Rib-β-*D*

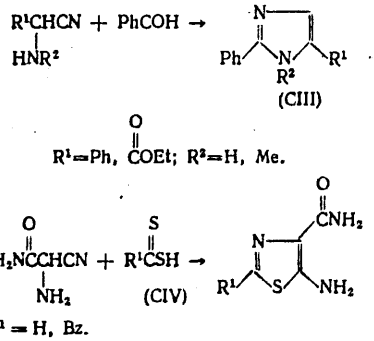
(XCIV)

In aqueous alkali solutions azomethines (XCV) are cyclised either to imidazolones (XCVI) or to oxazolimine (XCVII).[164] The first stage in the reaction of azomethine (XCVIII) with the olefin (XCIX) in the presence of sodium methoxide, which gives pyrrole (C) in the end, is apparently intramolecular attack by the methylene group on to the carbon atom of the cyano group in compound (XCVIII).[163] The α-hydroxyiminoketone (CI) can undergo cyclisation with a primary α-aminonitrile in the absence of water to give the

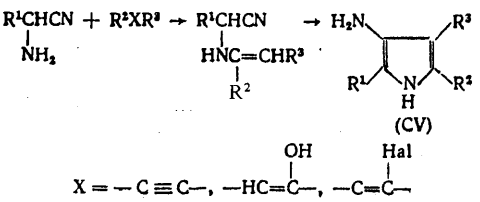
2-aminopyrazine-1-oxide (CII).[251]



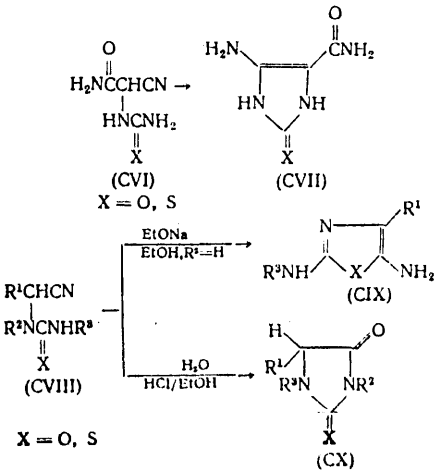
The synthesis of imidazoles (CIII) from secondary α-aminonitriles and benzaldehyde occurs in a different manner.[164] Dithiocarboxylic acids (CIV) constitute another group of condensation agents for α-aminonitriles.[149]



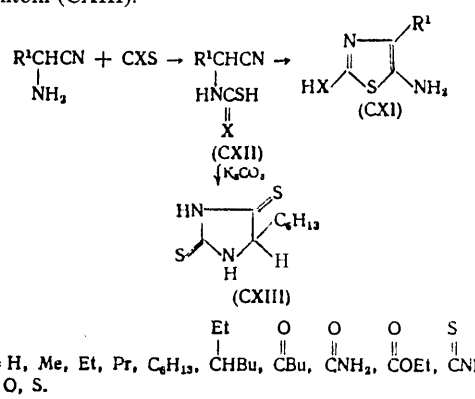
When α-aminonitriles are reacted with acetylenes or olefins that can undergo *cis*-elimination of water or hydrogen halides, 3-aminopyrroles (CV) are formed as final products.[252]



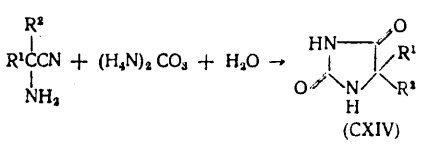
Heterocumulenes constitute a large group of reagents that react with both the amino group and cyano group of α-aminonitriles. A feature of these reagents is that they convert α-aminonitriles directly to aromatic five-membered heterocycles. Thus, for example, the monosubstituted urea and thiourea (CVI), which are obtained from 2-amino-2-cyanoacetamide and potassium cyanate and thiocyanate respectively, are cyclised to 2-oxo- [253] and 2-thio-5-aminoimidazole-4-carboxamides [254] (CVII) respectively. In turn, *N,N*-disubstituted ureas and thioureas (CVIII) in an ethanol solution of sodium ethoxide are cyclised to 5-aminooxazoles [160] and 5-aminothiazoles [148] (CIX). On the other hand, in the presence of hydrogen chloride compounds (CVIII) are converted to the hydantoin[160] and thiohydantoin [161] (CX).



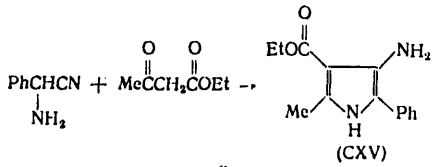
When treated with carbon disulphide[149,159,197,242] and carbon oxysulphide,[255] primary α-aminonitriles are converted to 2-mercapto- and 2-hydroxy-5-aminothiazoles (CXI). In the presence of potassium carbonate a dithiocarbamate of the type (CXII) is cyclised to the dithiohydantoin (CXIII).[256]



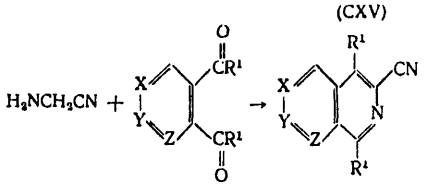
Hydantoins (CXIV) are the final products in the Bucherer–Bergs reaction.[103,157]



Condensation of 2-phenyl-2-aminoacetonitrile with ethyl acetoacetate gives the aminopyrrole (CXV).[257] The reaction of aminoacetonitrile with *o*-dicarbonyl compounds (CXVI), giving condensed pyridines (CXVII), occurs in a different manner.[258–261]



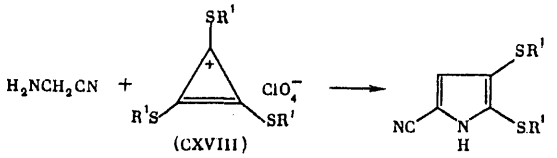
(CXV)



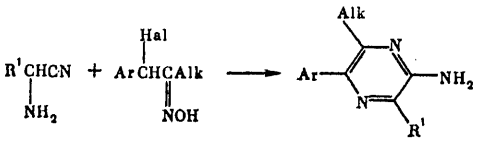
(CXVI) (CXVII)

X, Y, Z = CH, N.

Other bifunctional reagents such as cyclopropenyl cations (CXVIII) [262] and oximes (CXIX) [263] have also been used for the heterocyclisation of α-aminonitriles.



(CXVIII)



(CXIX)

V. Physicochemical properties of α-aminonitriles

Stretching vibrations from the cyano group of α-aminonitriles appear in the region 2210–2250 cm^{-1} in their IR spectra.[98,101,117,128,150,153] When hydroxyl or acetyl groups are present in the α-aminonitrile molecule, the intensity of this band is considerably reduced.[211] Thus, IR spectroscopy is not always a reliable method for confirming the structure of α-aminonitriles; in this respect a more promising method could be mass spectroscopy.[111]

The ^1H and ^{13}C NMR spectra,[20,136,138,140] microwave[3] and EPR [264] spectra of α-aminonitriles have been reported. In one study[265] information about the acid-base properties of aminoacetonitrile is given. It was shown that the experimental pK_a value (5.17) was in good agreement with the results of quantum-chemical calculations of the atomic charges.

VI. Biological activity of α-aminonitriles

At the present time the biological and biochemical properties of α-aminonitriles have been studied quite widely. It has been found, for example, that aminoacetonitrile inhibits different enzymes, including monoamino oxidase,[266–268] dimethylase,[269–271] glycine decarboxylase[272,273] and nitrilase.[258,274] Aminoacetonitrile also has an effect on the contraction of muscles[275–277] and the mechanical properties of bones[278–280] and it inhibits the introduction of gallium into tissues.[281]

In 1983 the first report was published on the antitumour activity of 2-amino-2-phenylacetonitrile derivatives.[66] Three compounds of this series proved to be highly effective towards carcinoma and seminoma in a clinical experiment.

A number of α-aminonitriles exhibit fungicidal[282] and herbicidal[144,154,283] activity.

References

1. D Jones *General Organic Chemistry* (Translated into Russian), Izd. Khimiya, Moscow, 1983, p. 233
2. V I Ivanskii *Khimiya Geterotsiklicheskikh Soedinenii* (The Chemistry of Heterocyclic Compounds), Izd. Vys. Shkola, Moscow, 1978, p. 147
3. J C Guillemin, J M Denis, M Bogey, J L Destombes *Tetrahedron Lett.*, 1986, **27**(10) 1147
4. S L Miller, G Schlesinger *Adv. Space Res.*, 1983, **3**(9) 47
5. C A Buehler, D E Pearson *Organic Syntheses* (Translated into Russian), Part 2, Izd. Mir, Moscow, 1973
6. P J Irurre, E R Herbera, B F Sanchez, et al. *Afinidad*, 1985, **42**(397) 270
7. P Van Deale *Meded. Vlaam. Chem. Ver.*, 1961, **23** 163; *Chem. Abs.*, 1962, **57** 16365
8. J-P Fleury, A Baysang, D Clerin *Bull. Soc. Chim. Fr.*, 1969, (11) 4108
9. K Takahashi *Senryo to Yakugin*, 1985, **30**(5) 128; *Chem. Abs.*, 1985, **100** 87191
10. A Strecker *Ann. Chem. Pharm.*, 1850, **75** 27
11. K V Vapiro, G L Mishchenko *Imennye Reaktsii v Organicheskoi Khimii* (Name Reactions in Organic Chemistry), Izd. Khimiya, Moscow, 1976, p. 495
12. H T Bucherer, W Steiner *J. Prakt. Chem.*, 1934, **140** 291
13. K Takahashi, H Saitoh, K Ogura, H Iida *Heterocycles*, 1986, **24**(10) 2905
14. H Distler, H Schlecht, BRD P. 2625935; *Chem. Abs.*, 1978, **88** 105785
15. M P Dave, J Patel, N A Laugalia, K A Thaker *J. Inst. Chem. (India)*, 1985, **57**(3) 113
16. F Seel, A Dessauer, G Simon, U Z Eder *Z. Naturforsch.*, 1982, **37B**(12) 1540
17. R Walther, R Hübner *J. Prakt. Chem.*, 1916, **93** 119
18. R P Iyer, R K Ratham, S P Kulkarni, M S Sonaselth *J. Heterocycl. Chem.*, 1986, **24**(4) 991
19. T E Koballa, E E Schmitz *Res. Discl.*, 1985, **253** 265; *Chem. Abs.*, 1985, **103** 37084
20. K Weinges, K P Klotz, H Droste *Chem. Ber.*, 1980, **113**(2) 710
21. M Mussim, I Beker, M Ungar, Israel P. 59048; *Chem. Abs.*, 1985, **102** 149784
22. W J Stepek, M M Nigro, S. African ZA P. 8402266; *Chem. Abs.*, 1986, **105** 148198
23. S Chuberek, French P. 1521741; *Chem. Abs.*, 1969, **71** 12611
24. J C Menendez, G G Trigo, M M Sollhuber *Tetrahedron Lett.*, 1986, **27**(28) 3285
25. K W Saunders, W H Montgomery, J C French, US P. 3167580; *Chem. Abs.*, 1965, **62** 13052
26. A Spaltenstein, T P Holler, P B Hopkins *J. Org. Chem.*, 1987, **52** 2977
27. T A Baer US P. 4517130; *Chem. Abs.*, 1985, **103** 104732
28. J L Boucher, L Stella *Tetrahedron*, 1985, **41**(5) 875
29. U H Pandya, R R Astik, K A Thaker *J. Inst. Chem. (India)*, 1979, **51** 127
30. A Commeyras, J Taillades, L Mion, et al., French P. 2405924; *Chem. Abs.*, 1979, **91** 140371

31. D M Stout, L A Black, W L Matier *J. Org. Chem.*, 1983, **48**(26) 5369
32. *3rd Symposium on the Syntheses of Organic Compounds* (Translated into Russian), Izd. Inostr. Lit., Moscow, 1952
33. T Honda, T Dosono, H Ohashi, K Aoki, Japanese P. Appl. 7 203 606; *Chem. Abs.*, 1972, **76** 176 426
34. F Becke, J Gnad, J Jung, BRD P. 2 044 642; *Chem. Abs.*, 1972, **76** 152 634
35. K Wakabayashi, M Itoh, Y Imai, J Oya, Japanese P. Appl. 7 106 615; *Chem. Abs.*, 1971, **75** 48 474
36. R A Firestone, D F Reinhold, M Sletziger, J M Chermerda, BRD P. 1 493 965; *Chem. Abs.*, 1971, **74** 141 326
37. A N Ghandhi, French P. 1 575 104; *Chem. Abs.*, 1970, **73** 14 241
38. V Machacek, G Svobodova, V Sterba *Coll. Czech. Chem. Commun.*, 1987, **52**(1) 140
39. S Chabereck, BRD P. 1 902 934; *Chem. Abs.*, 1970, **72**, 121 160
40. Y Senda, N Kajitani, Japanese P. Appl. 7 205 242; *Chem. Abs.*, 1972, **76** 112 746
41. W R Grace, B. P. 1 163 684; *Chem. Abs.*, 1970, **72**, 21 354
42. C P Morgan, J J Gadfrey, French P. 1 561 020; *Chem. Abs.*, 1970, **72** 54 811
43. K E Davis, K S Shim, BRD P. 1 805 404; *Chem. Abs.*, 1969, **71** 170 146
44. C E Greco, W Stamm, BRD P. 1 815 110; *Chem. Abs.*, 1969, **71** 101 351
45. R N Mesiah, French P. 1 532 168; *Chem. Abs.*, 1969, **71** 49 340
46. J Z Harper, D A Daniels, French P. 1 513 031; *Chem. Abs.*, 1969, **70** 87 078
47. J J Singer, M Weisberg, US P. 3 061 628; *Chem. Abs.*, 1963, **58** 7836
48. R W Foreman, G K Meloy, French P. 1 501 552; *Chem. Abs.*, 1969, **70** 3322
49. D A Daniels, J L Harper, T R Steadman, US P. 347 387; *Chem. Abs.*, 1970, **72** 21 348
50. A B Silaev, V M Svetlaeva, A P Teren'tev *Vestnik MGU Ser. Fiz-Mat i Estest. Nauk*, 1955, **10**(10) 115
51. A B Silaev, V M Svetlaeva, A P Terent'ev *Vestnik MGU Ser. Fiz-Mat i Estest. Nauk*, 1955, **10**(12) 109
52. W Glund, W Klempt, F Brodkorb, German P. 656 349; *Chem. Abs.*, 1938, **32** 3423
53. F Osama, K Wada, W Mihara, Japanese P. Appl. 7 414 423; *Chem. Abs.*, 1974, **80** 145 485
54. R Kuhn, W Kirschenlohr *Angew. Chem.*, 1955, **67** 786
55. K Takahashi, K Suenobu, K Ogura, H Iida *Chem. Lett.*, 1985, 1487
56. K Takahashi, A Tachiki, K Ogura, H Iida *Heterocycles*, 1986, **24**(10) 2835
57. R Iwata, T Ido, T Takahashi, et al *Appl. Radiat. Isol.*, 1987, **38**(2) 97 102
58. A Kozakowska, W Kula, T Tkaczynsky *Acta Pol. Pharm.*, 1974, **31**(5) 595; *Chem. Abs.*, 1975, **83** 28 153
59. K Mai, G Patil *Tetrahedron Lett.*, 1984, **25**(41) 4583
60. K Mai, G Patil *Org. Prep. Proced. Int.*, 1985, **17**(3) 183
61. K Weinges, H Blackholm *Chem. Ber.*, 1980, **113**(9) 3098
62. A Gvozhakova, J Schnittova *Acta Fac. Rerum Natur. Univ. Comenianae Chim.*, 1966, **11** 59
63. J S Sandhu, P S Sethi, M J Suresh *Ind. Chem. Soc.*, 1971, **48**(1) 91
64. Y Murao, T Ochiai, T Nakanome, Japanese P. Appl. 7 946 717; *Chem. Abs.*, **1979, 91** 57 536
65. S Harusawa, Y Hamada, T Shioiri *Tetrahedron Lett.*, 1979, 4663 H A Niepper, F Köhler, Swiss P. 637 828; *Chem. Abs.*, 1983,
66. **100**, 96 704
67. P Geneste, J-M Kamenka, P Dessapt *Bull. Soc. Chim. Fr.*, 1980, (3–4), Pt. 2 187
68. K Mai, G Patil *Synth. Commun.*, 1985, **15**(2) 157
69. S Waki, S Nakata, H Dandan, Japanese P. Appl. 7 988 220; *Chem. Abs.*, 1979, **91** 210 929
70. W L Matier, D A Owens, W T Cromer *J. Med. Chem.*, 1973, **16**(8) 901
71. B. P. 482 352; *Chem. Abs.*, 1938, **32** 6668
72. F Reinhold, U Heinrich, German P. 673 590; *Chem. Abs.*, 1939, **33** 6347
73. A Kotelko, B Zajczkowska *Acta Pol. Pharm.*, 1962, **19** 223; *Chem. Abs.*, 1963, **59** 7370
74. H Distler, K L Hock, Europ. P. Appl. 45 496; *Chem. Abs.*, 1982, 97 38 510
75. German P. 669 808; *Chem. Abs.*, 1939, **33** 5415
76. L A Yanovskaya, B I Kozyrkin, V F Kucherov, USSR P. 191 526; *Byul. Izobret.*, 1967, (4) 28
77. J Yoshimura, Y Ogo, T Sato *Bull. Chem. Soc. Jpn.*, 1965, **38**(11) 1809
78. E E Vittal, A S Gibin, A V Dombrovskii *Zhur. Obshch. Khim.*, 1975, **45**(8) 1872
79. J Gardent *C. R. Seances Acad. Sci.*, 1963, **256** 3140
80. D H R Barton, A Billion, J Boivin *Tetrahedron Lett.*, 1985, **26**(9) 1229
81. E C Evers, W O Freitag, J N Keith, et al. *J. Amer. Chem. Soc.*, 1959, **81**(17) 4493
82. D A Evans, G L Caroll, L K Truesdale *J. Org. Chem.*, 1974, **39**(7) 914
83. J W Zubrick, B I Dunbar, H D Durst *Tetrahedron Lett.*, 1975, (1) 71
84. B Uznanshi, W J Stec *Synthesis*, 1978, (2) 154
85. F Brunnmueler, M Kroner, BRD P. 3 242 193; *Chem. Abs.*, 1984, **101** 210 589
86. A I Ayi, R Guedj *J. Fluor. Chem.*, 1984, **24**(2) 137
87. Y Murao, T Ochiai, T Nakanome, Japanese P. Appl. 7 946 716; *Chem. Abs.*, 1979, **91** 57 537
88. V P Chekhun, E N Zvonkova, R P Evstigneeva, USSR P. 438 257; *Byul. Izobret.*, 1976, (7) 201
89. M L Dhanani, N K Undavia, K A Thaker *J. Inst. Chem. (India)*, 1974, (46), Pt. 6 187
90. J-M Bourgeois *Helv. Chim. Acta*, 1975, **59**, Fasc. 2 363
91. F Becke, P Pässler, BRD P. 1 950 280; *Chem. Abs.*, 1971, **75** 6346
92. F Becke, P Pässler, *Annalen*, 1970, **733** 27
93. K H X Mai, G Patil, US P. 4 551 537; *Chem. Abs.*, 1986, **104** 168 194
94. K H X Mai, G Patil, US P. 4 551 537; *Chem. Abs.*, 1986, **104** 168 195
95. K Mai, G Patil *Synth. Commun.*, 1984, **14**(14) 1299
96. J W Apsimon, R P Seguin *Tetrahedron*, 1979, **35** 2797
97. K Horst, W Sager *Angew. Chem.*, 1987, **99**(6) 595
98. J Morrison *Asymmetric Synthesis. Analytical Methods* (Translated into Russian), Izd. Mir, Moscow, 1987, p. 21
99. S S Naim, N H Khan, A A Siddiqui *Ind. J. Chem. Sec. B*, 1980, **19**(7) 622
100. Y Yamasaki, T Maekawa, T Ishihara, T Ando *Chem. Lett.*, 1985, (9) 1387

101. A J Cowper, R R Astik,, K A Thaker *J. Inst. Chem. (India)*, 1981, **53**, Pt. 4 195
102. J Huang, D F Bushey, M D Graves, et al. *J. Heterocycl. Chem.*, 1987, **24** 1
103. C Pedragal, G G Trigo, M Espada, et al. *J. Heterocycl. Chem.*, 1984, **21** 1527
104. J Kant, F D Popp, B C Uff *J. Heterocycl. Chem.*, 1985, **22** 1065
105. P Potier *Rev. Latinoamer. Quim.*, 1978, **9** 47
106. M Lounasmaa, A Koskinen *Tetrahedron Lett.*, 1982, **23** 349
107. A Koskinen, M Lounasmaa *Tetrahedron*, 1983, **39**(9) 1627
108. Y Nomura, T Shimura, Y Takeuchi *Bull. Chem. Soc. Jpn.*, 1964, **37**(6) 892
109. J Taillades, A Commeyras *Tetrahedron*, 1974, **30**(1) 127
110. M Bejaud, L Mion, J Taillades, A Commeyras *Tetrahedron*, 1975, **31**(5) 403
111. J S Sandhu, S Mohan, G Schroll *Acta Chem. Scand.*, 1971, **25**, Fasc.2 590
112. J C Guillemin, J M Denis *Chem. Commun.*, 1985, 951
113. L A Yanovskaya, Kh Shakhidayatov, E P Prokof'ev, et al. *Tetrahedron*, 1968, **24**(13) 4677
114. F L Logemann, G Shaw *Chem. Ind.*, 1980, (13) 541
115. V D Domkin, A A Kur'yanovich *Zhur. Obshch. Khim.*, 1976, **12**(4) 908
116. K Kadir, G Shaw, G Wright *J. Chem. Soc., Perkin Trans. I*, 1980, (12) 2728
117. P S Khokhlov, V A Kashemirov, A D Mikityuk, et al. *Zhur. Obshch. Khim.*, 1984, **54**(11) 2641
118. T Brown, G Shaw, G J Durant *J. Chem. Soc., Perkin Trans. I*, 1980, (10) 2310
119. E Catalucci, BRD P. 2 700 733; *Chem. Abs.*, 1977, **87** 117 596
120. G Duguay, J P Guemas, J C Meslin, et al. *J. Heterocycl. Chem.*, 1980, **17** 767
121. C M Darling, C P Chen *J. Pharm Sci.*, 1978, **67**(6) 860
122. N F Tullar, US P.2 393 723; *Chem. Abs.*, 1946, **40** 2465
123. M Fields, D E Waltz, S Rothchild *J. Amer. Chem. Soc.*, 1951, **73** 1000
124. H J F Weiss, B. P. 583 307; *Chem. Abs.*, 1947, **41** 2747
125. Y Otsuka, Japanese P. Appl. 7 441 317; *Chem. Abs.*, 1974, **81** 169 159
126. Kh Shakhidayatov *Zhur. Obshch. Khim.*, 1973, **9**(7) 1373
127. O W Bauer, J W Teter, US P. 2 552 026; *Chem. Abs.*, 1951, **45** 9074
128. K Kawashiro, H Yoshida, S Marimoto *Bull. Chem. Soc. Jpn.*, 1977, **50**(1) 2956
129. E C Taylor, J H Sun *Synthesis*, 1986, (10) 801
130. Yu M Kosyrev, N P Novoselov, N I Kirichenko, et al., USSR P. 232 233; *Byul. Izobret.*, 1969, (1) 21
131. L de Vries *J. Org. Chem.*, 1971, **36**(22) 3442
132. Japanese P. 95 952; *Chem. Abs.*, 1982, **97** 162 405
133. M Inone, S Enomoto *Bull. Chem. Soc. Jpn.*, 1982, **55**(1) 33
134. R Ciabatti, Europ. P. Appl. 97 839; *Chem. Abs.*, 1984, **101** 68 534
135. J C Jochims *Chem. Ber.*, 1963, **96** 980
136. K Weinges, F Kromm *Liebigs Ann. Chem.*, 1985, (1) 90
137. R Sarges, H R Howard, P R Kelbaugh *J. Org. Chem.*, 1982, **47**(21) 4081
138. K Weinges, G Brune, H Droste *Liebigs Ann. Chem.*, 1980, (1) 212
139. P K Subramanian, R W Woodward *Synth. Commun.*, 1986, **16**(3) 337
140. K Weinges, H Brachmann, P Stahrecker, et al. *Liebigs Ann. Chem.*, 1985, (3) 566
141. T A Hylton, F L Shenton, US P. 4 072 698; *Chem. Abs.*, 1978, **88** 152 276
142. H F Kung, C C Yu, J Billings, et al. *J. Med. Chem.*, 1985, **28**(9) 1280
143. M Acs, E Fogassy, F Faigl *Tetrahedron*, 1985, **41**(12) 2465
144. N Kametaka, N Nagato, K Hirimeto, et al., BRD P. Appl. 3 531 084; *Chem. Abs.*, 1986, **105** 173 046
145. M Makossa, J Winiarsky *Bull. Soc. Chim. Belg.*, 1987, **49**(4) 303
146. Y Tanaka, K Sakai, T Kouno, et al., Europ. P. 171 768; *Chem. Abs.*, 1986, **104** 163 736
147. M Lim, R S Klein *Tetrahedron Lett.*, 1981, **22**(1) 25
148. A H Cook, J Heilbron, E Smith *J. Chem. Soc.*, 1949 1440
149. M Yu Kolobov, V A Bakulev, V S Mokrushin, A T Lebedev *Khim. Geterotsikl. Soedin.*, 1987, (11) 1503
150. J F Mooze, US P 4 260 624; *Chem. Abs.*, 1981, **95** 25 080
151. T Winkler, W Lutz, H Kristinson *Liebigs Ann. Chem.*, 1985, (2) 433
152. R P Kreher, J Pfister *Chem.-Ztg.*, 1984, **108**(9) 275
153. M W Willard *J. Org. Chem.*, 1982, **47**(5) 886
154. J Schapira, J Pecheur, R Jacquier, BRD P. Appl. 3 001 433; *Chem. Abs.*, 1981, **94** 65 307
155. B V Suvorov, L A Krichevskii, V M Kagasov, et al. *Khimicheskie Sintezy na Osnove Odnouglerodnykh Molekul* (Chemical Syntheses Based on Single-carbon Molecules), Moscow, 1987
156. Kamaluddin, H Janagawa, F Egami, J Iudia *Biochem. Biophys.*, 1981, **18**(3) 215
157. T Irijura, K Nishino, S Suzue, et al., Japanese P. 10 206; *Chem. Abs.*, 1968, **68** 30 062
158. A F McKay, G Y Paris, D L Garmaise *J. Amer. Chem. Soc.*, 1958, **80** 6276
159. A H Cook, I M Heilbron, A L Levy *J. Chem. Soc.*, 1947, 1598
160. A H Cook, G D Hunter *J. Chem. Soc.*, 1952, 3785
161. A F McKay, C Podesva, M-E Kreling *J. Chem. Soc.*, 1962, **27** 2884
162. E R Young, BRD P. Appl. 2 940 037; *Chem. Abs.*, 1980, **93** 132 092
163. J R Ross, J W Sowell *J. Heterocycl. Chem.*, 1985, **22** 817
164. A C Davis, A L Levy *J. Chem. Soc.*, 1951, 3749
165. D L Leussing, N V Ryghavan *J. Amer. Chem. Soc.*, 1980, **102**(17) 5635
166. R S Hosmane *Tetrahedron Lett.*, 1984, **25**(4) 363
167. R S Hosmane, F N Burnett, M S Albert *J. Org. Chem.*, 1984, **49**(7) 1212
168. L A Pavlova, Yu A Davidovich, S V Rogozhin *Uspekhi Khim.*, 1986, **55**(11) 1803 [*Russ. Chem. Rev.*, 1986(11)]
169. T Brown, G Shaw *J. Chem. Soc., Perkin Trans. I*, 1983, (4) 809
170. B Ruiner, C Tapiro, J L Imbach *J. Carbohydrates, Nucleosides, Nucleotides*, 1976, **9**(1–2) 1
171. J L Montero, A Dhainaut, J L Imbach *J. Heterocycl. Chem.*, 1978, **15**(6) 929
172. D H Robinson, Europ. P. Appl. 66 909; *Chem. Abs.*, 1983, **98** 143 429
173. A Edenhofer *Helv. Chim. Acta*, 1975, **58**, Fasc. 7 2192
174. T Teitei *Austral. J. Chem.*, 1983, **36**(11) 2307
175. D Ranganathan, S Ranganathan, S Bamezai *Tetrahedron Lett.*, 1982, **23**(27) 2789
176. C J Barnett, US P.4 199 525; *Chem. Abs.*, 1980, **93** 94 970

177. D B Luten, Jr. *J. Org. Chem.*, 1939, **3** 588
178. A Goldberg, W Kelly, US P. 2493578; *Chem. Abs.*, 1950, **44** 3535
179. A A Goldberg, W Kelly, B. P. 593753; *Chem. Abs.*, 1948, **42** 2289
180. T Hamamoto, K Harada, Europ. P. Appl. 53400; *Chem. Abs.*, 1982, **97** 181771
181. M Nakai, K Harada, Y Mori, US P. 4269982; *Chem. Abs.*, 1981, **95** 62231
182. N V Konstantinova, USSR P. 956476; *Byul. Izobret.*, 1982, (33) 103
183. Yu M Shafran, V A Bakulev, V S Mokrushin, S G Alekseev *Khim. Geterotsikl. Khim.*, 1984, (9) 1266
184. Yu M Shafran, V A Bakulev, V S Mokrushin, P N Kondrat'ev, USSR P.1055741; *Byul. Izobret.*, 1983, (43) 79
185. V A Bakulev, V S Mokrushin *Khim. Geterotsikl. Soedin.*, 1986, (8) 1011
186. K Vaughan, R J La France, Y Tang, D L Hooper *Can. J. Chem.*, 1985, **63**(9) 2455
187. D L Hooper, H W Manning, R J La France, K Vaughan, *Can. J. Chem.*, 1986, **64**(2) 250
188. A M Pinchuk, L N Markovskii, E S Levchenko, V I Shevchenko *Zhur. Obshch. Khim.*, 1967, **37**(4) 852
189. A M Pinchuk, L N Markovskii, I M Kozinskaya *Zhur. Obshch. Khim.*, 1968, **38**(5) 1008
190. P L de Benneville, US P. 2743291; *Chem. Abs.*, 1956, **50** 16826
191. J Denkstein, V Kadarabek *Coll. Czech. Chem. Commun.*, 1966, **31**(7) 2915
192. M W Harman, US P. 2649470; *Chem. Abs.*, 1954, **48** 7629
193. K Yamashita, K Koen, J Nagaoka, Japanese P. Appl. 7514813; *Chem. Abs.*, 1976, **84** 135142
194. T Mitsui, Japanese P. Appl. 59130246; *Chem. Abs.*, 1984, **101** 192477
195. Yuasa Battery Co., Japanese P. Appl. 81118047; *Chem. Abs.*, 1982, **96** 35722
196. K Nakayasu, B Furaya, Y Hasaki, US P. 4299978; *Chem. Abs.*, 1982, **96** 104768
197. A H Cook, S F Cox, *J. Chem. Soc.*, 1949, 2337
198. E Tolksdorf, BRD P. 2717371; *Chem. Abs.*, 1979, **90** 138201
199. Japanese P. 57158743; *Chem. Abs.*, 1983, **98** 107779
200. A Commeyras, J Taillades, J Brugidou, et al., French P. 2565225; *Chem. Abs.*, 1986, **105** 153543
201. C B Warren, R D Minard, C N Matthews *J. Org. Chem.*, 1974, **39**(23) 3375
202. N K Undavia, M L Dhanani, K A Thaker *J. Inst. Chem. (India)*, 1978, **50**(1) 41
203. W H J Boesten, BRD P. 2637204; *Chem. Abs.*, 1977, **87** 39839
204. M E D Hillman, US P. 3560551; *Chem. Abs.*, 1971, **74** 87447
205. D Giraud-Clenet, J Anatol *C. R. Seances Acad. Sci., Ser. C*, 1966, **262**(2) 224
206. D W Wooley, J W B Hershey, H A Jodlowski *J. Org. Chem.*, 1963, **28**(8) 2012
207. D F Ewig, D G Neilson *J Chem. Soc., Sec. C*, 1966, (4) 390
208. N R Barot, J A Elvidge *J. Chem. Soc., Perkin Trans. I*, 1972, (7) 1009
209. J L Kraus *Synth. Commun.*, 1986, **16**(7) 827
210. RG Melik-Ogadzhanyan, R G Mirzoyan, A A Aroyan *Arm. Khim. Zhur.*, 1975, **28**(1) 53
211. Z Rappoport (Editor) *The Chemistry of the Cyano Group*, Interscience, London–New York–Sydney–Toronto, 1970
212. E N Zilberman *The Reactions of Nitriles* (Translated into Russian), Izd. Khimiya, Moscow, 1972
213. A C W Curran, R Crossley, US P. 3907899; *Chem. Abs.*, 1976, **84** 30643
214. M Paventi, J T Edward *Can. J. Chem.*, 1987, **65**(2) 282
215. Z Welwart *Compt. Rend.*, 1960, **250** 1870
216. H Ahlbrecht, H Dollinger *Synthesis*, 1985, (8) 743
217. Z E Overman, R M Burk *Tetrahedron Lett.*, 1984, **25**(16) 1635
218. J Sansoulet, C Tackx, Z Welwart *Compt. Rend.*, 1960, **250** 4370
219. T Thomson, T S Stevens *J. Chem. Soc.*, 1932, 2607
220. R Epsztein, N Le Goff *Tetrahedron*, 1985, **41**(22) 5349
221. W McMeeking, T S Stevens *J. Chem. Soc.*, 1933, 347
222. H Thies, H Schönenberger, P H Qasba *Arch. Pharm.*, 1969, **302**(11) 803; *Chem. Abs.*, 1970, **72** 42998
223. H Thies, H Schönenberger, P H Qasba *Tetrahedron Lett.*, 1965, (3) 163
224. E Münch, O. Schlichting, German P. 561156; *Chem. Abs.*, 1933, **27** 995
225. Z Welwart *International Congress on Aluminium*, Vol.1, Paris, 1955, p. 97; *Chem. Abs.*, 1958, **52** 19926
226. A Kotelko *Acta Pol. Pharm.*, 1962, **19** 109; *Chem. Abs.*, 1963, **59** 1482
227. S Yamada, H Akimoto, Japanese P. Appl. 7419243; *Chem. Abs.*, 1965, **82** 97816
228. S Yamada, H Akimoto *Tetrahedron Lett.*, 1969, (36) 3105
229. G Le Ny, Z Welwart *Compt. Rend.*, 1957, **245** 434
230. Z Welwart *Compt. Rend.*, 1951, **233** 1121
231. Z Welwart *Compt. Rend.*, 1954, **238** 2536
232. R Granger, H Orzalesi, Y Robbe *Trav. Soc. Pharm. Montpellier*, 1967, **27**(1) 15; *Chem. Abs.*, 1968, **68** 77818
233. H Reihlen, G Hessling, G Hühn, E Weinbrenner *Liebigs Ann. Chem.*, 1932, **493** 20
234. A Gaiffe, A Padovani *Compt. Rend., Ser. C*, 1969, **269**(2) 144
235. A Padwa, Y Y Chen, U Chiacehio, W Dont *Tetrahedron*, 1985, **41**(17), 3529
236. T Otohiko, U Kazumori, K Shuji, Y Kiyotaka *Bull. Chem. Soc. Jpn.*, 1980, **59** 1809
237. T Kato, M Sato *Yakugaku Zasshi*, 1972, **92**(12) 1515; *Chem. Abs.*, 1973, **78** 97451
238. P Verschave, J Vekemans, G Hoornaert *Tetrahedron*, 1984, **40**(12) 2395
239. J A Gauthier, I Z Jirkovsky, US P. 4492697; *Chem. Abs.*, 1985, **102** 132054
240. N J Cusack, G Shaw, F I Zogemann *J. Chem. Soc., Perkin Trans. I*, 1980, (10) 2316
241. B G Christensen, J Hannah, D H Shih, US P. 4189493; *Chem. Abs.*, 1980, **93** 8012
242. M H Elnagdi, S M Sherif, R M Mohareb *Heterocycles*, 1987, **26**(2) 497
243. E Gomez, C Evendafio, A McKillop *Tetrahedron*, 1986, **42** 2634
244. C Avendano, T Ramos, E Gomez-Molinero *J. Heterocycl. Chem.*, 1985, **22** 537
245. J Heyes, N Ward, B. P. 1373347
246. C J Rose, A T Ainsworth, B. P. 1421787
247. T C McKenzie, S M Rolfe *J. Heterocycl. Chem.* 1987, **24** 859
248. C K Chu, S Y Cutler *J. Heterocycl. Chem.*, 1986, **24**(2) 289
249. G Shaw, D N Butler *J. Chem. Soc.*, 1959, 4040
250. N J Cusack, G Shaw *Chem. Commun.*, 1970, (17) 1114
251. O W Lever, B R Vessal *J. Heterocycl. Chem.*, 1985, **22** 5

252. T Giorgio, P Gianbattista, US P. 4 198 502; *Chem. Abs.*, 1980, **93** 220 579
253. L H Smith Jr, P Yates *J. Amer. Chem. Soc.*, 1954, **76** 6080
254. G Weitzel, F Schneider, H Guglielmi, J Sander *J. Physiol. Chem.*, 1966, **346** 208
255. A H Cook, G D Hunter *J. Chem. Soc.*, 1949, 1443
256. A D Ainley, A Sexton *Biochem. J.*, 1948, **43** 468
257. G Tarzia, G Pansone, US P. 4 212 806; *Chem. Abs.*, 1981, **94** 83 936
258. A M Macadam, C J Knowles *Biotechnol. Lett.*, 1985, **7**(12) 865
259. S Mataka, K Takahashi, M Tashiro *J. Heterocycl. Chem.*, 1983, **20**(4) 971
260. S Mataka, K Takahashi, M Tashiro, Y Tsuda *Synthesis*, 1980, (10) 842
261. S Mataka, K Takahashi, Y Tsuda, M Tashiro *Heterocycles*, 1980, **14**(6) 789
262. S Yoneda, H Hirai, Z Yoshida *Heterocycles*, 1981, **15**(2) 865
263. C J Barnett, T L Emmick, R C Hoying, US P. 4 211 870; *Chem. Abs.*, 1980 **93** 220 777
264. D Griller, D C Nouhebel, J C Walton *J. Chem. Soc., Perkin Trans. II*, 1983, (9) 1373
265. R D Hancock, B S Nakani, F Marsicano *Inorg. Chem.*, 1983, **22**(18) 2531
266. I R Rowland, B G Lake, J C Philips, S D Gandolli *Mutant Res.*, 1980, **72**(1) 63
267. N Seiler, B Knoedyen, G Buik, S Sarhau, F Bolkenius *Adv. Polym. Res.*, 1983, **4** 135
268. B G Lake, I R Rowland, R A Harris, et al. *Adv. Exp. Med. Biol.*, 1982, **136**, Pt. B 1143
269. T Kawanishi, Y Ohno, A Takahashi, et al., *Arch. Toxicol.*, 1984, **56**(1) 7
270. G Diaz, I Maric, H M Goday, J A Castro *Arch. Toxicol.*, 1981, **47**(3) 159
271. C Stephen, B J Neuburger, M F Argus *Cancer Lett.*, 1980, **9**(2) 161
272. G Walker, G Sarogini, D Y Oliver *Biochem. Biophys. Res. Commun.*, 1982, **107**(3) 856
273. J Behavides, N Croci, M S Benedetti *Biochem. Pharmacol.*, 1983, **32**(2) 287
274. A M Macadam, C J Knowles *Biotechnol. Lett.*, 1985, **7**(12) 865 865
275. K Minami, K Shika *Yakugaku Zasshi*, 1984, **26**(3) 882; *Chem. Abs.*, 1985, **102** 91 189
276. W Schmidt *Z. Wiss, Ernst-Moritz-Arndt-Univ. Greifaw. Med. Reihe*, 1983, **32**(1–2) 27; *Chem. Abs.*, 1984, **101** 49 894
277. H G Vogel *Arzneim. Forsch.*, 1984, **34**(2) 213
278. S Oshima *Tsurumi Shigaku*, 1982, **8**(3) 345; *Chem. Abs.*, 1983, **98** 29 173
279. W Schmidt, D Wendler *Folia Morphol.*, 1982, **30**(2) 146
280. D Wendler, W Schmidt, W Gabler *Anat. Arz.*, 1980, **147**(5) 413; *Chem. Abs.*, 1982, **96** 81 093
281. S Kojima, Y Hamo, T Sasaki, A Kubodera *Fur. J. Nucl. Med.*, 1983, **98** 212 186
282. O Kirino, T Oishi, N Kameda, et al., BRD P. 2 442 239; *Chem. Abs.*, 1975, **83** 27 636
283. K Bauer, H Bieringer, G Frisch, et al., BRD P. Appl. 2 948 095; *Chem. Abs.*, 1982, **96** 7068

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Synthesis of pyrroles from aliphatic compounds

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ABSTRACT. The most recent information about the methods for constructing a pyrrole ring from functional aliphatic compounds has been classified and correlated.
The bibliography includes 196 references.

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I. Introduction

The pyrrole ring forms part of the molecular structure of many natural and biologically active compounds. Hence the constant interest in the chemistry of pyrroles is understandable. Since the last monographs[1–3] and reviews[4–7] appeared, covering different questions concerning the structure, reactivity, and synthesis of pyrroles, a large number of new studies in this field which require classification and correlation have been published in the literature.

The many methods for synthesising pyrroles can be divided into three main groups: cyclisation of functional aliphatic compounds, conversion of five-membered heterocyclic compounds containing one nitrogen atom in the ring, and conversions of other heterocycles.

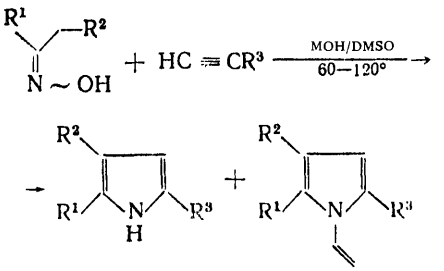
The methods for synthesising pyrroles by cyclisation of aliphatic compounds are usually classified[1,2] according to the number of carbon atoms provided to the pyrrole ring by the initial reagents: $C_2 + C_2$, $C_3 + C_1$, and $C_4 + N$ (C_4-N).

The methods for synthesising pyrroles from aliphatic compounds have undergone considerable development in recent years. They are the subject of the present review, which covers publications from 1980 to 1987 that have, as a rule, not yet appeared in monographs or reviews.

II. $C_2 + C_2$ reactions

1. Pyrroles from ketoximes and acetylene

In recent years there has been the most rapid development of a new general method for constructing a pyrrole ring which is based on the reaction, which was discovered at the beginning of the 1970s, between ketoximes and acetylenes in the system alkali metal hydroxide–DMSO [3,6] (it was suggested[8,9] that this synthesis should be called the Trofimov reaction)

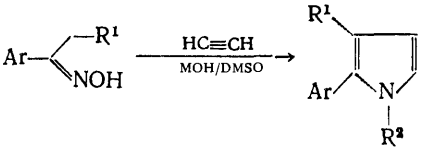


R^1, R^2 = Alk, Ar, etc.; R^3 = H, Ph; M = K, Na, Li.

The yields of pyrroles and *N*-vinylpyrroles (the latter are readily formed with excess acetylene) depend on the structure of the initial compounds and, as a rule, amount to 50–70%, while in favourable cases they reach 90%. A necessary condition for this reaction to take place is the presence of an α-CH_2 group in the ketoxime. Aldoximes do not form pyrroles but are converted to nitriles, amides, or salts of carboxylic acids.[3,6,10]

This simple and effective synthesis has made it possible to convert ketones in two stages to pyrroles with the widest range of substituents—alkyl,[3] alkenyl,[11] aryl,[3,12,13] hetaryl [3,14]—as well as to annelated pyrrole systems.[3,6] For the first time the simplest alkyl- and aryl-substituted pyrroles not containing functional groups became accessible, the majority of known methods for obtaining them being not very suitable. It is not surprising that the discovery of this reaction acted as a powerful stimulus for the development of pyrrole chemistry. Within a short time more than 120 studies were published in this field. The majority of them have already been covered in a review[6] and monograph.[3] We have therefore restricted ourselves here to examining the most recent information that has not appeared in these review publications.

In one study[15] the synthesis of the previously unknown 2-arylpyrroles and their 1-vinyl derivatives is reported.



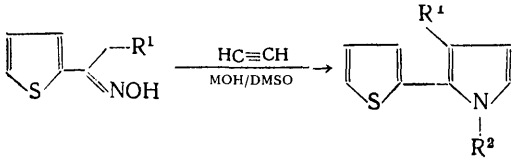
Ar = Ph, 4-RC_6H_4 (R = Me, Et, MeO, Cl, Br, iso-Pr, t-Bu), Bz;

R^1 = H, Me, C_6H_{13}, C_7H_{15}, C_8H_{17}, Ph; R^2 = H, CH = CH_2;

MOH = LiOH, KOH.

Pyrroles that are not substituted on the nitrogen atom are obtained in LiOH–DMSO (100 °C, 3 h) and their 1-vinyl derivatives are obtained in KOH–DMSO. By using an equimolar quantity of KOH relative to ketoxime and a tenfold excess of DMSO (from the total weight of the reagents) it is possible to reduce the reaction temperature considerably (to 50–60 °C) and obtain 3-alkyl-2-arylpyrroles and their 1-vinyl derivatives with total yields of up to 90%.[16]

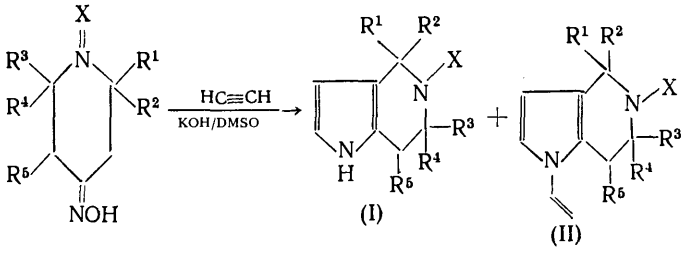
Oximes of a thiophene series and acetylene underwent the Trofimov reaction to give thienylpyrroles and the previously unknown 1-vinylthienylpyrroles in 50–70% yield.[17]



R^1 = H, Me, Et, Pr, Bu, C_6H_{13}; R^2 = H, CH = CH_2.

The reaction takes place smoothly at 100–130 °C and can be effected both at elevated pressure (1.0–1.6 MPa) and atmospheric pressure of acetylene. The ratio of pyrroles to their 1-vinyl derivatives formed in this synthesis is governed by the reaction conditions—its duration, the temperature system, concentration of acetylene, addition of water, and change in cation from the hydroxide.

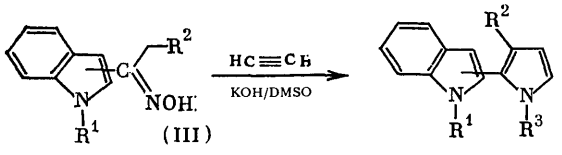
The heterocyclisation (50–100 °C, 4–5 h) of acetylene with piperidine oximes,[18–21] their *N*-hydroxy derivatives, and nitroxyl radicals[18,19] has been carried out.



X = H, Me, OH, O·; $R^1 = R^3$ = H, Me, Ph; $R^2 = R^4 = R^5$ = H, Me.

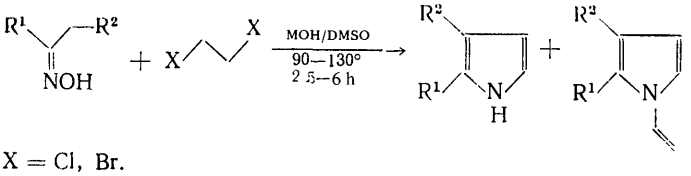
Tetrahydro-5-azaindoles (I) and (II), including those with a free valency (X = O) have been obtained in this way. A special feature of the reaction when X = OH is that it mainly gives tetrahydroazaindoles with a nitroxyl free-radical centre (compounds with a vinyloxy group at the 5-position are formed in very small quantities in the process).[18,19]

Reaction between acetylene and oximes of 2- and 3-acylindoles (III) gives 2- and 3-(pyrrolyl)indoles with yields of 30–45%.[22,23] The optimum conditions for synthesis are: temperature 100–105 °C (30 min to 2 h), ratio of ketoxime to KOH = 1:1.2.



R^1=H, Me; R^2=H, Me, Pr, Ph; R^3=H, CH=CH_2.

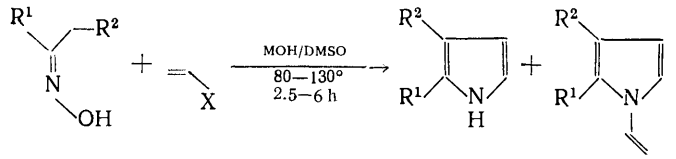
A variant of the reaction under discussion is the interaction between ketoximes and haloethanes, which gives pyrroles and their 1-vinyl derivatives with a total yield of 50–60%.[3,24,25]



X = Cl, Br.

Trofimov and Mikhaleva[3] achieved 94–95% selectivity with respect to the main product—a pyrrole—at the cost of a reduction in yield to 30%. As in the reaction with acetylene,[3,6] this was mainly achieved by adding small quantities of water (10–20%) to the reaction mixture.

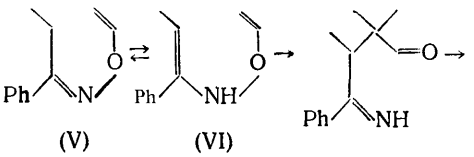
The reaction between ketoximes and vinyl halides occurs in a similar manner.[26,27]

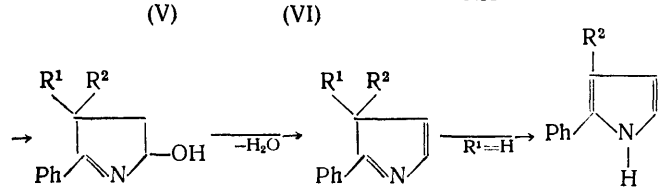


By varying the ratio of reagents and the conditions it is possible to carry out the reaction with a sufficient degree of selectivity to obtain either mainly pyrroles in about 40% yield or their 1-vinyl derivatives (yields up to 35%).

These variants of the Trofimov reaction, despite the lower yields of pyrroles, can in some cases prove to be more suitable for laboratory experiments, since they exclude the use of free acetylene.

One of the possible methods for forming pyrroles from ketoximes and acetylene in the superbasic catalytic system KOH–DMSO is a heteroatomic variant of the Claisen rearrangement of the intermediate *O*-vinyloxime (V), which undergoes isomerisation by proton transfer to give the *O*,*N*-divinylhydroxylamine (VI).[3]

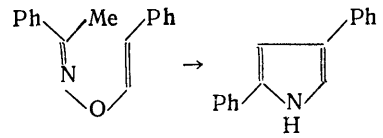




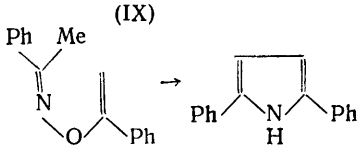
R^1 = Me; R^2 = Me; R^1 = H, R^1 = H, R^2 = iso-Pr.

It was shown[28] that *O*-vinylarylketoximes (V), which can be obtained in 50% yield from ketoximes and acetylene, on heating (100 °C) in KOH–DMSO are completely converted to the corresponding pyrroles even after 1.5 h. When isopropyl- and isobutyl-phenylketoximes were reacted with acetylene in the same system the reaction was stopped at the stage where 4*H*-2-hydroxy-2,3-dihydropyrroles (VII) were formed,[29] and on heating (70 °C, 5 h) compound (VII) (R^1 = R^2 = Me) with acetylene, the 3*H*-pyrrole (VIII) was isolated.[30]

Confirmation of this mechanism was also obtained[31] by rearrangement of the isomeric *O*-(phenylvinyl) acetophenone oximes (IX) and (X) in KOH–DMSO to give the corresponding pyrroles.

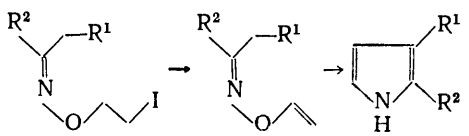


(IX)



(X)

O-(2-Iodoethyl)ketoximes (XI), obtained in two stages from ketones, on heating in the presence of t-BuOK and t-BuOH are converted to pyrroles (yields 65–74%).[32]

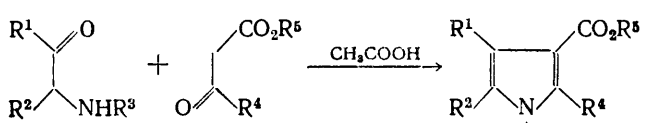


(XI) (XII)

It was possible to stop the reaction at the stage where the *O*-vinyloxime (XII) was formed, R^1 = H, R^2 = Ph (yield 41%), by lowering the concentration of t-BuOK and reducing the time of reaction. The pyrrole was obtained in 89% yield by thermolysis of oxime (XII).

2. Condensation of aminoketones with ketones

In recent years there has been further development of one of the most widely used methods for synthesising pyrroles—the Knorr synthesis, which in its original form is regarded as the condensation of α-aminoketones with carbonyl compounds that have active methylene groups adjacent to the carbonyl group such as in β-ketoesters and β-diketones.



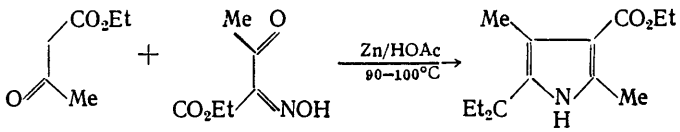
(XIII)

When phenylacylamines are reacted with methyl and ethyl acetoacetates, pyrroles (XIII) are obtained: (R^1 = Ar; R^2 = H; R^3 = H, Ar; R^4 = Me; R^5 = H, Me, Et),[33] (R^1 and R^3 = Me; R^2 = 4-ClC_6H_4O; R^4 = CH_2CO_2Et; R^5 = Et).[34]

The reaction of amino derivatives of sugars with dimethyl diacetylenedicarboxylate (DMADC) may be regarded as a unique version of the Knorr synthesis; this gives pyrroles with carbalkoxy substituents (XIII) (R^1 = H; R^2 = $(CHOH)_nCH_2OH$, *n* = 2, 3; R^3 = Alk, Ar; R^4 = Co_2Me; R^5 = Me).[35,36]

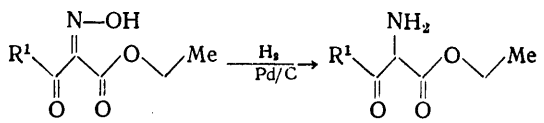
The aminoketone component of the reaction is most frequently obtained by reduction *in situ* of the corresponding monooxime, which in turn is formed by nitrosation of a ketone or β-dicarbonyl compound.[37–43]

The reducing agent most frequently used is zinc in acetic acid.

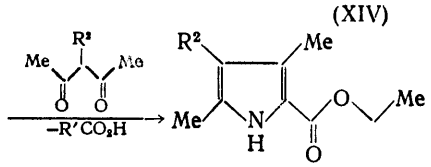


Although quite versatile, the Knorr synthesis does have some disadvantages. These are mainly the moderate yields of pyrroles (40–60%). The reaction efficiency is substantially reduced in the case of asymmetric β-dicarbonyl compounds, which usually form mixtures of different pyrroles.

The higher yields of pyrrole-2-carboxylates (60–70% for the main product synthesised from an asymmetric ketone and 75–90% from a symmetric ketone) in comparison with the method described by Kleinspen[5] (reduction *in situ* of diethyl oximinomalonate with zinc) were achieved by reaction of 1,3-diketones with diethyl aminomalonate (XIV), which was prepared in advance in boiling glacial acetic acid.[44] Reduction of oximinomalonate is carried out in ethanol solution in the presence of Pd/C.[44]

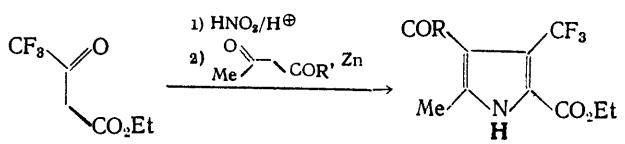


(XIV)



R′ = Me, EtO; R^2 = H, Me, Et, Pr.

The usual conditions for the Knorr synthesis are not very suitable for the synthesis of β-trifluoromethylpyrroles (yield 5%). The yield of these compounds can be increased by using a strong acid medium during nitrosation. In neutral solution ethyl trifluoroacetoacetate is enolised to a considerable extent. A strong acid medium shifts the tautomeric equilibrium towards the keto tautomer, which results in a greater yield of pyrroles (41–47%). A mixture of acetic and trifluoroacetic acids saturated with HCl is used as the solvent.[38]

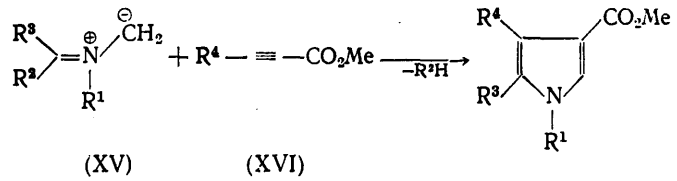


R = Alk, AlkO.

3. 1,3-Dipolar cycloaddition

Dipolar cycloaddition[45] has formed the basis for the development of many methods for synthesising pyrroles in recent years. 1,3-Dipolar cycloaddition of nitrile or azomethine ylides to dipolarophiles gives pyrroles either directly or via pyrroline derivatives. For this purpose it is possible to use mesoionic compounds which formally contain a system of azomethine ylide bonds. Thus, the azomethine ylide (XV), which is generated by reaction of α-cyanoaminosilanes [46] or α-(phenylthio)aminosilanes [47] with silver fluoride and also by alkylation of imidates with trimethylsilylmethyltriflate (DMF, 25 °C,

3 h) followed by desilylation of the resulting salts with caesium fluoride,[48] reacts with methyl propiolate or DMADC to form pyrroles.[46-48]



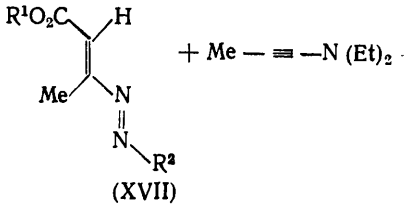
(XV) (XVI)

R^1 = Me, $PhCH_2$; R^2 = H, EtO, Me; R^3 = H, Me, Ph; R^4 = H, CO_2Me.

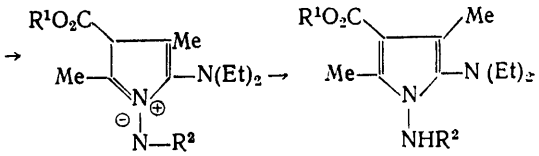
The reaction between compounds (XV) and (XVI) in the presence of silver fluoride takes place when there is a small excess of the latter in acetonitrile at 25 °C over a period of 10 h in the dark. The residue (pyrroline) formed after removal of solvent is oxidised by 2,3-dichloro-5,6-dicyano-*p*-benzoquinone to give the corresponding pyrroles in 62–65% yield.[46,47] The reaction takes place under similar conditions in the presence of anhydrous CsF, with a yield of pyrroles of up to 75%.[48]

N-Protonated azomethine ylides (XV) (R^1 = H, R^3 = Et, Bu, Ph; R^2 = NPh, $NC_6H_{11}S$) readily add on to electron-deficient acetylene compounds (dry acetonitrile, 20–25 °C, 16 h) forming the corresponding pyrroles (yield 44–96%).[49,50]

One of the most unusual examples of 1,3-cycloaddition of hetero-1,3-dienes to alkynes has been reported in one study;[51] 1,2-diaminopyrroles (XVIII) are obtained in 46–59% yield by reaction of diazabutadienes (XVII) with 1-propynyldiethylamine.



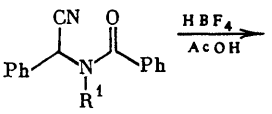
(XVII)



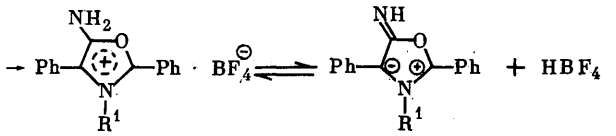
(XVIII)

R^1 = Me, Et; R^2 = Ts, $CO_2CMe_2CCl_3$.

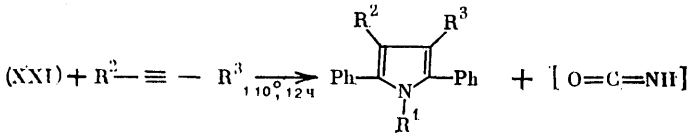
Acyclic analogues (XIX) of Reissert compounds have been used for the synthesis of pyrroles under both acidic and alkaline conditions.[52] Thus, the mesoionic compounds (XXI), which are formed by dissociation of hydrophobic salts of Reissert compounds (XX), undergo 1,3-dipolar cycloaddition to alkynes to give the corresponding pyrroles.



(XIX)

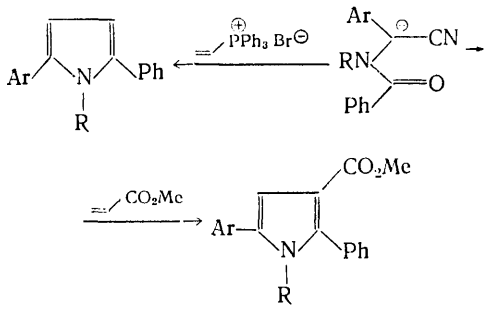


(XX) (XXI)



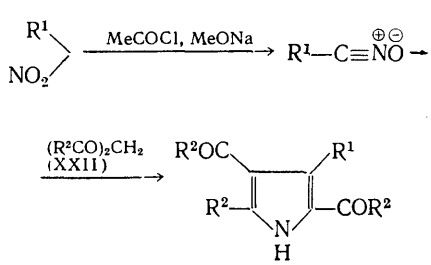
R^1 = Ph, Bz; R^2 = R^3 = H, CO_2Me.

Similar pyrroles are formed by reaction between methyl acrylate [52] or vinyltriphenylphosphonium cation[53,54] and anions which are products of the reactions of superbases (BuLi/THF, NaH/DMSO or DMF/NaH) with Reissert compounds. In the first case the reaction occurs at room temperature, in the second case heating is required (110 °C) for 24 h.



R = Ph, 3-$MeOC_6H_4$, 4-ClC_6H_4, C_6H_{13}, cyclo-C_6H_{11}; Ar = Ph, 4-ClC_6H_4, 3, 4-$Me_2C_6H_3$.

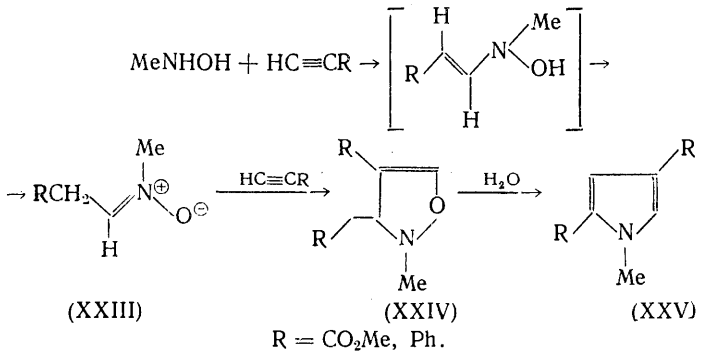
A 1,3-dipolar cycloaddition route is followed in the reaction of aliphatic nitro compounds, 1,3-diketones, and acetyl chloride (MeONa/MeOH, *N*,*N*-dimethylacetamide, 0–20 °C, 12 h), which gives diacylpyrrole derivatives in 35–85% yield.[55]



R^1, R^2 = Ph, 4-MeC_6H_4, 4-ClC_6H_4.

It is suggested[55] that the first stage of the reaction is formation of nitrile oxide, which as a result of 1,3-dipolar cycloaddition to 1,3-diketone (XXII) forms a pyrrole.

1,3-Dipolar cycloaddition of nitrones (XXIII), which are formed from methylhydroxylamine and methyl propiolate or phenylacetylene (80 °C, 12 h) gives the pyrrole (XXV).[56] When the reaction is carried out at 25 °C (24 h) it is possible to stop it at the stage involving formation of the intermediate isoxazoline (XXIV), which at 80 °C over a period of 12 h rearranges to pyrrole (XXV).



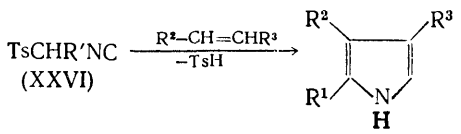
(XXIII) (XXIV) (XXV)

R = CO_2Me, Ph.

With alkyl-substituted acetylenes this reaction does not occur even with prolonged heating.[56]

4. Pyrroles from isonitriles

An effective method of obtaining pyrrole derivatives which are unsubstituted at the 1- and 5-positions is the base-catalysed addition of tosylmethylisocyanide (XXVI) to activated alkenes.[57,58]



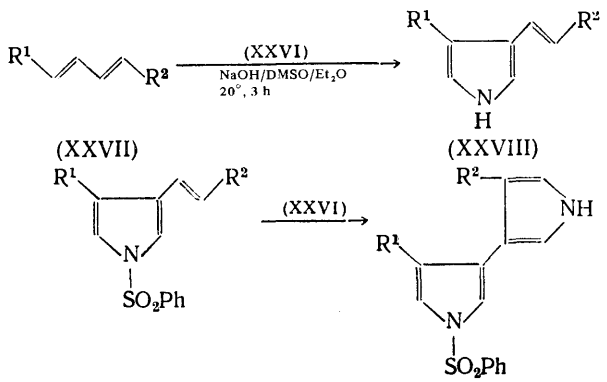
(XXVI)

R^1 = Me, CH_2=CH—CH_2, Bz; R^2 = Me, Ph;

R^3 = CO_2Me, Bz, C≡N.

The reaction can be carried out in superbasic systems—NaH in a DMSO—Et_2O mixture or in dimethoxyethane. The yields of pyrroles are 70–90%.

When 1,3-diene esters (XXVII) are used as the Michael acceptor, the addition to them of two molecules of isonitrile (XXVI) to give a bipyrrolyl is to be expected. However, under the given conditions only the 3,4-substituted pyrrole (XXVIII) is obtained in 80% yield.[59–61] The addition of the second isonitrile molecule does not occur apparently because of the reduction in electrophilicity of the α,β-unsaturated ester (XXVIII). A 3,3′-bipyrrolyl can only be obtained after addition of a $PhSO_2$ group to the nitrogen atom.

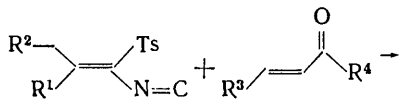


(XXVII) (XXVIII)

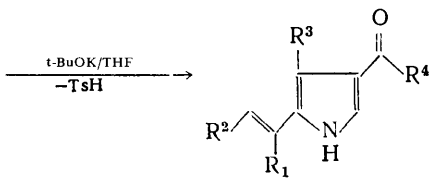
R^1 = Me, Et; R^2 = CO_2Me, CO_2Et.

If the reaction of isonitrile (XXVI) and the 1,3-diene ester is carried out in the presence of BuLi in THF (−70° to 0 °C, 2 h), the other isomer of pyrrole (XXVIII) (R^1 = CO_2Me, R^2 = Me) is obtained in 34% yield.[61]

Pyrroles (XXX), which have an alkenyl group at the α-position, are synthesised in high yield (83–96%) by the base-catalysed addition of 1-tosylalk-1-enylisocyanides (XXIX), readily formed by reaction of tosylmethylisocyanide with carbonyl compounds, to Michael acceptors.[62]



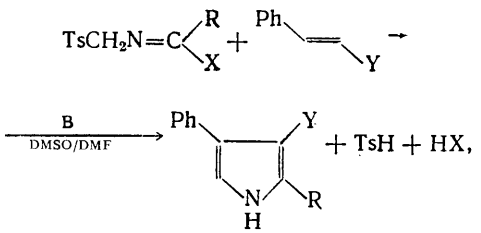
(XXIX)



(XXX)

R^1 = Me, Ph; R^2 = H; R^1R^2 = $(CH_2)_3$, $(CH_2)_4$, $(CH_2)_5$;
R^3 = H, Me, Ph; 2-furyl, 2-thienyl, MeCH = CH, PhCH = CH;
R^4 = Me, MeO, EtO, Ph, 2-furyl, 2-thienyl

Methyl isocyanoacetates (RO_2CCH_2NC) are quite frequently used for the synthesis of pyrrole-2-carboxylates.[63–65] The reaction takes place under the same conditions as for isonitriles (XXVI). *N*-(Tosylmethyl)imino derivatives[66] react in a similar manner with Michael acceptors.



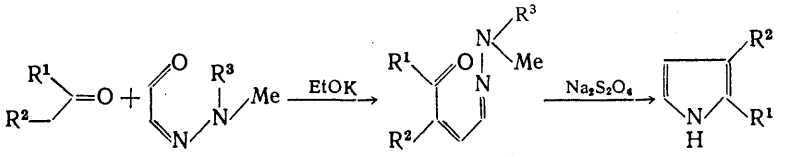
B = NaH, t-BuOK

R = Me, Ph, SMe, OMe; X = SMe, OMe; Y = COPh, CO_2Me, CN.

It appears that in this case the first stage involves removal of a proton from the activated methylene group, generating a 2-azaallyl anion $Ts\overline{C}-N=CRX$, which subsequently reacts with the unsaturated substrate either according to a 1,3-dipolar addition mechanism (after elimination of Ts^- or X^-) or according to a 1,3-anionic cycloaddition mechanism.

5. Reactions involving hydrazones and azoalkenes

Carbonyl compounds containing an active methylene group when reacted with glyoxal monohydrazones form hydrazones (XXXI),[67,68] which on treatment with sodium dithionite give pyrroles in 21–48% yield.[68]

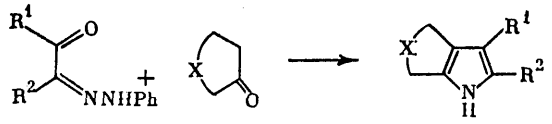


(XXXI)

R^1 = H, Alk, AlkO, Ar; R^2 = H; Alk, AlkO, CN, CO_2Alk; R^3 = Alk, Ar.

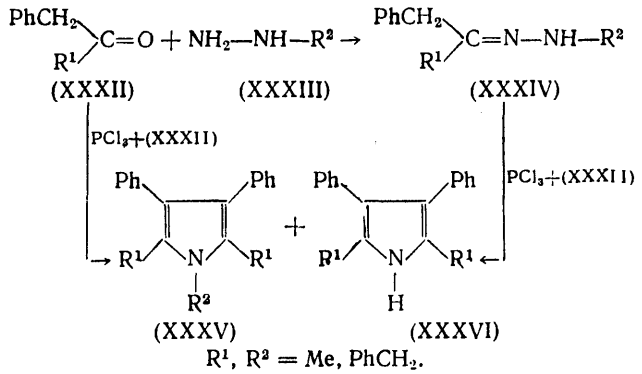
Compounds (XXXI) when treated with sodium borohydride are converted to alcohols, which on heating or in the presence of acids eliminate water to form *N*-aminopyrroles, and subsequently on hydrogenation give pyrroles unsubstituted on the nitrogen atom.[67]

Reductive condensation of phenylhydrazones with cyclic ketones in the presence of zinc and sodium acetate in acetic acid gives pyrrolocycloalkanes in 19–25% yield.[69]



R^1=Me, Et; R^2=CO_2Me, CO_2Et; X=$(CH_2)_3$, $(CH_2)_4$.

The reaction of enolisable ketones (XXXII) with their hydrazones (XXXIV) in the presence of two equivalents of PCl_3 (CH_2Cl_2, 20 °C or C_6H_6, 80 °C) results in the formation of a mixture of symmetrically substituted pyrroles (XXXV) and (XXXVI).[70] The yield (28–46%) and ratio of products depend on the structure of the reagents and the reaction conditions.



R^1, R^2 = Me, $PhCH_2$.

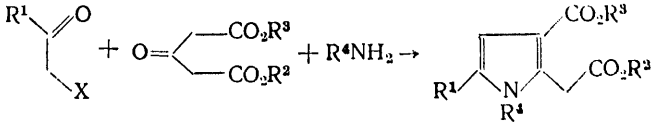
A mixture of pyrroles (XXXV) and (XXXVI) (1 : 1) is also obtained by direct reaction of the initial ketones (2 equivalents), hydrazine (XXXIII) (1 equivalent) and PCl_3 (3 equivalents).

Azoalkenes react with 1,3-dicarbonyl compounds.[71–88]

The reaction occurs via intermediate 1,4-adducts (XXXVII), which subsequently cyclise to a pyrrole by elimination of water. In a number of cases these intermediates have been isolated. The synthesis proceeds smoothly at room temperature and is complete after several hours. The process can be speeded up by heating the reaction mixture or by using a catalyst ($CuCl_2$,[71–80] Na_2CO_3 [81]). Aminocarbonyl-,[73,74] aryl-,[75–77] aroyl-,[72] arylsulphonyl-,[78,79] alkoxycarbonyl-,[71,80] and β-chloro-azoalkenes [81] have been used as the first reaction component. 1,3-Diketones,[71,73,75,77,79,81] β-ketoesters,[71,73,75,77,79,81] and 3-oxoalkanamides [72,74,76,78,80] have been used as the second components.

6. Reactions involving haloketones

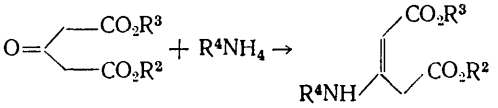
A series of studies have recently appeared which are devoted to extending the Hantzsch method,[82–95] which is based on the reaction of α-haloketones or α-haloaldehydes with β-ketoesters and amines.



R^1, R^4 = H, Alk; R^2, R^3 = Alk, Ar; X = Cl, Br.

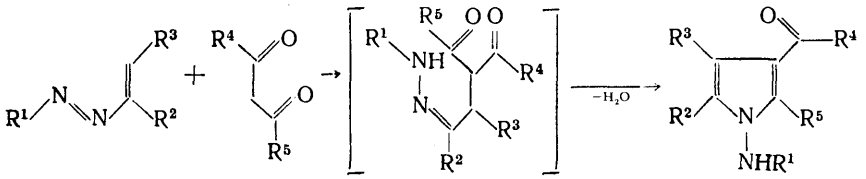
The reaction is carried out in the same water–dioxan or water–alcohol solution, in a two-phase system, or without any solvent at room temperature (prolonged standing of the mixture) as well as with heating for several hours. In some cases[95] the reaction is catalysed by carboxylic acids.

The probable reaction route[5] assumes the formation of aminocrotonate (XXXVIII) at the first stage.

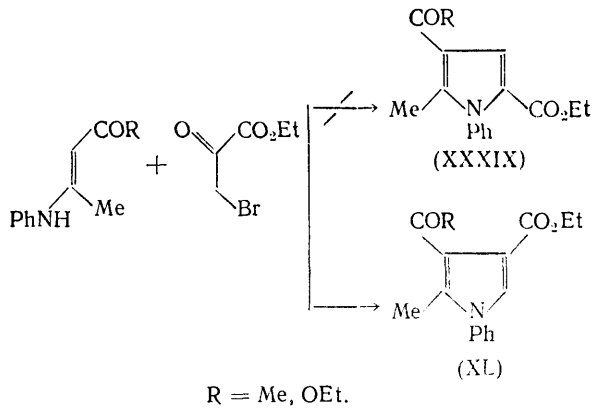


(XXXVIII)

In fact, such aminocrotonates have successfully been used as initial compounds for the synthesis of pyrroles.[96]



(XXXVII)

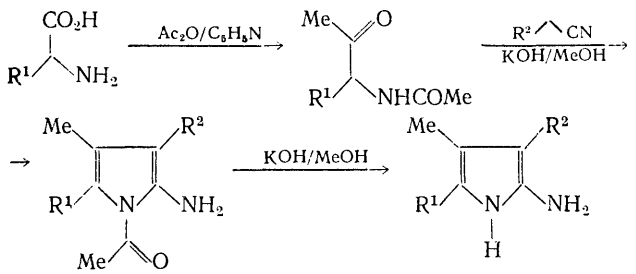


R = Me, OEt.

An unexpected result of this study was that instead of pyrrole (**XXXIX**) its isomer (**XL**) was formed in 72% yield. The reaction took place when the reagents were refluxed in ethanol for 30 min.

7. Reactions involving amino and nitrile groups

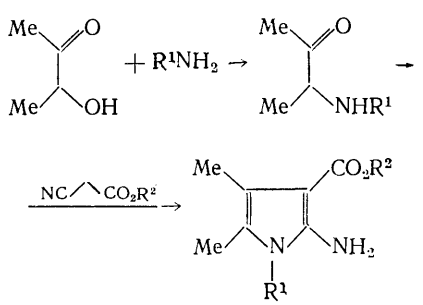
N-Acetyl-α-aminoketones, obtained from *L*- or *DL*-amino acids, when condensed with nitriles form substituted 2-amino-3-cyano-4-methylpyrroles (120 °C, 3–4 h).[97]



R^1 = Me, Pr, iso-Pr, Ph, Bz; R^2 = CN, SO_2R.

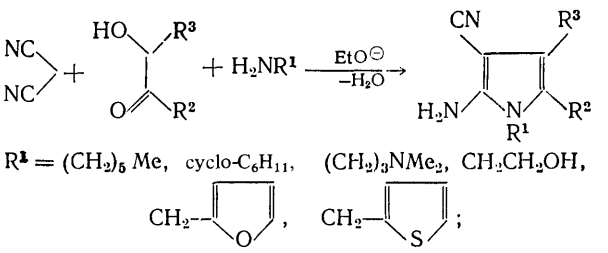
The pH of the medium must be kept within the range 9–10 and the temperature at 55–60 °C when decarbonylation takes place.

Condensation of 3-hydroxy-2-butanone with primary aryl- and alkyl-amines in boiling cyclohexane gives aminoketones, which react with cyanoacetates to give various 2-amino-3-carbalkoxy-4,5-dimethylpyrroles in 36–87% yield.[98]



R^1 = Alk, Ar; R^2 = Me, t-Bu.

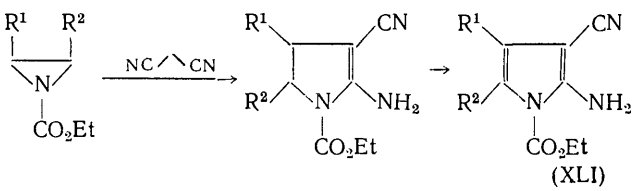
The reaction of hydroxyketones with amines and malononitrile, giving 2-amino-3-cyanopyrroles in yields up to 96%, also takes place via the intermediate formation of an aminoketone. The reaction is carried out in ethanol in the presence of sodium ethoxide.[99]



R^3 = $(CH_2)_5$Me, cyclo-C_6H_{11}, $(CH_2)_3NMe_2$, CH_2CH_2OH,

$R^1 = R^3$ = Me, Ph; $R^2R^3 = (CH_2)_4$, $(NH_2)_5$.

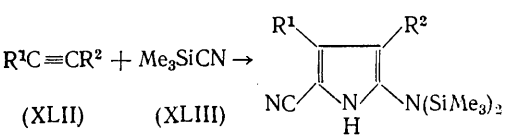
The reaction of malononitrile with 1-carbethoxyaziridines in the presence of sodium hydride (THF, 100 °C, 4 h) gives 2-amino-3-cyano-1-carbethoxy-4,5-dihydropyrroles (yield 45–50%), which are aromatised (chloranil, benzene, 80 °C, 3 h) to the corresponding pyrroles (XLI) in 30–90% yield.[100]



R^1 = H, Ph; R^2 = H, Me.

Pyrroles (XLI) (R^1 = Me, Ph; R^2 = H) were also obtained by counter-synthesis from malononitrile and *N*-phenacyl- or *N*-acetonyl-carbamates $R^1COCH_2NHCO_2Et$ on boiling the reagents in benzene in the presence of acetic acid and ammonium acetate or piperidine.

When trimethylsilylcyanide (XLIII) is reacted with alkynes (XLII) (N_2, 20 h) in the presence of palladium or nickel catalysts, 5-aminopyrrole-2-carbonitriles are obtained in high yield.[101]



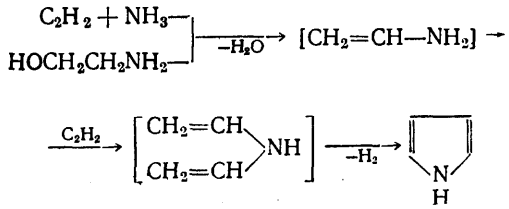
R^1 = H, Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4, 2-thienyl, 2-$MeOC_6H_4$;
R^2 = Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4, 2-thienyl.

There has been a study of the reaction of nitrile (XLIII) with silylacetylenes (XLII) (R^1 = $Me_3SiC{\equiv}C$, $CH_3(CH_2)_5$, Ph, Me_3Si; R^2 = $SiMe_3$),[102] (120–160 °C, 9–12 h) in the presence of palladium catalysts to give 2-amino-5-cyanosilylpyrroles (yield 49–84%).

8. Reactions involving enamines and imines

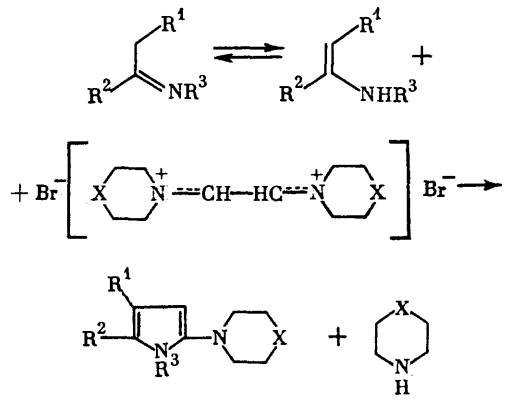
The Chichibabin reaction—the catalytic interaction of acetylene with ammonia—remains one of the most promising methods for obtaining unsubstituted pyrrole.[2] In recent years definite progress has been made in this direction. By varying the catalysts and reaction conditions it has been possible to increase the yield of pyrrole to 10.4% (cadmium calcium phosphate catalyst).[103] The same catalyst has been used for the condensation of acetylene with aniline (410–430 °C),[104] with a 15–17% yield of 2-phenylpyrrole.

It has been proposed[103] that at the first stage of the reaction between acetylene and ammonia, vinylamine is generated, which then reacts with acetylene to give divinylamine, which cyclises to pyrrole.



Such a scheme is consistent with the synthesis of pyrrole from mono- and di-ethanolamines, which presumably involves the intermediate formation of mono- and di-vinylamines.[105,106] The reaction takes place at a high temperature on a complex catalyst: Al_2O_3 (95%), ZnO (2%), Cr_2O_3 (3%). The yield of pyrrole is 10% from monoethanolamine and 18.5% from diethanolamine.

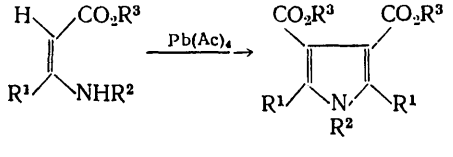
Enamines react under mild conditions (CH_2Cl_2, 20 °C, 2 h) with certain *bis*-iminium salts, forming aminopyrroles in good yield.[107]



R^1=CO_2Et, CO_2CMe_3, Ph; R^2= Me, Ph; R^3=H, Alk; X=O, NMe.

The formation of pyrroles in this reaction is due to double electrophilic attack by the dication on the nitrogen atom and β-carbon atom of the enamine. The 2,3-dihydropyrroles thus obtained eliminate an amine during the synthesis and are converted to α-aminopyrroles. When R^1 = H, pyrroles are not formed. This supports the conclusion[107] that α-aminopyrroles containing a hydrogen at C(4) are unstable compounds.

Oxidation of enaminoesters (XLIV) with an equivalent quantity of lead tetra-acetate (CH_2Cl_2, 20 °C, 3–7 h) results in the formation of symmetrically substituted pyrroles (XLV).[108–110]



(XLIV) (XLV)

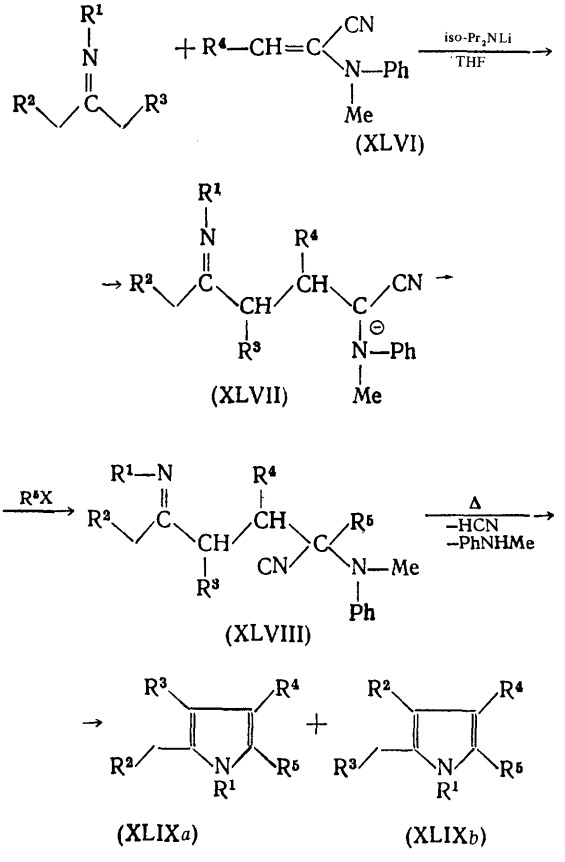
R^1 = CO_2Me, Me, Ph; R^2 = Me, Pr, Bu, $PhCH_2$, 4-ClC_6H_4, R^3 = Me, Et.

In the opinion of Vernon and co-workers,[108] the new C–C bond is formed by two-electron oxidation of enamine (XLIV).

The yields of the pyrroles synthesised from β-aminocrotonates amount to 20–40%. The oxidation of β-aminocinnamates is less effective (yields of pyrroles 10–20%) and only takes place in an atmosphere of nitrogen.

The reaction of 2-(*N*-methylanilino)-2-alkenonitriles (XLVI) with ketimine anions followed by alkylation or protonation of the intermediate carbanion (XLVII) and culminating in the pyrolysis of adduct (XLVIII) gives pyrroles.[111]

Asymmetrically substituted ketimines (R^2 = n-Pr, R^3 = H) form a mixture of pyrroles (XLIXa, b) in the ratio 85 : 15. It is possible to obtain pyrroles (XLIXa) selectively by deprotonation at –78 °C.



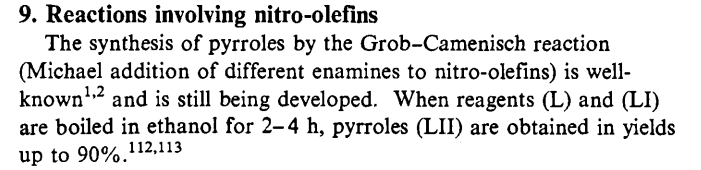
(XLVI) (XLVII) (XLVIII)

(XLIXa) (XLIXb)

R^1 = Me, cyclo-C_6H_{11}, iso-Pr, $PhCH_2$;
R^2 = H, Me, Pr; R^3 = H, Me, Pr; R^2R^3 = $(CH_2)_3$, $(CH_2)_4$;
R^4 = H, Et; R^5 = H, Me, Et, Pr; X = OH, I, Br.

9. Reactions involving nitro-olefins

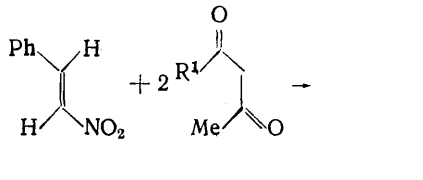
The synthesis of pyrroles by the Grob–Camenisch reaction (Michael addition of different enamines to nitro-olefins) is well-known[1,2] and is still being developed. When reagents (L) and (LI) are boiled in ethanol for 2–4 h, pyrroles (LII) are obtained in yields up to 90%.[112,113]



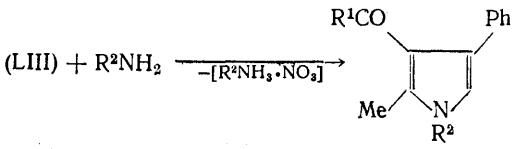
(L) (LI) (LII)

X-acceptor: COMe, CO_2Me, CO_2Et; R^1 = Me, Ph; R^2 = H, Me; R^3 = H, Me, Ph; R^4 = Me, Bu, Ph, $PhCH_2$, 4-$AlkOC_6H_4$.

1,3-Dicarbonyl compounds are being used for the reaction with nitro-olefins with increasing frequency.[114,115] Thus, the reaction of ethyl acetoacetate and pentane-2,4-dione with β-nitrostyrene in a solution of MeONa/MeOH gives the *bis*-dihydrofuran intermediate (LIII). Treatment of the latter with ammonia or amines in methanol gives 3-acylpyrroles in high yield.

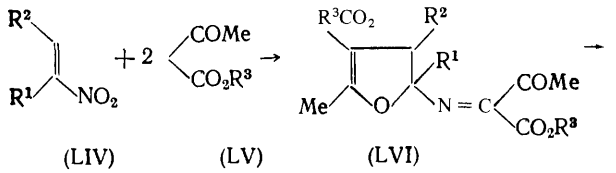


(LIII)

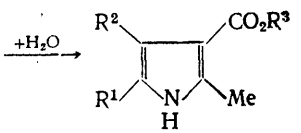


R^1 = Me, OEt; R^2 = H, Alk, Ar.

Acylpyrroles (LVII) are obtained by two methods—by hydrolysis of polyfunctional dihydrofurans (LVI) formed by reaction of nitro-olefins (LIV) with twice the amount of acetoacetates (LV) [116]

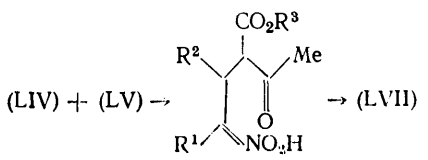


(LIV) (LV) (LVI)



(LVII)

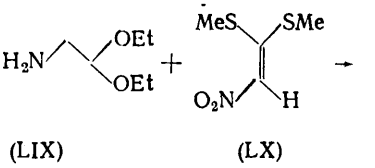
and by reduction of the nitronic acid (LVIII), which is an adduct of compounds (LIV) and (LV), with different reducing agents (Zn/HCl, $Zn/ZnCl_2$/HCl, 2-phenylethanethiol/benzene).[116]



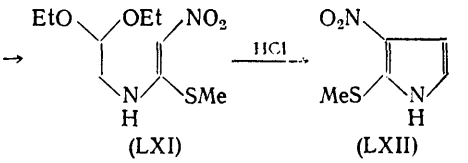
(LVIII)

R^1, R^3 = Alk; R^2 = Ar

The 3-nitropyrrole (LXII) was obtained in 58% yield by reaction of aminoacetaldehyde acetal (LIX) with 1,1-di(methylthio)-2-nitroethene (LX).[117] In this case the acyclic intermediate (LXI) is first formed and in the presence of HCl it cyclises to the pyrrole.

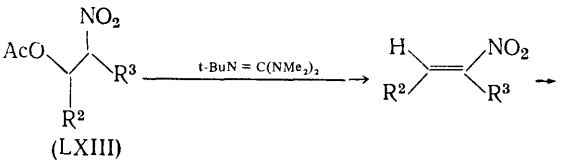


(LIX) (LX)

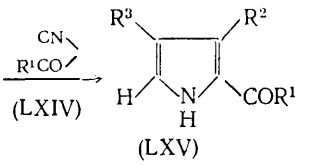


(LXI) (LXII)

The base-catalysed reaction between α-isocyanoacetates (LXIV) and nitroalkenes or their precursors—β-acetoxynitro compounds (LXIII)—gives pyrroles (LXV) in 55–95% yield.[118]



(LXIII)



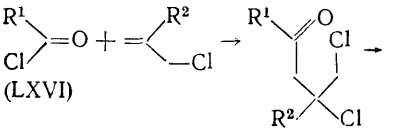
(LXIV) (LXV)

R^1 = EtO, t-BuO, Me_2N; R^2 = H, Me, Et, 4-$MeOC_6H_4$, 4-$PhCH_2OC_6H_4$; R^3 = Me, $CH_2CH_2CO_2Me$

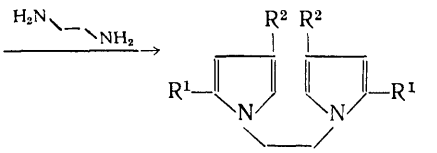
III. C_3 + C_1 reactions

1. Pyrroles from β,γ-dihaloethanes and amines

In a refinement of the Kost–Ibragimov–Mamedov method,[119–122] the intermediate products (LXVII) from the electrophilic addition of carboxylic acid chlorides (LXVI) to allyl and methallyl chlorides ($AlCl_3$, dichloroethane, −20° to 25 °C) when treated with diamines (aqueous NaOH, 70–80 °C, 6 h) form *bis*-pyrrole compounds.[123]



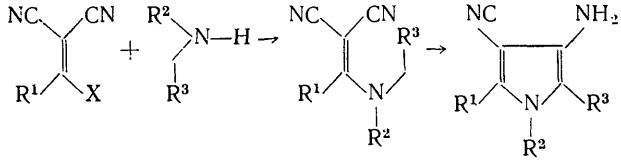
(LXVI) (LXVII)



R^1 = cyclo-C_6H_{11}, cyclo-$C_6H_{10}NH_2$; R^2 = H, Me

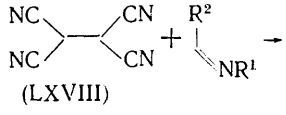
2. Reactions involving a cyano group

β-Aminopyrroles that have a CN group at the β'-position are obtained by reaction of α,β-unsaturated dinitriles with secondary amines containing functional groups; the intermediates are either isolated or not isolated.[124]

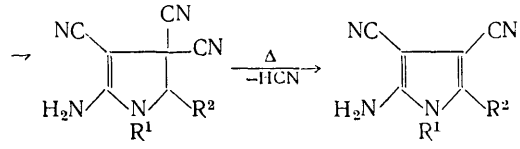


X = Cl, AlkO; R^1 = H, Alk, Ar; R^2=H, Alk, Ar; R^3 = CN, CO_2H, CO_2Alk.

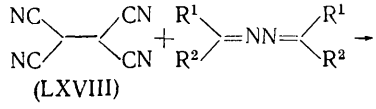
A convenient and simple method for the synthesis of pyrroles that contain amino and cyano groups is based on the reaction between tetracyanoethane (LXVIII) and azomethines or azines.[125-127] The reaction occurs in water–alcohol and alcohol media or in DMSO, giving 3-cyanodihydropyrroles, which on gentle heating in DMF eliminate a molecule of hydrocyanic acid and are converted to the corresponding pyrroles in high yield.



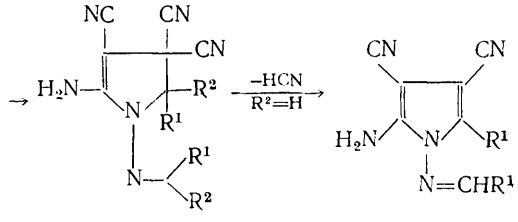
(LXVIII)



R^1 = Ph, 4-HOC_6H_4; R^2 = Ph, 2-furyl, 2-HOC_6H_4.



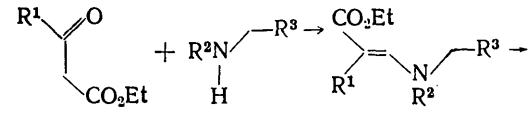
(LXVIII)



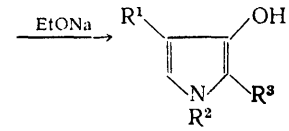
R^1 = Pr, iso-Pr, Ph, 2-furyl, 3-pyridyl, R^2 = H

3. Reactions of amino acids and their derivatives with 1,3-dicarbonyl compounds

Hydroxypyrroles (LXX) [128-130] are synthesised by Dieckmann cyclisation (NaOEt/EtOH, boiling for 3 h) of enaminodicarboxylates (LXIX), which are formed by reaction of amino acid amides and esters with β-ketoesters [128] or with diethyl ethoxymethylenemalonate.[129,130]



(LXIX)



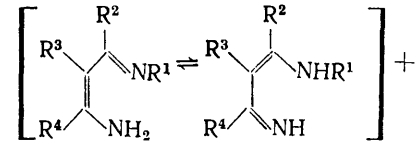
(LXX)

R^1=H, Ph, CO_2Et; R^2=H,Me,Ph,Bz; R^3=$CONH_2$, CONHMe, CO_2Et, CO_2CMe_3, CH_2CO_2Et

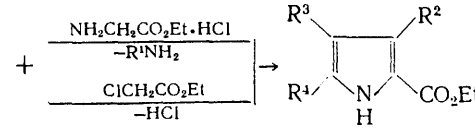
A number of pyrroles have been obtained from amino acids and 1,3-diketones [131-132] and also from α-(aminomethylene)cyclohexanone.[133] Cyclisation of the intermediates often occurs simply by heating.[133]

4. Reactions of azabutadienes

Azabutadienes (LXXI) react with glycine ethyl ester hydrochloride (80 °C, 4 h) or ethyl chloroacetate (100 °C, 6 h) in pyridine, giving in both cases pyrrole-2-carboxylates (LXXIII).[134] The regiospecificity of the reaction suggests that only one of the tautomeric diimine forms, namely (LXXII), participates in it.



(LXXI) (LXXII)



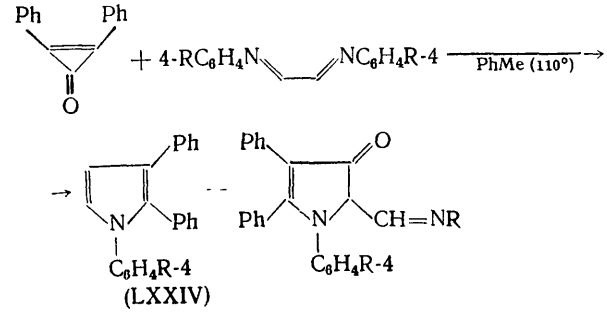
(LXXIII)

R^2 = Ph, 4-ClC_6H_4; R^3 = H, Me;

R^4 = Pr, Ph, 4-MeC_6H_4, cyclo-C_6H_{11}.

In the first case heterocyclisation probably takes place by transamination of diimine (LXXII) with the amino group of glycine.

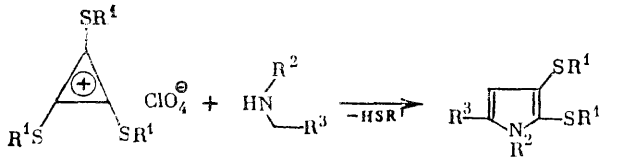
1,4-Diazabutadienes form the pyrrole (LXXIV) as a by-product (5–17%) by reaction with 2,3-diphenylcyclopropen-1-one. The main route in this case is formation of pyrroline-4-ones.[135]



(LXXIV)

5. Reactions involving cyclopropanes

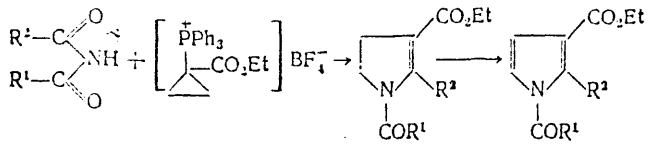
Condensation of *tris*-(t-butylthio)cyclopropenyl salts (LXXV) with secondary amines in the presence of the superbasic system t-BuOK – DMSO at 20–25 °C gives pyrroles (LXXVI) in 40–80% yield.[136–138]



(LXXV) (LXXVI)

R^1 = t-Bu; R^2 = Me, Et; R^3 = Me, CN, Ph, CO_2Me; R^2R^3 = $(CH_2)_3$, $(CH_2)_4$.

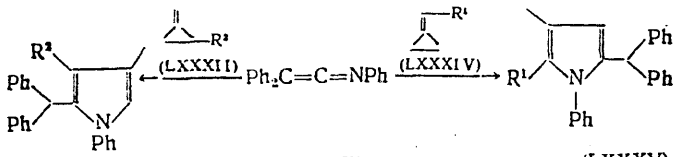
Anions of acyclic imides (LXXVII) (NaH, xylene, 20 °C) and cyclopropylphosphonium salts (LXXVIII) give Δ^2-pyrrolines, which are dehydrogenated with 2,3-dichloro-5,6-*p*-benzoquinone to the corresponding pyrroles (LXXX).[139]



(LXXVII) (LXXVIII) (LXXIX) (LXXX)

R^1 = H, Me, Ph; R^2 = H, Me, Ph

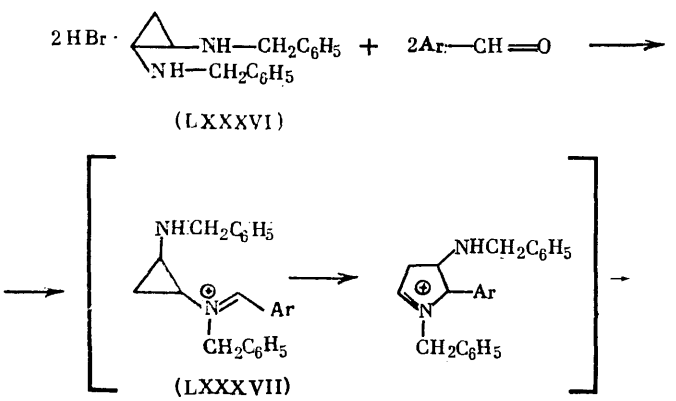
The [3 + 2]-cycloaddition of methylenecyclopropanes (LXXXII) and (LXXXIV) to the ketenimine (LXXXIII) (125 °C, 22–30 h), catalysed by $(PhP)_4Pd$, gives pyrroles (LXXXI) and (LXXXV) in 77–96% yield.[140]



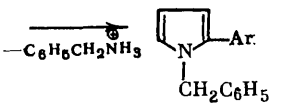
(LXXXI) (LXXXIII) (LXXXV)

R^1 = H, Me; R^2 = Me

Reaction of hydrobromide salts of 1,2-cyclopropanediamine (LXXXVI) with a twofold excess of aromatic aldehydes (MeOH or EtOH, NaOAc, 20–25 °C, 15 h) goes to completion with the formation of 2-arylpyrroles (LXXXVIII).[141]



(LXXXVI) (LXXXVII)



(LXXXVIII)

Ar = Ph; 4-$NO_2C_6H_4$; 4-$(Me)_2NC_6H_4$; 2,4,6-$(Me)_3C_6H_2$; 2-pyridyl.

The benzylidenammonium ions (LXXXVII) formed at the first stage of the reaction are converted to pyrrolinium ions, which are aromatised with elimination of benzylamine.

IV. C_4 + N(C_4–N) reactions

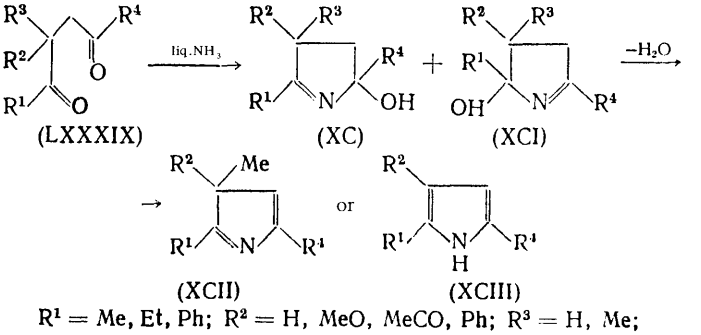
1. Reactions of 1,4-dicarbonyl compounds

The formation of pyrroles from 1,4-dicarbonyl compounds by treatment with ammonia or amines (the Paal–Knorr synthesis) is one of the most common methods for obtaining substituted pyrroles. Interest in it continues unabated. In recent years it has been developed further in several studies.[142–161] In particular, a large number of pyrroles have been obtained from hexane-2,5-dione.[143,144,148,149,156,161] Apart from simple alkyl- and aryl-amines, aminoalcohols,[144,146,147] aminoacetals,[144] amino acids and their derivatives,[146,147,156,157] sulphamoylbenzoic acid derivatives,[143] and amides[150–152] have been used in the condensation.

Reaction of 1,4-diketones with hydroxylamine and hydrazines gives 1-hydroxy- and 1-amino-pyrroles respectively.[5]

As a rule, cyclisation is carried out by boiling the reagents in an acidic medium. Acetic acid is used the most frequently for this purpose.[141,142,145,149,150–152] The method has virtually no limitations. In a number of cases it is possible to obtain (dioxan, 100 °C, 3 h) pyrroles with bulky substituents[145,149] which are difficult to prepare by another method because of steric hindrance.

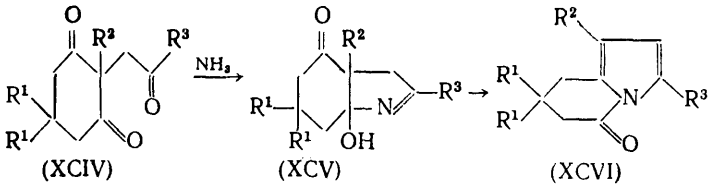
In some cases the Paal–Knorr reaction can be stopped at intermediate stages. Thus, the reaction of diketone (LXXXIX) (R^2 = R^3 = Me) with liquid ammonia results in the formation of a mixture of 2-hydroxy-3,4-dihydro-2*H*-pyrroles (XC) and (XCI), which are readily dehydrated (boiling in methylene chloride, basic Al_2O_3, 8 h) to the 3*H*-pyrrole (XCII). Less substituted diketones (LXXXIX) (R^2 = Me, R^3 = H) give the analogous hydroxypyrrolines (XC) and (XCI) (R^2 = Me, R^3 = H), which are dehydrated to the 1*H*-pyrrole (XCIII) on standing for several days.[162]



(LXXXIX) (XC) (XCI) (XCII) (XCIII)

R^1 = Me, Et, Ph; R^2 = H, MeO, MeCO, Ph; R^3 = H, Me; R^4 = Me, Ph.

The hydroxypyrroline intermediates (XCV) have also been isolated in the reaction of cyclic 2-(acylmethyl)1,3-diketones (XCIV) with liquid ammonia.[163]

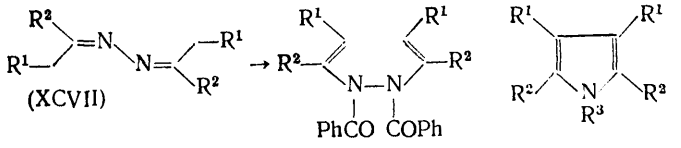


(XCIV) (XCV) (XCVI)

On heating in acetic acid in the presence of ammonium acetate or without a solvent up to the melting point, hydroxypyrrolines (XCV) rearrange to pyrroles (XCVI) in high yield. This rearrangement may occur either by dehydration to a 3*H*-pyrrole with two successive 1,5-acyl shifts or by transannular interaction between the amide nitrogen atom and the carbonyl group.

2. Pyrroles from azines

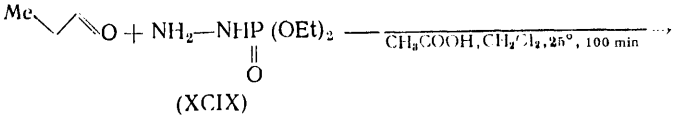
There is a continuous development of methods for the synthesis of pyrroles based on the Piloty reaction. When this reaction is used in its original form, the yields of pyrroles are usually low since strong acid media are used, and it is not possible to convert aldazines to pyrroles. Therefore, in one study[164] azines (XCVII) of enolisable aldehydes and ketones were first converted to *N,N'*-dibenzoyl-*N,N'-bis*(enyl)hydrazines (XCVIII) (by reaction with benzoyl chloride and pyridine in benzene), which on boiling in xylene gave *N*-benzoylpyrroles. Hydrazinolysis of the latter in isopropyl alcohol (80 °C, 1–3 days) yielded *N*-unsubstituted pyrroles.[164]



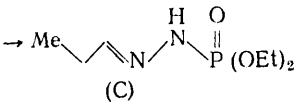
(XCVII) (XCVIII)

$R^1 = H$, Me, Et; R^2 = Me, Et; $R^1R^2 = (CH_2)_5$; R^3 = COPh, H

Reaction of propanal with diethyl phosphorohydrizidate (XCIX) gives the hydrazone (C).

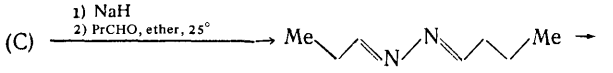


(XCIX)

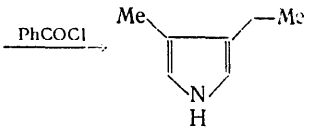


(C)

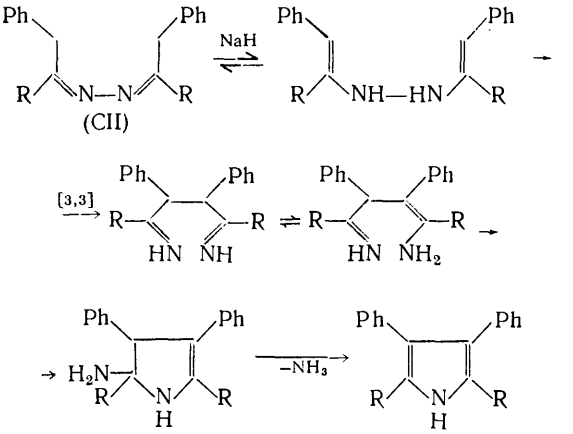
The sodium salt of (C) reacts with butanal to form the asymmetric azine (CI), which after reaction with benzoyl chloride cyclises to a pyrrole.[164]



(CI)



Azines (CII) of carbonyl compounds that contain a readily enolisable benzyl group can undergo thermolysis by catalysis with sodium hydride to give pyrroles.[165,166]

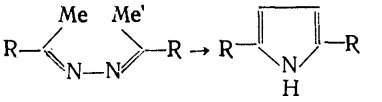


(CII)

R = Me, Et, Pr, iso-Pr, Ph

At the first stage of the cyclisation azine (CII) is converted to a dienehydrazine. An alkaline catalyst, not displacing the equilibrium itself, considerably increases the rate of the tautomeric conversion. At the next stage a [3,3]-sigmatropic shift occurs and after that (via several stages accompanied by elimination of ammonia) the pyrrole is formed. The probability that the stage involving C–C bond formation occurs as a [3,3]-sigmatropic shift is borne out by the fact that pyrrole formation takes place by thermolysis without a catalyst.

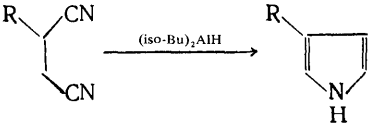
The thermal (150–170 °C) uncatalysed rearrangement of methylarylketazines to 2,5-diarylpyrroles [167] has also been reported.[167]



R = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, α-naphthyl

3. Reactions involving a nitrile group

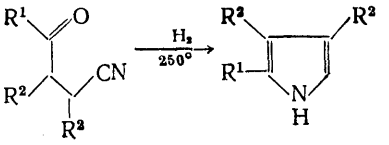
Succinonitriles (CIII) when treated with diisobutylaluminium hydride followed by hydrolysis (NaH_2PO_4, 100 °C, 0.5 h) are converted to pyrroles (CIV) in 34–57% yield.[168]



(CIII) (CIV)

R = iso-Pr, Bu, Ph, 2-ClC_6H_4

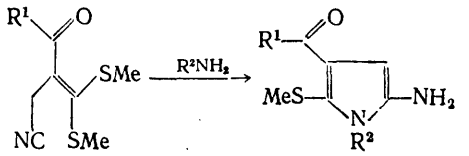
Alkylpyrroles (CVI) are obtained by gas-phase reductive cyclisation of ketonitriles (CV) in the presence of Group VIII metals (Rh, Pd, Pt, Ni).[169]



(CV) (CVI)

R^1 = Alk; R^2 = H, Alk

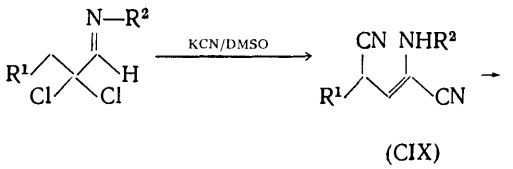
Cyclisation of α-acylketene *S*,*S*-acetals (CVII) with amines (EtOH, 75 °C, 1–1.5 h) gives pyrroles (CVIII) in 41–61% yield.[170]



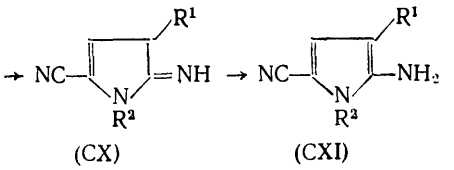
(CVII) (CVIII)

R^1 = Ph, 4-ClC_6H_4, 4-$HO_2CC_6H_4$; R^2 = Me, Et, Bz

Cyclisation of 1,3-dicyanoenamines (CIX), obtained from α,α-dichloroaldimines by treatment with KCN–DMSO (120 °C, 2 h) gives 2-amino-5-cyanopyrroles (CXI) (43–71% yield).[171] Pyrrole formation occurs as a result of intramolecular attack by the amine nitrogen on the CN group and prototropic rearrangement of the intermediate 2-iminopyrroline (CX).



(CIX)

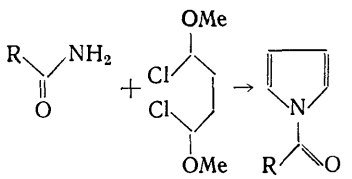


(CX) (CXI)

R^1 = Me, Et; R^2 = iso-Pr, t-Bu

4. Reactions of halogen-containing compounds

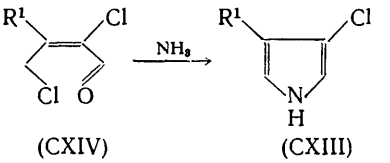
Some primary amides are converted to *N*-acylpyrroles (yield 55–85%) by reaction with 1,4-dichloro-1,4-dimethoxybutane (CXII) in the presence of an ion-exchange resin (MeCN, 45–60 °C, 12 h).[172]



(CXII)

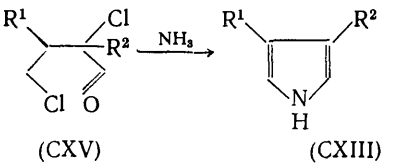
R = Me, Pr, $C_{17}H_{35}$, Ph.

The condensation of chloroaldehydes (CXIV) and (CXV) with ammonia in diglyme gives pyrroles (CXIII).[173–175]



(CXIV) (CXIII)

R^1 = H, Cl

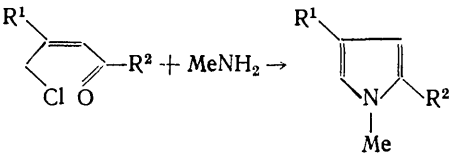


(CXV) (CXIII)

R^1 = HCl; R^2 = Ar

If 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) is used as the catalyst it is possible to carry out the reaction at room temperature.[176]

2,4-Substituted pyrroles (CXVII) are obtained by reaction of chloropropenyl ketones (CXVI) with primary amines.[177]

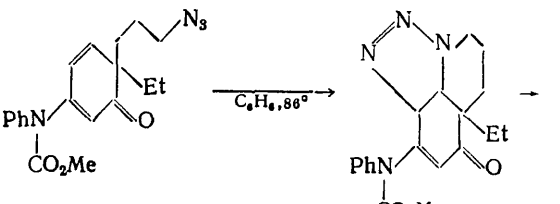


(CXVI) (CXVII)

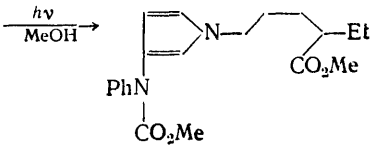
When secondary amines are used, only replacement of the chlorine atom by an amino group occurs.[177]

5. Pyrroles from azides

Irradiation of the triazoline (CXIX), which was derived by intramolecular conversion of azide (CXVIII), in methanol solution gave the pyrrole (CXX) in 75% yield.[178]

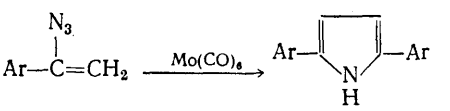


(CXVIII) (CXIX)



(CXX)

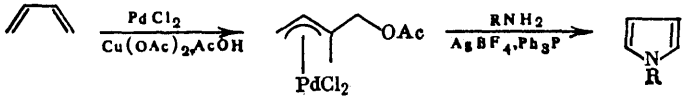
Reaction of the vinylazide (CXXI) with molybdenum hexacarbonyl in protic and aprotic solvents occurs with the formation of 2,5-diarylpyrrole.[179]



(CXXI)

6. Other reactions

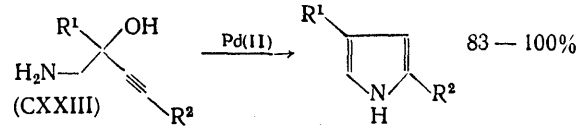
The reaction of dienes with $PdCl_2$ and $Cu(OAc)_2$ in acetic acid gives stable palladium π-allyl complexes (CXXII), which on treatment with primary amines in the presence of 1 equivalent of $AgBF_4$ and 0.1 equivalent of triphenylphosphine form pyrroles in 13–54% yield.[180]



(CXXII)

R= Et, Bz.

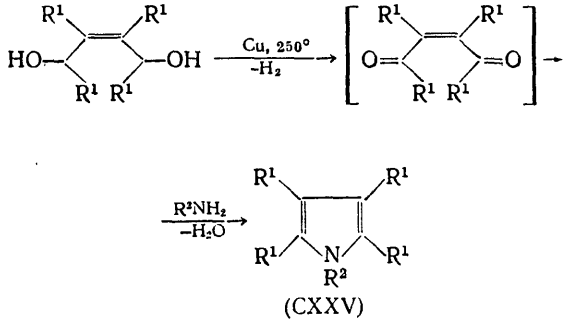
Cyclisation of the acetylenic aminoalcohols (CXXIII) to pyrroles (CXXIV) has been successfully carried out in the presence of palladium [$PdCl_2$ or $Pd(OAc)_2$].[181] A $Pd(Ph_3P)_4$ complex is less effective.



(CXXIII) (CXXIV)

$R^1 = C_6H_{13}$, Ph; R^2 = H, Et, iso-Pr

N-Substituted pyrroles (CXXV) are obtained in good yield by gas-phase cyclocondensation (250 °C) of 2-butene-1,4-diols with primary amines, catalysed by transition metals, in particular, by Cu.[182] At the first stage of the reaction the butenediol is probably dehydrated to a dialdehyde or diketone, which then reacts with the amine.

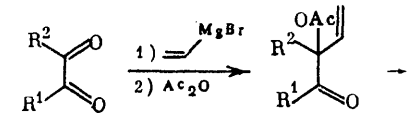


(CXXV)

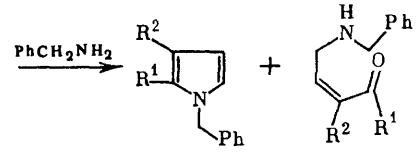
R^1, R^2 = H, Alk, Ar

The possibility of using a reduced fused iron catalyst for the gas-phase synthesis of pyrrole and its derivatives from butanediol, ammonia, and hydrogen has been investigated.[183] At 250–310 °C a mixture consisting of pyrrolidine, *N*-butylpyrrolidine, n-butylamine, n-butanol, 4-(1-pyrrolidyl)-butanol, 1,4-dipyrrolidinebutane, di-n-butylamine, pyrrole, and *N*-butylpyrrole was formed with a total yield of 10–15%. It has been suggested[183] that at lower values of the partial pressure of hydrogen, pyrrole and its derivatives could become the main reaction products.

α-Acetoxy-α-vinylalkanones (CXXVI) (products derived from the reaction of α-dicarbonyl compounds with vinylmagnesium bromide and acetic anhydride) react with benzylamine in the presence of $Pd(PPh_3)_4$



(CXXVI)

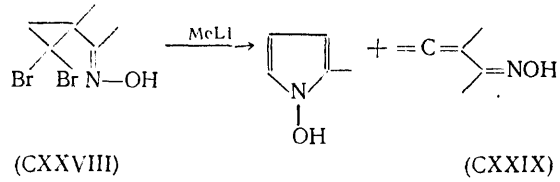


(CXXVII)

R^1 = H, Me, Ph; R^2 = H, Me, Ph; R^1R^2 = $(CH_2)_4$.

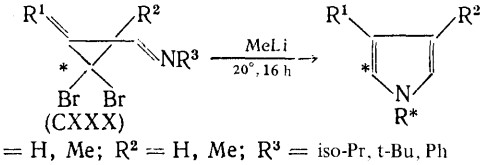
(xylene, THF) to give *N*-benzylpyrroles in 43–65% yield.[184] In addition to pyrroles, aminoketones (CXXVII) are also formed; however, they are not a source of pyrrole.

From oximes of alkyl dibromocyclopropyl ketones (CXXIII) and MeLi were isolated *N*-hydroxypyrroles and allenes (CXXIX),[185] which Santelli considered to be intermediates.



(CXXVIII) (CXXIX)

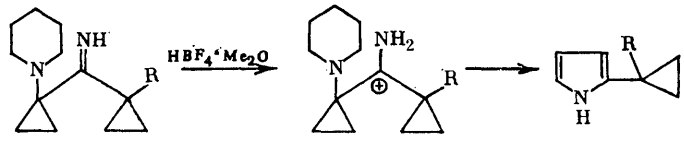
It was shown subsequently[186,187] using dibromocyclopropanimines (CXXX) that pyrroles are formed in similar reactions as a result of a carbene-carbene rearrangement. Imines with a labelled carbon atom were used to demonstrate the mechanism.



(CXXX)

R^1 = H, Me; R^2 = H, Me; R^3 = iso-Pr, t-Bu, Ph

On heating dicyclopropylketimines (CXXXI) in xylene in the presence of a dimethyl ether—fluoroboric acid complex, pyrroles (CXXXIII) are formed with yields of 32 and 42%.[188]

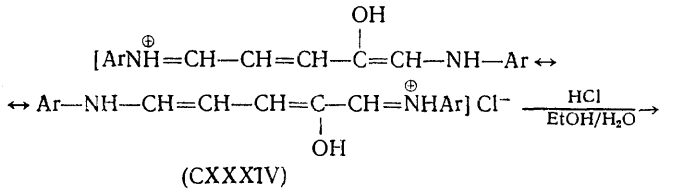


(CXXXI) (CXXXII) (CXXXIII)

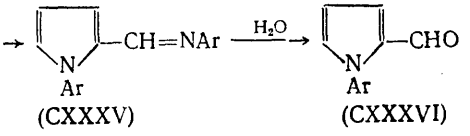
R= H, SPh.

The reaction starts with formation of the carbocation (CXXXII).

N-Arylpyrrole-2-carbaldehydes (CXXXVI) were obtained by acid hydrolysis of salts (CXXXIV).[189]



(CXXXIV)



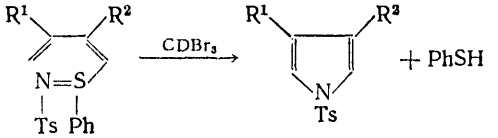
(CXXXV) (CXXXVI)

Ar = Ph, 3-$O_2NC_6H_4$; 4-$O_2NC_6H_4$;

4-Me-3-$O_2NC_6H_3$, 4-MeC_6H_4, 4-BrC_6H_4, 4-ClC_6H_4

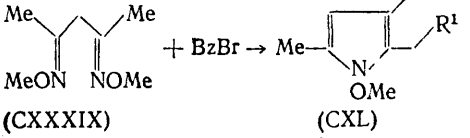
When an ethanol solution of the salts was heated without acid, the intermediate anils (CXXXV) were isolated, readily hydrolysing to aldehydes (CXXXVI) in the presence of acids.

A 1 : 1 mixture of the *N*-tosylpyrrole (CXXXVIII) and thiophenol is obtained from *S*-butadienylsulphimines (CXXXVII) (130 °C, 0.5 h, $CDCl_3$).[190] The reaction takes place with preparative yields in different solvents, but the best results are obtained in phenylisocyanate, which combines with thiophenol.



(CXXXVII) (CXXXVIII)

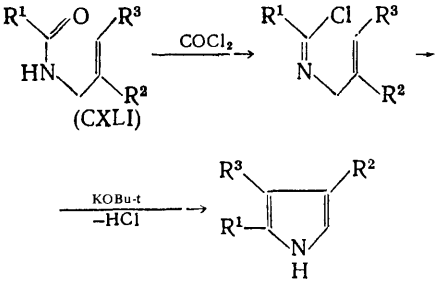
Condensation of benzyl bromide with the diketoxime dimethyl ether (CXXXIX) (HCl, H_2O, CH_2Cl_2, 30 °C, 12 h) gives pyrroles (CXL).[191]



(CXXXIX) (CXL)

$R^1 = H$, $R^2 = Bz$, $R^1 = Bz$, $R^2 = H$

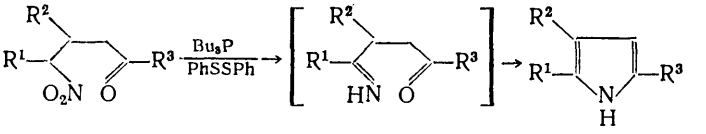
Pyrroles with various substituents are obtained by reaction of *N*-allylamides (CXLI) with $COCl_2$ and then with t-BuOK.[192,193]



(CXLI)

R^1 = Ph, 2-furyl, 2-thienyl, 2-HOC_6H_4, t-Bu; R^2 = H, Me; R^3 = H, Me.

The intramolecular cyclisation of iminoketones (CXLIII), which are formed by reduction of nitroalkanones (CXLII) with tributylphosphine and diphenyl sulphide (THF, 20 °C) gives pyrroles (CXLIV) in high yield.[194,195]



(CXLII) (CXLIII) (CXLIV)

R^1 = Me, CO_2Et; R^2 = Me, Ph; R^3 = Ph, Me

Thus, the methods for constructing a pyrrole ring from aliphatic compounds continue to undergo rapid development. Along with an improvement of the known synthetic methods based on the classical reactions of Knorr, Paal–Knorr, Hantzsch, Chichibabin, and Piloty, there is a constant search for new preparative reactions which can form a pyrrole ring from the most accessible starting materials and under the mildest possible conditions. A particularly rapid development is taking place at present for the recently discovered formation of pyrroles from ketoximes when treated with acetylene or its equivalents (vinyl halides, dihaloethanes) in the presence of superbasic systems of the type KOH–DMSO. This reaction has opened up a simple route to groups of pyrroles that were previously difficult to obtain, including *N*-vinylpyrroles, which are now being synthesised rapidly and studied in detail.

In the present-day synthesis of pyrroles from aliphatic compounds the following trends prevail: 1) there is a wider use of acetylenic compounds or their equivalents (especially acetylenes with strong acceptor substituents and conjugated diacetylenes) as starting materials; 2) different ketone derivatives (oximes, imines, hydrazones, β-nitro derivatives, etc.) are involved in synthesis; 3) there is a change to reagents and catalysts having superbasicity,[196] such as KOH–DMSO, t-BuOK–DMSO, dimsyl sodium, NaH–THF, $NaNH_2$–NH_3, lithium diisopropylamide, etc.; this achieves a substantial increase in the yield of pyrroles, an acceleration of different base-catalysed processes, and in a number of cases gives rise to new reactions.

References

1. A Gossauer *Die Chemie der Pyrrole*, Springer Verlag, Berlin–Heidelberg–New York, 1974, p. 433
2. R A Jones, G P Bean *The Chemistry of Pyrroles*, Acad. Press, London–New York–San Franciso, 1977, p. 525
3. B A Trofimov, A I Mikhaleva *N-Vinilpirroly* (*N*-Vinylpyrroles), Izd. Nauka, Novosibirsk, 1984, p. 262
4. R J Sundberg *Comprehensive Heterocyclic Chemistry*, Vol. 4 (Edited by A R Katritzky et al.), Pergamon Press, Oxford–New York, 1984, p. 313
5. A H Jackson *General Organic Chemistry* (Translated into Russian), Vol. 8, Izd. Khimiya, Moscow, 1985, p. 332
6. B A Trofimov, A I Mikhaleva *Khim. Geterotsikl. Soed.*, 1980, 1299
7. J M Patterson *Synthesis*, 1976, 281
8. Ya P Stradyn' *Khim. Geterotsikl. Soed.*, 1979, 1567
9. Ya P Stradyn' *Khim. Geterotsikl. Soed.*, 1981, 1412

10. B A Trofimov *Geteroatomnye Proizvodnye Atsetilena. Novye Polifunktsional'nye Monomery, Reagenty i Poluprodukty* (Heteroatomic Derivatives of Acetylene, New Polyfunctional Monomers, Reagents, and Intermediates), Izd. Nauka, Moscow, 1981, p. 319
11. A I Mikhaleva, M V Sigalov, G A Kalabin *Tetrahedron Lett.*, 1982, **23** 5063
12. L N Sobenina, Candidate's Thesis in Chemical Sciences, Irkutsk Institute of Organic Chemistry, Siberian Branch, USSR Academy of Sciences, Irkutsk, 1983, p. 216
13. S E Korostova, A I Mikhaleva *Zhur. Org. Khim.*, 1982, **18** 2620
14. B A Trofimov, A I Mikhaleva, R I Polovnikova, et al. *Khim. Geterotsikl. Soed.*, 1981, 1058
15. S E Korostova, L N Sobenina, R N Nesterenko, et al. *Zhur. Org. Khim.*, 1984, **20** 1960
16. S E Korostova, A I Mikhaleva, L N Sobenina, et al. *Khim. Geterotsikl. Soed.*, 1985, 1501
17. S E Korostova, A I Mikhaleva, R N Nesterenko, et al. *Zhur. Org. Khim.*, 1985, **21** 406
18. B A Trofimov, A I Mihaleva, R N Nesterenko, et al. *Tezisy Dokladov VII Vsesoyuznoi Konferentsii po Khimii Atsetilena* (Abstracts of Reports at the VIIth All-Union Conference on Acetylene Chemistry), Erevan, 1984, p. 110
19. B A Trofimov, A B Shapiro, R N Nesterenko, et al. *Khim. Geterotsikl. Soed.*, 1988, 350
20. T N Borisov, A V Varlamov, N S Prostakov *Tezisy Dokladov I Vsesoyuvnoi Konferentsii po Khimii, Biokhimii i Farmakologii Proizvodnykh Indola* (Abstracts of Reports at the Ist All-Union Conference on the Chemistry, Biochemistry, and Pharmacology of Indole Derivatives), Tbilisi, 1986, p. 39
21. T N Borisov, Candidate's Thesis in Chemical Sciences, P Lumumba People's Friendship University, 1987, 152
22. M A Yarovskaya, V V Druzhinina, E V Snetkova, and Yu G Bundel' *Khim. Geterotsikl. Soed.*, 1983, 356
23. V V Druzhinina, Candidate's Thesis in Chemical Sciences, Izd. MGU, Moscow, 1983, p. 161
24. S E Korostova, A I Mikhaleva, L N Sobenina, et al. *Zhur. Org. Khim.*, 1986, **27** 492
25. B A Trofimov, A I Mikhaleva, A N Vasil'ev, et al. *Khim. Geterotsikl. Soed.*, 1985, 59
26. I A Aliev, D G Almamedova, B R Gasanov, A I Mikhaleva *Khim. Geterotsikl. Soed.*, 1984, 1359
27. I A Aliev, A I Mikhaleva, M V Sigalov *Sulfur Lett.*, 1984, **2**(2) 55
28. B A Trofimov, S E Korostova, A I Mikhaleva, et al. *Khim. Geterotsikl. Soed.*, 1983, 273
29. B A Trofimov, S E Korostova, A I Mikhaleva, et al. *Khim. Geterotsikl. Soed.*, 1983, 276
30. B A Trofimov, S G Shevchenko, S E Korostova, et al. *Khim. Geterotsikl. Soed.*, 1985, 1573
31. M A Yurovskaya, A Z Afanas'ev, Yu G Bundel', et al. *Khim. Geterotsikl. Soed.*, 1984, 1077
32. D Dhanak, C B Reese, S Romana, G Zappia *Chem. Commun.*, 1986, 903
33. G Filacchioni, L Cecci, G C Porreta, et al. *Farmaco. Ed. Sci.*, 1983, **38** 619
34. P Rubio Zurita, Spanish P. 502 650; *Chem. Abs.*, 1982, **97** 162 811
35. E Pando, M C Garcia Bala, C Martin Madero *Afinidad*, 1983, **40**(387) 445
36. E Pando, C Martin Madero, C Vergara *An. Quim., Ser. C*, 1980, **76**(1) 53
37. Central Glass Co., Japanese P. 59 167 568; *Chem. Abs.*, 1985, **102** 78 719
38. H Ogoshi, M Homma, K Yokota, et al. *Tetrahedron Lett.*, 1983, **24** 929
39. J V Cooney, E J Beal, R N Hazlett *Org. Prep. Proceed. Int.*, 1983, **15** 292
40. P S Clezy, M W Duncan, B N Ravi, L. van Thuc *Austral. J. Chem.*, 1986, **39** 399
41. M F Chen, S F MacDonald *Can. J. Chem.*, 1974, **52** 1760
42. Laboratoires Pharmedical SA, BRD P. 3 242 203; *Chem. Abs.*, 1983, **99** 122 290
43. J B Paine, D Dolphin *J. Heterocycl. Chem.*, 1975, **12** 1317
44. J B Paine, D Dolphin *J. Org. Chem.*, 1985, **50** 5598
45. A Padwa *1,3-Dipolar Cycloaddition Chemistry*, Wiley, New York, 1984, p. 1521
46. A Padwa, Y-Y Chen, W Dent, H Nimmesgern *J. Org. Chem.*, 1985, **50** 4006
47. A Padwa, W Dent, H Nimmesgern, et al. *Chem. Ber.*, 1986, **119** 813
48. A Padwa, G Haffmanns, M Tomas *Tetrahedron Lett.*, 1983, **24** 4303
49. O Tsuge, S Kanemasa, K Matsuda *Chem. Lett.*, 1985, 1411
50. O Tsuge, S Kanemasa, K Matsuda *J. Org. Chem.*, 1986, **51** 1997
51. K Burger, S Rottegger *Tetrahedron Lett.*, 1984, **25** 4091
52. W E McEwen, A V Grossi, R J MacDonald, A P Stamegna *J. Org. Chem.*, 1980, **45** 1301
53. J V Cooney, W E McEwen *J. Org. Chem.*, 1981, **46** 2570
54. J V Cooney, B D Bearer, W E McEwen *J. Heterocycl. Chem.*, 1985, **22** 635
55. S Zen, K Harada *Chem. Pharm. Bull.*, 1982, **30** 366
56. A Padwa, G S K Wong *J. Org. Chem.*, 1986, **51** 3125
57. G Holland, US P. 4 282 242; Chem. Abs., 1981, **95** 187 068
58. G Genda, H Muro, S Nakayama, et al., Japanese P. 6 130 571; Chem. Abs., 1986, **105** 60 520
59. P Magnus, Y S Or *Chem. Commun.*, 1983, 26
60. P Magnus, T Gallagher *Chem. Commun.*, 1984, 389
61. S P J Van Nispen, O Mensink, A M van Leusen *Tetrahedron Lett.*, 1980, **21** 3723
62. J Moskal, A M van Leusen *J. Org. Chem.*, 1986, **51** 4131
63. K Sakai, M Suzuki, K Nunami, N. Yoneda *Chem. Pharm. Bull.*, 1980, **28** 2384
64. Nippon Soda Co., Japanese P. 59 212 468; *Chem. Abs.*, 1985, **102** 149 104
65. Nippon Soda Co., Japanese P. 5 885 861; *Chem. Abs.*, 1983, **99** 122 293
66. H A Houwing, A M van Leusen *J. Heterocycl. Chem.*, 1981, **18** 1127
67. L A Mayring, T Severin *Chem. Ber.*, 1981, **114** 3863
68. Du Pont de Nemours Co., Israel P. 61 768; *Chem. Abs.*, 1985, **102** 95 535
69. T O Lash, K A Bladel, M C Johnson *Tetrahedron Lett.*, 1987, **28** 1135
70. G Baccolini, C Sandali *Chem. Commun.*, 1987, 788
71. O Attanasi, P Filippone, A Mei, F Zerra-Zanetti *Synth. Commun.*, 1986, **16** 343
72. O Attanasi, M Grossi, F Zerra-Zannetti *Org. Prep. Proced. Int.*, 1986, **18** 1
73. O Attanasi, P. Filippone, A Mei, et al. *Synthesis*, 1985, 157

74. O Attanasi, P Filippone, A Mei, S Santeusanio *Synthesis*, 1984, 671
75. O Attanasi, P Bonifazi, E Foresti, G Pradella *J. Org. Chem.*, 1982, **47** 684
76. O Attanasi, S Santeusanio *Synthesis*, 1983, 742
77. O Attanasi, P Bonifazi, F Buiani *J. Heterocycl. Chem.*, 1983, **20** 1077
78. O Attanasi, F R Perrulli *Synthesis*, 1984, 874
79. O Attanasi, F R Perrulli, F Zerra-Zanetti *Heterocycles*, 1985, **23** 867
80. O Attanasi, P Filippone, A Mei, S Santeusanio *Synthesis*, 1984, 873
81. T L Gilchrist, B Parton, J A Stevens *Tetrahedron Lett.*, 1981, **22** 1059
82. D A Robinson, J Chen Chen, BRD P. 2942140; *Chem. Abs.*, 1980, **93** 150113
83. M J Dagani, US P. 4565876; *Chem. Abs.*, 1985, **105** 42636
84. M J Dagani, US P. 4388468; *Chem. Abs.*, 1983, **99** 105120
85. Y Cai, W Dong *Yiyao Gongye* 1983, (5) 3; *Chem. Abs.*, 1983, **99** 139683
86. J T F Kao, E M Marlett, US P. 4383117; *Chem. Abs.*, 1983, **99** 38359
87. G Bottaccio, S Campolmi, V Carletti, A Marchi, Europ. P. 92487; *Chem. Abs.*, 1984, **100** 174654
88. M J Dagani, Europ. P. 72441; *Chem. Abs.*, 1983, **99** 22312
89. J T F Kao, Canadian P. 1146564; *Chem. Abs.*, 1983, **99** 139758
90. J T F Kao, R E Farritor, US P. 4374255; *Chem. Abs.*, 1983, **98** 160584
91. R Albert, S A Willemsen, G van der Veken, US P. 4363918; *Chem. Abs.*, 1983, **98** 143271
92. Ethyl Corp., Japanese P. 58177964; *Chem. Abs.*, 1984, **100** 68165
93. G Bottaccio, S Campolmi, V Carletti, M Marchi, Europ. P. 105664; *Chem. Abs.*, 1984, **101** 54915
94. M J Dagani, J T F Kao, Europ. P. 89393; *Chem. Abs.*, 1984, **100** 51446
95. E M Marlett, US P. 4455433; *Chem. Abs.*, 1984, **101** 110727
96. C G Kazembe Takawiva, D A Taylor *Tetrahedron*, 1980, **36** 2125
97. R J Mattson, L C Wang, J W Sowell *J. Heterocycl. Chem.*, 1980, **17** 1793
98. J A S Lacks, J R Ross, S M Bayomi, J W Sowell *Synthesis*, 1985, 291
99. H Pichler, G Folkers, H J Roth, K Eger *Liebigs Ann. Chem.*, 1985, 1485
100. M Sonoda, N Kuriyama, Y Tomioka, M Yamazaki *Chem. Pharm. Bull.*, 1982, **30** 2357
101. N Chatani, T Hanafusa *Tetrahedron Lett.*, 1986, **27** 4201
102. T Kusumoto, T Hiyama, K Ogata *Tetrahedron Lett.*, 1986, **27** 4197
103. D Yusipov, Abstract of Doctorate Thesis in Chemical Sciences, M V Lomonosov Moscow Institute of Technology and Chemical Technology, 1987, p. 40.
104. A K Kulimov, D Yusipov, K M Akhmerov, A B Kuchkarov *Dokl. Akad. Nauk UzSSR*, 1984, (5) 40
105. K M Akhmerov, D Yusipov, A B Kuchkarov, K Akhmedov, USSR P. 514820; *Byul. Izobret.*, 1976, (19) 54
106. K M Akhmerov, D Yusipov, A B Kuchkarov, K Akhmedov *Khim. Geterotsikl. Soed.*, 1974, **428**
107. S Baroni, R Straid, M L Saccarello *J. Heterocyclic Chem.*, 1980, **17** 1221
108. J M Vernon, R M Carr, M A Sukari *J. Chem. Res. S*, 1982, 115
109. R M Carr, R O C Norman, J M Vernon *J. Chem. Soc., Perkin Trans. I*, 1980, 156
110. M A Sukari, J M Vernon *Tetrahedron*, 1983, **39** 793
111. H Ahlbrecht, A von Daacke *Synthesis*, 1984, 610
112. A Gomes-Sanchez, M Mancerai, F J Caballero, J Bellanato *An. Quim. Ser. C*, 1983, **79**(2) 175
113. H Meyer *Liebigs Ann. Chim.*, 1981, 1534
114. A Gomes-Sanchez, B M Stiefel, R Fernandez-Fernandez, et al. *J. Chem. Soc., Perkin Trans. I*, 1982, 441
115. A Gomes-Sanchez, B M Stiefel, R Fernandez-Fernandez, Spanish P. 500331; *Chem. Abs.*, 1982, **97** 92129
116. F Boberg, K H Garburg, K J Gorlich, et al. *Liebigs Ann. Chem.*, 1985, 239
117. M L Roantree, R C Young, Europ. P. 5985; *Chem. Abs.*, 1980, **93**, 46411
118. D H R Barton, S Z Zard *Chem. Commun.*, 1985, 1098
119. A G Ismailov, E I Mamedov, USSR P. 498295; *Byul. Izobret.*, 1976, (1) 82
120. A G Ismailov, E I Mamedov *Uchenye Zapiski. Min. Vysshego i Srednego Spetsial'nogo Obrazovaniya AzSSR, Ser. Khim. Nauk*, 1975, (2) 54
121. A G Ismailov, R D Goyushov *Uchenye Zapiski. Min. Vysshego i Srednego Spetsial'nogo Obrazovaniya AzSSR, Ser. Khim. Nauk*, 1975, (1) 30
122. I I Ibragimov, A N Kost, M M Guseinov, et al. *Khim. Geterotsikl. Soed.*, 1976, 790
123. E I Mamedov, A G Ismailov, V G Ibragimov, R D Goyushov *Khim. Geterotsikl. Soed.*, 1983, 1561
124. K Gewald, H Schaefer, E Schindler, GDR P. 138976; *Chem. Abs.*, 1980, **93** 71547
125. O E Nasakin, V V Alekseev, V K Promonenkov, et al. *Khim. Geterotsikl. Soed.*, 1981, 402
126. O E Nasakin, V V Alekseev, P B Teren'tev, et al. *Khim. Geterotsikl. Soed.*, 1983, 1062
127. O E Nasakin, V V Alekseev, P B Terent'ev, et al. *Khim. Geterotsikl. Soed.*, 1983, 1067
128. G Kresze, A Bizhiv *Dokl. Bolg. Akad. Nauk*, 1982, **35** 1387
129. J B Doherty, M N Chang, C P Dorn, US P. 443175; *Chem. Abs.*, 1984, **100** 191732
130. J B Doherty, M N Chang, C P Dorn, Europ. P. 72013; *Chem. Abs.*, 1983, **99** 22311
131. S Mataka, K Takahashi, Y Tsuda, M Tashiro *Synthesis*, 1982, 157
132. Du Pont de Nemours Co., Israel P. 56243; *Chem. Abs.*, 1983, **99**, 70557
133. N J Bach, E C Kornfeld, US P. 4235776; *Chem. Abs.*, 1981, **94** 121320
134. J Barluenga, V Rubio, V Gotor *J. Org. Chem.*, 1982, **47** 1696
135. M Takahashi, T Funaki, H Honda, et al. *Heterocycles*, 1982, **19** 1921
136. Nippon Soda Co., Japanese P. 8051065; *Chem. Abs.*, 1981, **94** 30559
137. S Yoneda, H Hirai, Z Yoshida *Heterocycles*, 1981, **15** 865
138. Z Yoshida, Japanese P. 7944669; *Chem. Abs.*, 1980, **98** 6404
139. W Flitsch, K Pandl, P Russkamp *Liebigs Ann. Chem.*, 1983, 529
140. H J Weintz, P Binger *Tetrahedron Lett.*, 1985, **26** 4075

141. H Quast, W Saal, J Stawitz *Angew. Chem.*, 1981, **93** 619
142. G Zoller, R Beyerle, U Schindler, et al., Europ. P. 124067; *Chem. Abs.*, 1985, **102** 131904
143. D Lenke, C D Mueller, K H Geiss, J U Bliesgher, BRD P. 2914615; *Chem. Abs.*, 1981, **94** 83939
144. W J Thompson C A Buhr *J. Org. Chem.*, 1983, **48** 2769
145. W Hua, M Zhu *Xuaxue Tongbao*, 1982, (5) 281; *Chem. Abs.*, 1982, **97** 182142
146. W Hua, L Chen, X Peng, et al. *Beijing Daxue Xuebao, Ziran Kexueban*, 1984, (2) 35; *Chem. Abs.*, 1985, **102** 6097
147. M Salmon, O Villarino, A Jimenez, R Zawadski *Rev. Soc. Quim. Mex.*, 1980, **24**(1) 32
148. Dainippon Pharmaceutical Co., Japanese P. 8270864; *Chem. Abs.*, 1982, **97** 162808
149. T Sato, M Uchida, F Tafusa, K Nakagawa, Japanese P. 7979271; *Chem. Abs.*, 1980, **92** 41752
150. C Bernhart, J P Gagnol, P Gautier, US P. 4329343; *Chem. Abs.*, 1982, **97** 72250
151. H Damarne, C Bernhart, M Serre, French P. 2492374; *Chem. Abs.*, 1982, **97** 127492
152. Japanese P. 57139063; *Chem. Abs.*, 1983, **98** 107153
153. C Bernhart, J P Gagnol, P Gautier, S. African ZA 81004880; *Chem. Abs.*, 1982, **97** 92131
154. N Filipovic-Marinic, G Nalic *Liebigs Ann. Chem.*, 1984, 199
155. W T Hua *Hua Wsuch Tung Pao*, 1980, 662; *Chem. Abs.*, 1981, **94** 174785
156. T Tanaka, T Wakabayashi, A Otsu, S Kurozumi, Europ. P. 2392; *Chem. Abs.*, 1980, **92** 76277
157. Nippon Soda Co., Japanese P. 80118458; *Chem. Abs.*, 1981, **95** 7047
158. B Li, S Zhang *Gaedeng Xuexiao Xuebao*, 1985, **6** 513; *Chem. Abs.*, 1986, **104** 129728
159. B Li, S Zhang *Gaedeng Xuexiao Xuebao*, 1985, **6** 341; *Chem. Abs.*, 1986, **104** 129729
160. B Li, S Zhang *Gaedeng Xuexiao Xuebao*, 1985, **6** 917; *Chem. Abs.*, 1986, **105** 152868
161. US P. 4551540; *Chem. Abs.*, 1986, **105** 114895
162. P K Chiu, K H Lui, P N Maini, M P Sammes *Chem. Commun.*, 1987, 109
163. M P Sammes, P N Maini, A R Katritzky *Chem. Commun.*, 1984, 354
164. J E Baldwin, J C Bottaro *Chem. Commun.*, 1982, 624
165. I I Grandberg, O Yu Kutsenko, USSR P. 1101441; *Byul. Izobret.*, 1984, (25) 57
166. I I Grandberg *Zhur. Org. Khim.*, 1983, **19** 2439
167. Yu V Shurukhin, N A Klyuev, I I Grandberg *Zhur. Org. Khim.*, 1985, **21** 2057
168. J H Babler, K P Spina *Tetrahedron Lett.*, 1984, **25** 1659
169. Europ. P. 66346; *Chem. Abs.*, 1983, **98** 125866
170. S Apparao, H Ila, H Junjappa *Synthesis*, 1981, 65
171. R Verhe, N De Kimpe, L De Buyck, et al. *Tetrahedron*, 1980, **36** 131
172. S D Lee, M A Brook, T H Chan *Tetrahedron Lett.*, 1983, **24** 1569
173. A Heda, H Nagasaki, J Takakura, S Kojima, Europ. P. 92890; *Chem. Abs.*, 1984, **100** 103170
174. A Heda, H Nagasaki, J Takakura, S Kojima, International P. 8401773; *Chem. Abs.*, 1984, **101** 171082
175. Nippon Soda Co., Japanese P. 59130864; *Chem. Abs.*, 1984, **101** 191685
176. Nippon Soda Co., Japanese P. 5978160; *Chem. Abs.*, 1984, **101** 171083
177. G M Bairamov, S P Godzhaev, R D Goyushev *Azerb. Zhur. Khim.*, 1985, (2) 79
178. A G Schulz, C K Sha *J. Org. Chem.*, 1980, 2041
179. T Kobayashi, M Nitta *Nippon Kagaku Kaishi*, 1985, 451
180. J E Backväll, J E Nyström *Chem. Comm.*, 1981, 59
181. K Utimoto, H Miwa, H Nozaki *Tetrahedron Lett.*, 1981, **22** 4277
182. H Mening, M Fisher, K Baer, BRD P. 3309355; *Chem. Abs.*, 1985, **102** 45769
183. G A Kliger, O A Lesik, E V Marchevskaya, et al. *Khim. Geterotsikl. Soed.*, 1987, 195
184. B M Trost, E Keinan *J. Org. Chem.*, 1980, **45** 2741
185. C Santelli *Tetrahedron Lett.*, 1980, 2893
186. J Arct, L Skatteebøl *Tetrahedron Lett.*, 1982, **45** 2741
187. Y H Brinker, M Boxberger *J. Chem. Res. Synop.*, 1983, (4) 100
188. H H Wasserman, R P Dion *Tetrahedron Lett.*, 1983, **24** 3409
189. B R D'Arcy, K G Lewis, C E Mulquiney *Austral. J. Chem.*, 1985, **36** 953
190. Y Gaoni *Tetrahedron Lett.*, 1982, **23** 2051
191. S Shatzmiller, R Lidor *Synthesis*, 1983, 590
192. S Cherkofsky, US P. 4267190; *Chem. Abs.*, 1982, **96** 68810
193. H Koenig, A Franke, F F Friekel, BRD P. 2835439; *Chem. Abs.*, 1980, **93** 132363
194. D H R Barton, W B Motherwell, S Z Zard *Tetrahedron Lett.*, 1984, **25** 3707
195. D H R Barton, W B Motherwell, E S Simon, S Z Zard *J. Chem. Soc., Perkin Trans. I*, 1986, 224
196. B A Trofimov *Zhur. Org. Khim.*, 1986, **22** 1991

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Heterometallic sulphide-bridged transition metal clusters

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ABSTRACT. The literature data on heterometallic clusters with sulphide bridges are described systematically and discussed. The methods for the specific synthesis of clusters and the dependence of their geometry on the electronic structure of their metallic core are examined. The possibilities for the modelling of catalytic systems and materials of the type of magnetic semiconductors and superconductors are discussed.

The bibliography includes 140 references.

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I. Introduction

In recent years, there has been an appreciable growth of interest, both here and abroad, in the study of clusters—polynuclear compounds in which three and more atoms of transition or non-transition elements are linked to one another via metal–metal bonds, bridging ligands, or both.[1] These systems are remarkable because they are shielded by the ligands, throughout the lattice, from cooperative interactions typical of solid state chemistry; clusters are therefore fairly soluble and can be investigated by the usual methods of coordination chemistry. On the other hand, when the number of metal atoms within the cluster is sufficiently large, fragments corresponding to the packing of metallic lattices (triangles, tetrahedra, squares, trigonal bipyramids, octahedra, etc.) arise. All parts of the metallic surface with chemisorbed organic ligands are thus modelled.[2] As a result of the latter factor, clusters became promising starting materials for practical application in the preparation of polymetallic coatings as well as homogeneous and immobilised catalysts.

Among compounds of this kind, heterometallic clusters (HMC) containing several atoms of different metals are especially interesting.[3,4] Sulphide-bridged heterometallic clusters (SHMC) occupy an important place among the HMC. In particular, the active component of the cofactor of the enzyme nitrogenase consists of sulphide-bridged tetrahedra containing iron and molybdenum atoms. Molybdenum atoms fix nitrogen molecules preferentially, while the cluster as a whole, together with the $Fe_4S_4(SR)_4^{4-}$ clusters, ensures electron transfer in the process involving the reduction of nitrogen to ammonia.[5]

Furthermore, the presence in one HMC molecule of atoms of different metals in precisely known (and frequently specified) proportions makes it possible to obtain materials of the type of mixed sulphides with a high degree of homogeneity and the required ratio of the elements. Examples of such practically important systems are provided by the chalcochromites $M^{II}Cr_2X_4$ with a spinel structure, which have the properties of magnetic semiconductors.[6] Superconducting systems, the socalled "Chevrel phases", containing the Mo_6S_8 clusters (an octahedron of molybdenum atoms incorporated in a cubane structure made up of sulphur atoms), which are linked to one another by heterometallic M atoms (Pb, Sn, Cu, Ag, and the lanthanides), also incorporated in cubane structures made up of sulphur atoms have attracted much attention recently.[7]

One of the main problems in the study and application of sulphide-bridged heterometallic clusters is their synthesis, whose principles will be examined in the present review. We may note that the methods for the specific synthesis of various types of HMC,[8–10] including optically active HMC,[10,11] have become available only in the most recent years and so far do not constitute a well constructed system.

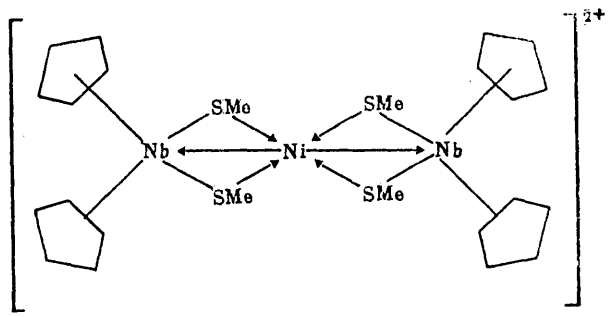
An important aspect of the specific synthesis of SHMC is the "cluster design" principle—the stepwise growth of the cluster core as a result of the employment of mono- and di-nuclear sulphur-containing metal complexes as ligands in relation to other metals (M′). Here one must take into account the electronic characteristics of the "building blocks" such as the presence of unshared electron pairs in the sulphur atoms or the metal atoms participating in the formation of new bonds with M′, the presence of S–S and M–M bonds in which an M′ atom can be inserted, and the presence of unoccupied or semioccupied orbitals of the metal atoms for which new dative bonds with M′ may be formed. Together with steric factors, these factors will be examined in the discussion of the synthesis and structure of clusters, the data being grouped in accordance with the nature of the principal "building blocks" within each Section in order of the arrangement of the heterometals in the Periodic System.

Since the complexity of the composition and geometry of the SHMC imposes special requirements as regards unambiguity in the determination of the structure of the complexes, this review discusses mainly clusters which have been obtained in the form of analytically pure single crystals and have been identified by full X-ray diffraction analysis. Literature data up to 1985 inclusive are incorporated.

II. Sulphide-bridged heterometallic clusters based on sulphur-containing complexes of group VA metals

The mononuclear trianion VS_4^{3-} functions as the central complex-forming agent in reactions with $(Me_4N)_2FeX_4^{2-}$ (X = Cl or SPh) in acetonitrile. This has resulted in the formation[12,13] of the trianions $X_2Fe(S)_2V(S)_2FeX_2^{3-}$ containing the Fe–V–Fe metal chain (for X = Cl, the length of the V–Fe bond is 2.727 Å) with two pairs of sulphide bridges and terminal X groups at the iron atoms. The clusters are paramagnetic (μ_{eff} = 4.96 B.M. for X = Cl and 4.80 B.M. for X = SPh).

The mononuclear sandwich fragments Cp_2M (Cp = C_5H_5), containing the SR groups which are forced to assume a position in the bisector plane between two cyclopenta-dienyl rings using the frontier orbitals with the $1a_1$, b_2, and $2a_1$ symmetries (their energies increase in this sequence) can serve as terminal complex-forming agents.[14] Thus the coordination of the two chelating ligands $Cp_2Nb(SMe)_2$ is observed when the readily displaced water molecules at the Ni(II) ion are substituted. The nickel atoms in the complex $[Cp_2Nb.(SMe)_2Ni(SMe)_2NbCp_2](BF_4)_2$ are linked to the four sulphur atoms of the SMe groups (the Ni–S bond lengths are 2.186–2.206 Å) and form direct Nb–Ni bonds (2.78 Å) via orbitals located in the bisector plane of the angle between the rings:[15,16]



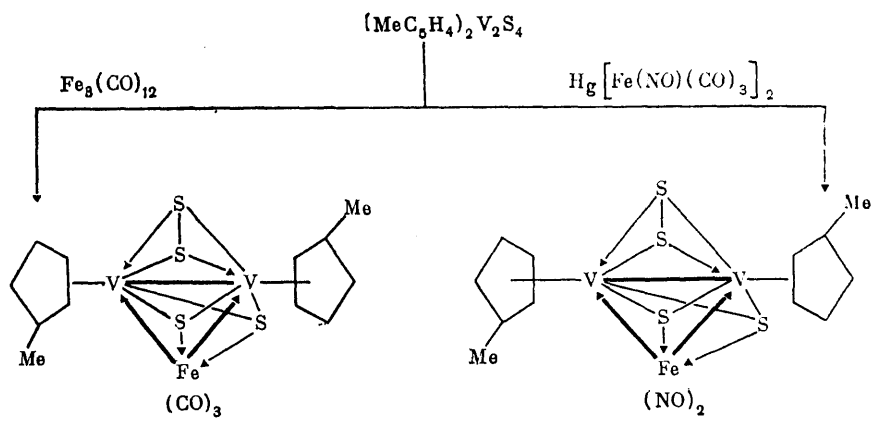
The complexes $(RC_5H_4)_2V_2S_4$,[18] obtained by treating $(RC_5H_4)_2.V_2S_5$ [19] with tributylphosphine, have been used recently as the starting materials for the synthesis of SHMC.[17] According to X-ray diffraction data, the complex $(RC_5H_4)_2V_2S_4$ (where R = iso-Pr) contains two sulphide bridges and the V–S–S–V fragment having a short V–V bond (2.610 Å). As a consequence of the electron deficiency, significant additional $\overline{S-V}$ π-bonding is observed, which shortens the V–S bonds (2.217–2.280 Å). The presence of unoccupied orbitals in $(MeC_5H_4)_2V_2S_4$ in combination with the presence of sulphide groups involved in different types of bonding, ensures a rich chemistry of this complex.

Thus the initial tetrasulphide complex $(MeC_5H_4)_2V_2S_4$ reacts with $IrCl(N_2)(PPh_3)_3$, affording the trinuclear cluster $(MeC_5H_4)_2V_2.(\mu,\eta^2\text{-}S_2)(\mu_3\text{-}S)_2IrCl(PPh_3)$, in which the iridium atom is located in a square planar environment (according to NMR data).[17]

Table 1. The principal geometrical characteristics of the vanadium-containing SHMC.[17,21]

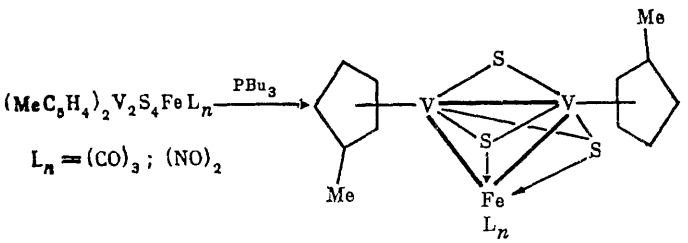
Compound	Bond length, Å (average values)					
	V–V	V–M	V–(μ_3-S)	M–(μ_3-S)	V–(μ,η^2-S)	V–(μ-S)
$(MeC_5H_4)_2V_2S_4Fe(CO)_3$	2.510	2.896	2.318	2.256	2.406	—
$(MeC_5H_4)_2V_2S_4Fe(NO)_2$	2.482	2.849	2.347	2.230	2.398	—
$(MeC_5H_4)_2V_2S_3Fe(CO)_3$	2.506	2.843	2.315	2.266	—	2.235
$(MeC_5H_4)_2V_2S_3Fe_2(NO)_2$	2.957	2.750	2.280	2.241	—	—
$[(MeC_5H_4)_2V_2S_4]_2Ni$	2.484	2.817	2.334	2.193	2.403	—

The addition of the CpCo fragment with formation of the triangular diamagnetic cluster $(MeC_5H_4)_2V_2S_4CoCp$ takes place in the reactions of $(MeC_5H_4)_2V_2S_4$ with $CpCo(C_8H_{12})$, $CpCo(CO)_2$, $[CpCo(CO)]_2$, or with the $CpCo(CO)I_2/Zn$ system (the yield reaches 25% in the last case). The trinuclear cluster $(MeC_5H_4)_2V_2(\mu,\eta^2\text{-}S_2).(\mu_3\text{-}S)_2Fe(CO)_3$ has been obtained by the reaction of $(MeC_5H_4)_2V_2S_4$ with $Fe_3(CO)_{12}$ [17] [or with $Fe(CO)_5$ in the presence of Me_3NO [20]] [$Fe_3S_2(CO)_9$ and $Fe_2S_2(CO)_6$ are formed as side products]:



The nitrosyl cluster $(MeC_5H_4)V_2(\mu,\eta^2\text{-}S_2)(\mu^3\text{-}S)_2Fe(NO)_2$, isoelectronic with the carbonyl-containing cluster, has been obtained by the reaction of $(MeC_5H_4)_2V_2S_4$ and $Hg[Fe(CO)_3(NO)]_2$ in tetrahydrofuran (THF) at 20 °C. The yield rises to 60% when $Fe(CO)_2.(NO)_2$, generated from $(PPh_3)_2N^+.Fe(CO)_3NO^-$ and $NOBF_4$ in the presence of Et_3N,[17,21] is used. When both diamagnetic clusters with the V_2Fe core are formed, the S_2 fragment changes the type of its coordination, being converted from the μ,η^1-bridging fragment (a two-electron donor) to the μ,η^2-bridging fragment (a six-electron donor). This is accompanied by an appreciable lengthening of the V–(μ-S) bond (to 2.318–2.347 Å) and the V–(μ,η^2-S) bond (to 2.406–2.398 Å) (Table 1). Apparently both facts (the rotation of the S_2 group and the lengthening of the V–S bonds) are determined by the decrease in the additional $\overline{V\text{–}S}_{bridge}$ π-bonding, since the unshared electron pairs of the sulphur atoms are used for the formation of the bond with the iron atom. Furthermore, the rotation of the disulphide bridge from the position along the V–V bond to the position at right angles appreciably diminishes (for steric reasons) the length of the V–V bond (2.510 and 2.482 Å respectively) compared with the length of the V–V bond in the initial dimer (V–V = 2.610 Å). The formation of new V–Fe bonds (2.8956 and 2.849 Å) does not interfere with the strengthening of the V–V bond, probably as a consequence of the interaction of the unoccupied orbitals of the vanadium atoms with the occupied orbitals of the iron atom.

When both clusters with the V_2Fe core are treated with tributylphosphine, the S_2 group loses one sulphur atom, affording the trisulphide clusters $(MeC_5H_4)_2V_2(\mu\text{-}S)(\mu_3\text{-}S)_2FeL_n$:[17,20]



In the tricarbonyl cluster, the overall geometry of the $V_2Fe(\mu_3\text{-}S)_2$ fragment [V–V = 2.505 Å, V–Fe = 2.8132 Å, and V–(μ_3-S) = 2.308–2.312 Å] remains the same as in the initial tetrasulphide cluster. However, the V–S bond (2.242 Å) of the V(μ-S)V group is strengthened as a result of the $\overline{V\text{–}S}$ π-bonding, since an electron deficiency arises on the vanadium atom as a consequence of the replacement of the six-electron donating $\mu,\eta^2\text{-}S_2$ group by the formally two-electron-donating bridge μ-S.

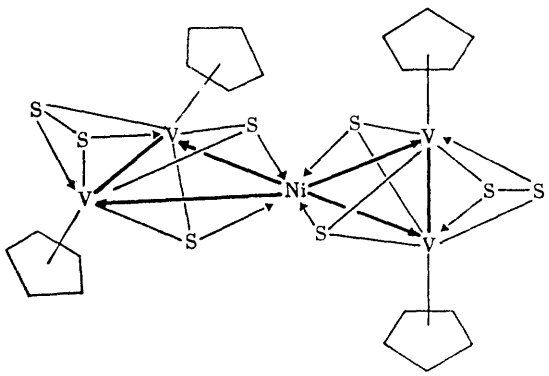
On the other hand, the active disulphide groups are capable of undergoing reactions involving the insertion of new metal atoms. Thus treatment of $(MeC_5H_4)_2V_2S_4Fe(CO)_3$ with $Pt(C_2H_4)L_2$ (L = PPh_3) at 25 °C leads to the insertion of the platinum atom in the S–S bond and the formation of the cluster $(MeC_5H_4)_2V_2.(\mu_3\text{-}S)_4Fe(CO)_3Pt(PPh_3)_2$.[17]

The nitrosyl cluster $(MeC_5H_4)_2V_2S_4Fe(NO)_2$ also contains the active $V_2(\mu,\eta^2\text{-}S_2)$ group, and its reaction with $Hg[Fe(CO)_3(NO)]_2$ or the direct interaction of $(MeC_5H_4)_2V_2S_4$ with $Hg[Fe(CO)_3(NO)]_2$ under severe conditions (in boiling toluene) leads to the addition of two Fe(NO) groups and the formation of the tetranuclear cluster $(MeC_5H_4)_2V_2S_4Fe_2(NO)_2$.[17,21]

The core of the molecule consists of the distorted V_2Fe_2 tetrahedron (V–V = 2.957 Å, V–Fe = 2.750 Å, and Fe–Fe = 2.590 Å), having μ_3-sulphide bridges over each face [$(Fe\text{–}S)_{av}$ = 2.241 Å; $(V\text{–}S)_{av}$ = 2.280 Å] and involving the additional coordination of the π-MeC_5H_4 ring at each vanadium atom and of one nitrosyl group at each iron atom. The cluster contains 58 electrons and its magnetic moment (μ_{eff} = 1.98 B.M. at 27 °C) is reduced compared with the spin-only value of 2.84 B.M. for two unpaired electrons, probably owing to antiferromagnetic exchange interactions. The paramagnetic (2.8 B.M.) 60-electron tetrahedral cluster $(MeC_5H_4)_2V_2S_4Co_2(NO)_2$ is in its turn formed readily (yield up to 95%) in the direct reaction of $(MeC_5H_4)_2V_2S_4$ with $Co(CO)_3(NO)$ in boiling toluene.[21]

The mixed paramagnetic 59-electron cluster $(MeC_5H_4)_2V_2S_4CoFe.(NO)_2$ has been obtained by the transmetallation of the cluster with the V_2Fe_2 core in the reaction with $Co(CO)_3(NO)$ in the presence of Me_3NO.[21] On treatment with metallic zinc and $[CoI(NO)_2]_x$,[17] the trisulphide cluster $(MeC_5H_4)_2V_2S_3Fe(NO)_2$ affords the diamagnetic cluster $(MeC_5H_4)V(\mu_3\text{-}S)_3FeCo_2(NO)_6$, which has 66 electrons and, according to the authors,[17] is constructed similarly to [the anion of] the block Roussin salt $Fe_4S_3(NO)_7^-$.[22]

The attempts to obtain the trinuclear cluster containing the V_2Ni core were unsuccessful and the reactions of $(MeC_5H_4)_2V_2S_4$ with nickel-containing reagents—$Ni(CO)_4$, $(COD)_2Ni$, $[CpNi(CO)]_2$, $Ni(CO)_2(PPh_3)_2$, or $Ni(CO)_2(Ph_2PC_2H_4PPh_2)$—resulted in the formation of the pentanuclear cluster $(MeC_5H_4)_4V_4S_8Ni$ with the V_4Ni metallospiran core:[17]



The peripheral S_2 bridging groups can split off one sulphur atom on treatment with a small excess of PPh_3, giving rise to the cluster $[(MeC_5H_4)_2V_2S_3]_2Ni$ with the V_4NiS_6 core.[17] Finally, insertion in the S–S bond is observed in reactions with one or two moles of $Pt(C_2H_4)(PPh_3)_2$ and leads to the growth of the core as a result of the addition of one or two $Pt(PPh_3)_2$ fragments. The clusters $[(MeC_5H_4)_2V_2S_4]_2Ni[Pt(PPh_3)_2]$ and $[(MeC_5H_4)_2V_2S_4]_2Ni[Pt(PPh_3)_2]_2$ have been identified by chemical analysis and IR and ^1H NMR spectroscopy and probably do not contain Pt–V bonds.[17]

$(MeC_5H_4)_2V_2S_5$, in which the short V–V bond (2.658 Å) is supplemented by the μ-S, $\mu,\eta^1\text{-}S_2$, and $\mu,\eta^2\text{-}S_2$ bridges (i.e. one S_2 fragment is coordinated along the V–V bond and the other is coordinated at right angles to it), can be used directly for the preparation of $(MeC_5H_4)_2V_2S_4$ derivatives.[19] However, the yields of the heterometallic clusters are in this case very low.

III. The synthesis and geometry of sulphide-bridged heterometallic clusters obtained using sulphur-containing group VIA metal complexes as ligands

The dinuclear chromium complexes $(C_5Me_5)_2Cr_2S_5$ [23] and (to an especially large extent) the antiferromagnetic complexes $Cp_2Cr_2.(SCMe_3)_2S$ and $(MeC_5H_4)_2Cr_2(SCMe_3)_2S$ described below are used

for the synthesis of chromium-containing SHMC. The complex $(C_5Me_5)_2Cr_2S_5$ [23] differs from the vanadium complex of analogous composition by the fact that it contains, apart from the μ-S and μ,η^2-S_2 bridges, the unusual S_2 bridge which is linked to two chromium atoms only via one sulphur atom [the second sulphur atom is linked to it by a weakened single bond (2.101 Å) which is probably of the donor–acceptor type]. As a result, this bridge is a two-electron ligand and the chromium atoms have the d^2 electronic configuration. The complex is diamagnetic probably as a result of the strong antiferromagnetic exchange reactions via the direct Cr–Cr bond (2.489 Å). The peripheral sulphur atom is then readily split off on treatment with PPh_3, affording the tetrasulphide complex $(C_5Me_5)_2Cr_2S_4$.[24] The sulphur atom is readily abstracted also in the reaction with $Co_2(CO)_8$, which leads to the formation of the diamagnetic cubane-like cluster $(C_5Me_5)_2Cr_2(\mu_3\text{-}S)_4Co_2(CO)_2$ (I).[25] The cluster is stable in air and contains 60 electrons. When it was treated with PR_3 (R = Ph or OMe), the products of the substitution of one and two CO groups were isolated:[26]

$$\underset{\text{(I)}}{(Me_5C_5)_2Cr_2S_4Co_2(CO)_2} \xrightarrow{PR_3} (Me_5C_5)_2Cr_2S_4Co_2(CO)(PR_3) + \underset{\text{(II)}}{(Me_5C_5)_2Cr_2S_4Co_2(PR_3)_2}$$

$PR_3 = PPh_3,\ P(OMe)_3.$

According to X-ray diffraction data, in the bisphosphine derivative (II) [$PR_3 = P(OMe)_3$] the core of the molecule consists of a distorted Cr_2Co_2 metallotetrahedron (Co–Co = 2.511 Å, Co–Cr = 2.638 to 2.660 Å, and Cr–Cr = 2.872 Å) with tridentate-bridging sulphide ligands over each face (Co–S = 2.155–2.179 Å and Cr–S = 2.256 to 2.278 Å).[26] The 60-electron clusters $Cp_2Cr_2(\mu_3\text{-}S)_4Mo_2(C_5Me_5)_2$ and $(C_5Me_5)_2Cr_2(\mu_3\text{-}S)_4Mo_2Cp_2$ with a pseudocubane core, containing chromium and molybdenum atoms, are formed in the photochemical reaction of $(C_5Me_5)_2M_2S_n$ (M = Cr, n = 5; M = Mo, n = 4) with the dinuclear complexes $Cp_2M'_2(CO)_4$ (M′ = Cr or Mo) containing M′≡M′ triple bonds.[27] On the other hand, if the rings in the dimeric carbonyls also contain methyl groups, then stable paramagnetic trinuclear clusters $(C_5Me_5)_3CrMo_2(\mu_3\text{-}S)(\mu\text{-}S)_3$ are formed.[27]

$Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (III), in which chromium(III) atoms are separated by a short distance (Cr–Cr = 2.689 Å), have been used for the synthesis of a large series of magnetically active SHMC. It is formed in the reaction of chromocene with t-butanethiol and its antiferromagnetic properties are described (μ_{eff} falls from 0.96 B.M. to zero in the temperature range 295–79 K) by the exchange parameter $-2J$ = 430 cm^{-1} for the spins of the Cr(III) ions equal to 3/2.[28,29] The methylated analogue $(MeC_5H_4)_2Cr_2$.·$(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (IIIa), which is also antiferromagnetic ($-2J$ = 478 cm^{-1}), was obtained in accordance with the same scheme from $(MeC_5H_4)_2Cr$.[30] From the formal point of view, it means that, after the formation of the Cr–Cr single σ-bond, two half-occupied orbitals, on which the magnetic properties depend, are present at each chromium atom. On the other hand, together with the presence of the unshared electron pairs in the sulphide and thiolate bridges, the presence of the above half-occupied orbitals determines the chemical behaviour of the complexes (III) and (IIIa).

1. Ferromagnetic clusters with the Cr_2Pd core

The complexes (III) and (IIIa) readily react under mild conditions (benzene, 20 °C) with $(PPh_3)_2PdCl_2$, affording the dark-green crystalline complexes $(RC_5H_4)_2Cr_2(SCMe_3)_2(S)(Cl)_2Pd(PPh_3)$ (R = H or Me). The composition of the clusters formally corresponds to 1 : 1 adducts, but, in contrast to the initial dinuclear complexes, the new clusters manifest ferromagnetic exchange interactions [μ_{eff} = 4.11 (296 K)–4.57 (79 K) B.M. and $+2J$ = 28 cm^{-1} for R = H; μ_{eff} = 3.87 (296 K)–4.20 (95 K) B.M. and $+2J$ = 11 cm^{-1} for R = Me).[13] According to X-ray diffraction data for the cluster with R = Me, the preferred rearrangement takes place in the resulting clusters in conformity with Pearson's principle:[32] the Cl atoms (hard Lewis bases) pass from the palladium atom (a soft Lewis base) to the chromium(III) atoms (hard Lewis bases). The $SCMe_3$ groups (soft Lewis bases), which previously served as bridges between the chromium atoms, then becomes bridges between the chromium and palladium atoms. The chelate ligand $(PPh_3)Pd(SCMe)_2$ (Pd–S = 2.350 and 2.381 Å), coordinated to to chromium atoms via thiolate bridges (Cr–S = 2.396 and 2.403 Å; Cr...Pd = 3.230 and 3.380 Å), is ultimately formed. The chromium atoms in this situation are coordinated to the π-MeC_5H_4 rings and the chlorine atoms (Cr–Cl = 2.308 Å) located in the *trans*-positions relative to the Cr_2Pd plane. As a result of such ligand environment of each chromium atom [the MeC_5H_4(centre)–Cr–Cr angle is 124.5° instead of 180° in compound (III)], the effective overlap of the d_{z^2} orbitals, which mainly determines the bonding of the chromium atoms in the dinuclear complexes (III) and (IIIa), becomes impossible. The Cr...Pd distances in the clusters are also large for bonding and, in the absence of M–M bonds, the antiferromagnetic contribution to the exchange interactions diminishes sharply and it is found possible to observe the ferromagnetic exchange via the sulphide bridge (the Cr–S–Cr angle is 121.77°).

2. The $(CpCrSCMe_3)_2S.ML$ adducts

The course of the interaction of the complex (III) with metal carbonyls is determined by the coordination number of the corresponding metal [CN(M)]. For CN(M) = 6, any adducts in which the $M(CO)_5$ is linked to the virtually unaltered complex (III) (Cr–Cr = 2.73 Å) via a sulphide bridge (M–S = 2.58 Å for M = Mo or W) are formed for $M(CO)_6$ (M = Cr, Mo, or W) with CN(M) = 6 on UV irradiation. Ultimately the magnetic properties remain unaltered ($-2J$ = 440 cm^{-1}).[33,34] The reaction of compound (III) with $Mn_2(CO)_{10}$ takes place analogously in THF at 10 °C, where the $Mn_2(CO)_9$ fragment is generated under the influence of UV irradiation.[35] It adds to the sulphide bridge in the initial chromium complex (III) in the *cis*-position relative to the Mn–Mn bond. Here CN(M) is also six and the dichromium fragment remains almost unchanged (Cr–Cr = 2.739 Å, Cr–$SCMe_3$ = 2.35 Å, Cr–S = 2.31 Å) like the magnetic properties ($-2J$ = 440 cm^{-1}), although the Mn–S distance is smaller (2.448 Å) than the Mo–S distance in the adducts described above.

Finally, as a result of the photochemical reaction of compound (III) under mild conditions ($h\nu$, 7°C), cyclopentadienylmanganese tricarbonyl $CpMn(CO)_3$ with CN(M) = 6 (the Cp ring occupies three coordination sites) also gives rise to a simple adduct of the initial complex, with $CpMn(CO)_2$ "suspended" under it and linked via a sulphide bridge only, the Mn–S bond being shortened to 2.334 Å. The geometry of the dichromium fragment is virtually unchanged on coordination of the manganese atom (Cr–Cr = 2.704 Å, Cr–$SCMe_3$ = 2.350–2.364 Å, and Cr–S = 2.295 Å).[36] All these adducts have a common geometrical feature involving the coordination of the "suspended group" to an M atom having an octahedral environment (i.e. for a coordination number of 6), the possibility of further interaction of the M atom (Mo, W, or Mn) with the thiolate sulphur atom being sterically blocked by two carbonyl groups.

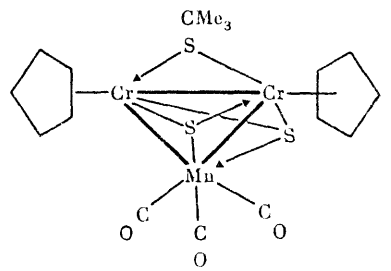
3. Triangular clusters with the Cr_2M core

The reactions involving complexes in which CN(M) is less than 6, i.e. when there is a possibility of the interaction of the orbitals of the M atom with the thiolate sulphur atom in the intermediates, proceed differently.

Thus the photochemical reaction of compound (III) with $Fe(CO)_5$ in THF takes place with the loss of two CO groups and one t-butyl group, the $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Fe(CO)_3$ cluster (IV) being formed.[37] Replacement of the S–CMe_3 σ-bond in it by the Fe–S bond alters little the geometry of the $Cp_2Cr_2S_2(SCMe_3)$ fragment compared with compound (III) (Cr–Cr = 2.707 Å). However, the appearance of the paramagnetic Fe(I) ion with the d^7 electronic configuration leads to the non-equivalence of the Cr–Fe bonds (2.726 and 3.110 Å) and to the magnetic properties being described by three parameters of the antiferromagnetic exchange interactions ($-2J_{Cr-Cr}$ = 380 cm^{-1}, $-2J_{Cr-Fe}$ = 2600 cm^{-1}, and $-2J_{Cr\ldots Fe}$ = 170 cm^{-1}). Apparently the half-occupied and occupied $Fe(CO)_3$ orbitals participate in the interaction with the two half-occupied orbitals in the dichromium fragment, forming a two-electron (single) Fe–Cr bond (2.726 Å) with one of the chromium atoms and a one-electron (bond order 1/2) Fe–Cr bond (3.110 Å) with the other atom.

Although the Mn atom in the above adduct of compound (III) with the $Mn_2(CO)_9$ fragment has CN(M) = 6, on UV irradiation under more severe conditions (boiling benzene or THF) there is a possibility of the dissociation of the Mn–Mn bond with decrease of CN(M) to five:[38]

$$(C_5H_5)_2Cr_2(SCMe_3)_2S\cdot Mn_2(CO)_9 \xrightarrow[C_6H_6,\ 80^\circ]{(III)}$$



(V)

This results in the formation of the antiferromagnetic metallocyclic cluster $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Mn(CO)_3$, whose composition is analogous to the iron-containing cluster (IV) but which differs in geometry and magnetic properties. Thus both Cr–Mn distances correspond to the presence of M–M′ bonds, although some non-equivalence, induced by the symmetry of the $Mn(CO)_3$ fragment relative to Cr_2S_2, is in fact observed in them (2.716 and 2.828 Å). On passing from the iron- to the manganese-containing cluster, in which the Mu(I) ion has the d^6 electronic configuration, the electron is apparently removed from the antibonding orbital, which leads to a marked stabilisation of the metallic core in compound (V). The Mn(I) ion is diamagnetic and the magnetic properties of the cluster (V) correspond to antiferromagnetic exchange interactions with the parameter $-2J_{Cr-Cr}$ = 670 cm^{-1}, which is much greater than for the $Cp_2Cr_2(SCMe_3)_2SML$ adducts (~440 cm^{-1}). Since the Cr–Cr bond in compound (V) (2.646 Å) has hardly changed compared with compound (III) (2.689 Å), the intensification of the exchange interactions can be evidently explained by the involvement of the bridging manganese atom.

The antiferromagnetic cluster $Cp_2Cr_2(SCMe_3)(\mu_3\text{-}S)_2FeCp$ (the iron atom in the cluster has the d^6 electronic configuration), which is formed in the form of dark-brown crystals on prolonged irradiation (17 h) of a boiling solution of compound (III) and $[CpFe(CO)_2]_2$ in THF (reactant ratio 2 : 1), is an isoelectronic analogue of the cluster (V).[39]

In contrast to the Cr, Mo, W, Mn, and Fe carbonyls or the cyclopentadienyl-manganese and -iron carbonyls, whose reactions with $Cp_2Cr_2(SCMe_3)_2S$ require UV irradiation and elevated temperatures, the dinuclear cobalt carbonyl $Co_2(CO)_8$ reacts with the dichromium complexes (III) and (IIIa) even at room temperature. The complex $Co_2(CO)_8$ exists in solutions in the non-bridged form [CN(Co) = 5] with a readily dissociating Co–Co bond (E = 9 kcal mol^{-1} [40] and the coordination with the sulphur atoms and the replacement of the S–CMe_3 bond in compound (III) or (IIIa) by the S–Co bond therefore proceed especially readily. The cluster $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Co(CO)_3$ (A), having a composition analogous to that of the iron-containing cluster (IV) and the manganese-containing cluster (V), should then be formed. However, owing to the d^8 electronic configuration of Co(I), the intermediate (A) must contain two electrons in the antibonding orbital of the metallic core. As a result, both Cr–Co bonds must have a bond order of 0.5 (or one bond is single and the other does not exist). Stabilisation of the intermediate (A) is readily achieved by splitting off of one carbonyl group on evacuation or heating of the reaction mixture, which results in the formation of the cluster $Cp_2Cr_2(SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2$ (VI).[35] According to X-ray diffraction data, compound (VI) has a stable metallic core with short Cr–Co bonds, which are almost equivalent (2.579 and 2.592 Å), since the two CO groups are distributed symmetrically relative to the pairs of chromium and sulphur atoms. The length of the Cr–Cr bond (2.617 Å) is changed relatively little (by 0.07 Å) compared with the initial complex (III). Therefore the increase in the parameter $-2J$ to 530 cm^{-1} is determined by the presence of the diamagnetic bridging cobalt atom.

The cluster $(MeC_5H_4)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2$, whose structure differs from that of the non-methylated analogue by the appearance of the crossed conformation of the rings instead of the eclipsed conformation, has been obtained analogously. Furthermore, on methylation of the ring, a slight but distinct strengthening of the metallic core compared with compound (VI) is observed (Cr–Cr = 2.590 and 2.617 Å, Cr–Co = 2.530, 2.569, 2.579, and 2.592 Å respectively). The antiferromagnetic exchange interactions are also found to have become more intense ($-2J$ = 578 cm^{-1}).[38]

Thus the introduction of the methyl substituent into the cyclopentadienyl ring strengthens the core and intensifies the exchange interactions, which is apparently associated with the increase in the electron density at the chromium atoms. This agrees with data for the electrochemical oxidation of $(RC_5H_4)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)Co.(CO)_2$. According to voltametric and microcoulometric data, both clusters give rise to two reversible one-electron oxidation waves in dimethylformamide (DMF) at potentials of 0.63 and 1.47 V (for R = H) and 0.44 and 1.10 V (for R = Me).

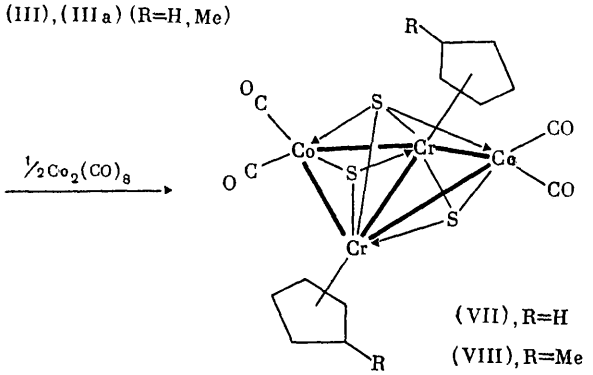
4. "Metallobutterfly" clusters with a Cr_2M_2 core

After the formation of compound (VI) and its methylated analogue, the remaining half-occupied orbitals of the chromium atoms can participate in further Cr–M bonding during the growth of the cluster core as a result of the reaction with an additional amount of $Co_2(CO)_8$, which leads to the formation of diamagnetic clusters having the general composition $(RC_5H_4)_2Cr_2(S)_3Co_2(CO)_4$, where R = H [compound (VII)] or Me [Compound (VIII)] with a metallic

core made up of two chromium atoms and two cobalt atoms.[39] We may note that, together with the replacement of the S–CMe_3 σ-bond in compound (VI) by a new S–Co bond, a μ_4-S bridge is produced by using yet another electron pair at the μ_3-sulphide bridge:

$$(C_5H_4R)_2Cr_2(\mu\text{-}SCMe_3)_2S \xrightarrow{1/2\,Co_2(CO)_8} (RC_5H_4)_2Cr_2(SCMe_3)(\mu\text{-}S)_2Co(CO)_2 \longrightarrow$$

(III), (IIIa) (R=H, Me)



(VII), R=H

(VIII), R=Me

There are no electrons in the antibonding orbitals of the Cr–Co bonds in the 62 electron clusters (VII) and (VIII) with the "metallobutterfly" core and all the Cr–Co bonds are therefore short and virtually equalised [2.617 and 2.622 Å in compound (VII) and 2.614–2.636 Å in compound (VIII)] by virtue of the symmetrical disposition of both $Co(CO)_2$ groups relative to the Cr_2S_2 fragment. The electrons participating in the formation of the Cr–Cr σ-bond are not then involved and the removal of the bulky CMe_3 groups, which hinder the mutual approach of the chromium atoms, shortens the Cr–Cr bonds to 2.544 Å (in both clusters).

The products of the formal replacement of the 13-electron $Co(CO)_2$ fragments in the cluster (VII) are the 15-electron CpNi fragments formed by the reaction of $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ (III) with the dinuclear cyclopentadienylnickel carbonyl $[CpNi(CO)]_2$, which, like the isolobal $Co_2(CO)_8$ complex, exists in solution in a non-bridged form [CN(Ni) = 5] and probably readily dissociates at the Ni–Ni bond. Therefore, as for $Co_2(CO)_8$, the reactants interact in equimolar amounts even at room temperature with formation of the 66-electron cluster $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Ni_2Cp_2$ (IX).[41] The cluster has an asymmetric "metallobutterfly" core with Cr–Ni distances non-equivalent in pairs (cf. 2.620 and 2.844 Å) and contains four superfluous electrons compared with $Cp_2Cr_2(S)_3Co_2(CO)_4$ (VII). These electrons are apparently located in the antibonding orbitals of the metallic core and not only the Cr–Ni bonds are lengthened, despite the smaller covalent radius of nickel compared with cobalt, but also the Cr–Cr bond [2.620 instead of 2.544 Å in compound (XVII)]. In addition, this leads to the appearance of antiferromagnetic properties ($-2J$ = 418 cm^{-1}).

5. Heterometallic tetrahedral clusters

The clusters $(\pi\text{-}C_5Me_5)_2Cr_2(S)_4Co_2(PR_3)_2$, containing the tetrahedral Cr_2Co_2 core, were described above.[25] An analogous cluster can be obtained by introducing a fourth sulphur atom instead of two carbonyl groups into the "metallobutterfly" $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2.(CO)_4$ (VII) in the reaction with t-butanethiol:[39]

$$(C_5H_5)_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2(CO)_4 + Me_3CSH \rightarrow (C_5H_5)_2Cr_2(\mu_3\text{-}S)_4Co_2(CO)_2.$$

A 60-electron diamagnetic cluster with an analogous structure has been obtained by the formal replacement of one Co(CO) fragment by the isoelectronic CpCr fragment. The cluster $Cp_3Cr_3(\mu_3\text{-}S)_4Co.(CO)$ (X) and its methylcyclopentadienyl analogue have been synthesised by treating the metallotriangular clusters $(RC_5H_4)_2Cr_2.(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2$ of type (VI) (R = H or Me) with diphenylacetylene which leads to the binding of some of the cobalt atoms (probably in the form of stable acetylene complexes).[42] The pseudocubane core is readily loosened on methylation of the Cp rings (the bond lengths in the Cr_3CoS_4 cores with R = H or Me are respectively Cr–Co = 2.650 and 2.692 Å and Cr–Cr = 2.810 and 2.816 Å). The M–S bonds are then found to be extremely short (Co–S = 2.163 and 2.171 Å and Cr–S = 2.244 and 2.263 Å), which indicates the undoubted occurrence of the additional $\overleftarrow{M\text{–}S}$ π-interaction.

The M–M′ bonds are loosened even more after the introduction of additional electrons into the metallic core of new electron-donating ligands, for example, on formation of the cluster $Cp_3Cr_3.(\mu_3\text{-}O)(\mu_3\text{-}S)_3Co(CO)_3HOOCCMe_3$ (XI).[43] It is produced as a result of the treatment with trimethylacetic acid of the reaction mixture of compound (III) and $Co_2(CO)_8$ in benzene [the mixture is obtained without concentration *in vacuo* and without heating, i.e. under conditions where the intermediate containing the $Co(CO)_3$ fragments may be obtained—see above]. As a result of the addition of two carbonyl groups, the metallotetrahedron (XI) is found to have four electrons more than in compound (X). They occupy antibonding orbitals of the metallic core but influence mainly bonds involving the cobalt atom. Not only the Cr–Co bonds (2.875, 3.219, and 3.230 Å), but also the Co–S (2.47 Å) and Co–O (2.16 Å) bonds are found to be greatly lengthened. On the other hand, in the metallotriangle Cp_3Cr_3 the Cr–Cr bond lengths (2.692–2.884 Å) are found to be within the limits characteristic of the trichromium fragment in the metallotetrahedral cluster (X). Trimethylacetic acid is a convenient reagent, binding some of the heterometal atoms occurring in the triangular clusters without the cleavage of the CpCr bond and with retention of the sulphide bridges. Thus treatment of the metallotriangular cluster $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)Fe(CO)_3$ (IV) with Me_3CCOOH yielded the heterometallotetrahedral cluster $Cp_3Cr_3.(\mu_3\text{-}S)_4Fe(OOCCMe_3)$ (XII), which contains a carboxylate group at the Fe atom linked only via one oxygen atom (Fe–O = 1.896 Å, C–O = 1.32 Å, and C–O = 1.25 Å) and is a structural analogue of the cluster $Cp_3Cr_3(\mu_3\text{-}S)_4Co(CO)$ (X) with a similar geometry (Fe–Cr = 2.758 Å, Cr–Cr = 2.830 Å, Fe–S = 2.218 Å, and Cr–S = 2.270 Å).[44] However, the replacement of the 11-electron Co(CO) fragment by the 9-electron $Fe(OCOCMe_3)$ fragment renders the cluster (XII) electron-deficient [58 electrons instead of the 60 electrons in compound (X)]. The two upper degenerate orbitals, which are occupied in compound (X), are found to be half-occupied in compound (XII), which is consistent with the observed paramagnetism of the cluster (μ_{eff} = 2.81 B.M.) and is close to the spin-only value for two unpaired electrons and is independent of temperature.

We may note that the reaction of compound (IV) with benzoic acid under the same conditions leads to the loss of the cyclopentadienyl ligands and of the thiolate bridge. All the metal atoms and one μ_3-sulphide bridge are then retained and the complex $Cr_2Fe.(\mu_3\text{-}S)(OOCPh)_6$ is formed.[44] The reactions of benzoic acid with the adducts $Cp_2Cr_2(SCME_2)_2S.ML_n$ [ML_n = $Cr(CO)_5$ or $Mn_2(CO)_9$] led to the analogous complexes in which the iron atom was replaced by the Cr(II) and Mn(II) atoms. The complexes are antiferromagnetic and the exchange parameters $-2J_{Cr...Cr}$ (54, 84, and 60 cm^{-1}

respectively) and $-2J_{Cr...M}$ (6, 36, and 28 cm^{-1})[44] exceed approximately by a factor of 2 the corresponding values for the known μ_3-oxo-bridged analogues.[45] This indicates an appreciable contribution of the exchange via the central bridging atom compared with the exchange via the carboxylate bridges and the small exchange parameters clearly indicate the absence of direct M–M bonds.

6. Pentanuclear heterometallospiran clusters

The cluster $[(MeC_5H_4)_2V_2S_4)_2Ni$ having the structure of a heterometallospiran with the $V_4(\mu_3\text{-}S)_4Ni$ core was described above.[17] It is the first representative of chromium-containing metallospiran clusters having the cobalt central atom. It arose very unexpectedly in the reaction of the metallotriangle $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2Co(CO)_2$ (VII) with Me_3CCOOH under severe conditions (xylene, 100 °C). This results in the binding of some of the cobalt atoms in the form $[Co(OOCCMe_3)_2]_n$ and the formation of the brown crystals of the antiferromagnetic cluster $[Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2Co$ (XIII) [μ_{eff} falls from 3.26 (292 K) to 2.19 (81 K) B.M.].[43] According to the results of full X-ray diffraction analysis, the two metallotriangular Cr_2Co fragments in the spiran core are arranged at an angle of 94.6° and are joined by the common cobalt atom. On the one hand, the geometry of each triangular fragment is similar to that observed in the initial triangle (VI). The dichromium fragments $Cp_2Cr_2(\mu\text{-}SCMe_3)(S)_2$ (designated henceforth by Q) remain almost unchanged under these conditions (Cr–Cr = 2.679 and 2.665 Å) (Table 2). On the other hand, pronounced loosening and asymmetry of the lengths of the Cr–Co heterometallic bonds are observed (2.766 and 2.744 Å in one triangle and 2.809 and 2.959 Å in the other).

If the dinuclear five-electron fragment Q is regarded as an unusual antiferromagnetic chelate ligand, then the cluster (XIII) is a formal product of the substitution of two CO groups in the initial compound (VI) by the fragment Q, the sulphur atoms occupying the places of the CO groups. As a result of such bonding, a 19 electron environment arises at the cobalt atom, the one superfluous electron loosening the Co–Cr and Co–S bonds [the Co–S bonds in compound (XIII) are lengthened on average by 0.075 Å compared with the initial compound (VI)]. We may note that, as in the metallotriangular cluster (IV) with the Cr_2Fe core, this occurs despite the general electron deficiency of the cluster (one half-occupied orbital remains in each chromium atom as before, which ensures the antiferromagnetic properties of the cluster).

The removal of an electron from the antibonding orbitals takes place on formal replacement of the central Co(II) ion by the Fe(II) ion. Such a cluster, $[Cp_2Cr_2(SCMe_3)(\mu_3\text{-}S)_2]_2Fe$ (XIV), has been obtained by the reaction of two moles of compound (III) with one mole of $Fe(CO)_5$ on prolonged UV irradiation in boiling THF, the reaction proceeding (according to IR spectroscopic data) via the intermediate formation of the triangular cluster $Cp_2Cr_2(SCMe_3).(\mu_3\text{-}S)_2Fe(CO)_3$ (IV) described above.[39] The cluster (XVI) was isolated in the form of fine black-green prisms, stable in air, by recrystallisation from a THF–heptane mixture; the composition of the cluster was established by elemental analysis, its IR spectrum being virtually identical with that of the cluster (XIII). The cluster (XIV) is antiferromagnetic and its μ_{eff} diminishes from 3.32 to 2.37 B.M. in the temperature range 290–80 K. Unfortunately, the crystals of the cluster (XIV) proved to be unsuitable for X-ray diffraction study.

The methylcyclopentadienyl analogue $[(MeC_5H_4)_2Cr_2(\mu\text{-}SCMe_3).(\mu_3\text{-}S)_2]_2Fe$ (XV) was obtained by the prolonged reaction of compound (IIIa) with $[CpFe(CO)_2]_2$ for a 4 : 1 reactant ratio in boiling toluene.[46] In this case the geometry of the metallic core of the cluster is determined to an appreciable extent by the steric effects

Table 2. Comparison of the principal geometrical parameters of the metallospiran clusters $[(RC_5H_4)_2Cr(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2M$.

Parameter	Central metal atom M in metallospiran				
	Cr(R=H)	Mn(R=H)	Mn(R=Me)	Fe(R=Me)	Co(R=H)
Cr–Cr (distance in peripheral fragments), Å	2.665	2.690	2.726; 2.657	2.693; 2.658	2.679; 2.665
Cr–M, Å	2.933; 2.889	2.947; 2.936	2.839–3.104	2.736–2.982	2.774–2.959
Cr–$SCMe_3$, Å	2.361–2.354	2.388–2.356	2.302–2.414	2.392–2.313	2.341–2.353
Cr–(μ_3-S), Å	2.302–2.327	2.307–2.323	2.250–2.372	2.275–2.329	2.248–2.270
M–(μ_3-S), Å	2.328–2.337	2.393–2.383	2.318–2.502	2.167–2.234	2.243–2.275
CrSRCr, deg	68.82	69.90	69.2–69.9	68.39–69.89	69.44–69.49
CrSCr, deg	70.02–70.62	71.00	70.9–72.1	71.92–70.08	71.08–71.23
CrSM, deg	76.6–78.1	77.6–77.7	73.6–82.0	73.75–81.03	75.25–80.42
Angle between Cr_2M planes, deg	90	90	109.60	113.80	94.60

of the MeC_5H_4...S repulsion (2.9–3.1 Å), leading to a marked change of the angle between the Cr_2Fe triangles (to 113.8°). This effect probably determines the non-equivalence of the Fe–Cr and Fe–S distances in the spiran core: Fe–Cr = 2.749 and 2.827 Å and Fe–S = 2.166 and 2.242 Å in one triangle and Fe–Cr = 2.910 and 2.969 Å and Fe–S = 2.293 and 2.368 Å in the other. Bearing in mind the difference between the covalent radii of iron and cobalt (1.34 and 1.29 Å), the Fe–Cr distances in compound (XV) indicate some stabilisation of the heterometallic bonds in the core compared with compound (XIII), i.e. on removal of an electron from the antibonding orbitals of the metallic core. The geometry of the $(MeC_5H_4)_2Cr_2(\mu\text{-}SCMe_3)(S)_2$ = Q′ fragments (especially the middle distance Cr–Cr = 2.675 Å) then remains very close to that found in compound (III). The cluster (XV) exhibits antiferromagnetic properties.

The same steric effects of the methyl groups in the rings are observed in the analogous cluster $[(MeC_5H_4)_2Cr_2(SCMe_3)(\mu_3\text{-}S)_2]_2Mn$ (XVI) containing the central Mn(II) ion. The cluster (XVI) was obtained by the reaction of compound (IIIa) in boiling toluene with manganocene Cp_2Mn, which readily loses the Cp ligands.[46] Owing to the short MeC_5H_4...S contacts (2.95–3.12 Å), the planes of the Cr_2Mn triangle are rotated by an angle of 109.6°. Not only do the Mn–Cr bonds differ under these conditions but also the lengths of the Cr–Cr bonds are not the same, a shorter Cr–Cr bond (2.657 Å) corresponding to the greatly lengthened Mn–Cr bonds (3.104 and 3.019 Å). The opposite picture is observed for the other triangle: a lengthened Cr–Cr bond (2.726 Å) corresponds to the shortened Mn–Cr bonds (2.839 and 2.967 Å). It is notable that all the Mn–Cr and Mn–S bonds (2.318–2.502 Å) are significantly lengthened compared with the corresponding bonds in the trinuclear cluster $QMn(CO)_3$. This is apparently due to the greater amount of ionic character in the bonds with a high-spin Mn(II) ion (d^5 electronic configuration). This idea agrees with the magnetic properties: μ_{eff} diminishes from 2.51 to 1.26 B.M. in the temperature range 295–80 K, which is described by the antiferromagnetic exchange parameters $-2J_{Cr-Cr}$ = 668 cm^{-1} and $-2J_{Cr-Mn}$ = 418 cm^{-1} for the spins of the Cr(III) and Mn(II) ions of 3/2 and 5/2 respectively.

The steric nature of the distortions in the geometries of the clusters (XV) and (XVI) is demonstrated by the removal of these distortions on passing to the non-methylated cluster $[Cp_2Cr_2.$ $.(SCMe_3).(S)_2]_2Mn$ (XVIII), which has been obtained by the reaction of two moles of compound (III) with one mole of $CpMn(CO)_3$ under severe conditions (on UV irradiation in boiling toluene).[47] The adduct $Cp_2Cr_2(SCMe_3)_2S.MnCp(CO)_2$ is formed as an intermediate and reacts with a second molecule of compound (III), affording the cluster (XVII) in the form of dark-green prisms. In compound (XVII), the angle between the Cr_2Mn planes is 90° and the geometry of the fragments Q remains unchanged (Cr–Cr = 2.690 Å and Cr–S = 2.307–2.324 Å), but, owing to the increased amount of ionic character, the Cr–Mn (2.947 and 2.936 Å) and Mn–S (2.393 and 2.324 Å) bonds are found to be lengthened compared with the triangular cluster $QMn(CO)_3$ (V).

The homonuclear cluster $[Cp_2Cr_2(SCMe_3)(S)_2]_2Cr$, containing the central Cr(II) ion (d^4 electronic configuration), which has been obtained by the reaction of compound (III) with C_6H_6 $Cr(CO)_3$ in THF on UV irradiation (not only the carbonyl groups but also the photolabile arene ligand are then substituted), has virtually the same geometry.[48] The peripheral Cr–Cr bonds are extremely short (2.665 Å) compared with the Cr_{periph}–Cr_{centr} bonds (2.933 and 2.889 Å). However, when account is taken of the difference between the covalent radii of Cr and Mn (1.46 and 1.34 Å respectively), the latter bonds are strengthened compared with Cr–Mn in compound (XVII). This can apparently be explained by the decrease in the amount of ionic character in the bonds on passing from d^5 to d^4.

We may note that the metallospiran clusters Q_2M (M = Cr, Mn, Fe, or Co) represent a new class of complex with chelate antiferromagnetic ligands Q, the character of the bonding of which to the central metal depends on the electronic configuration of M and the steric effect of the methyl substituents in the cyclopentadienyl ligands at the chromium atom.

The series of the structurally characterised clusters with the Cr_4Co, Cr_4Fe, Cr_4Mn, and Cr_4Cr cores presented here is supplemented by the clusters with the Cr_4V and Cr_4Ni cores. The vanadium-containing cluster has been obtained by the reaction of $V(BH_4)_2$ with compound (III) in the presence of Et_3N:[39]

$$2\,(C_5H_5)_2Cr_2(SCMe_3)_2S \xrightarrow[Et_3N]{V(BH_4)_2} [(C_5H_5)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2V.$$
(III)

The brown antiferromagnetic crystals have been characterised by elemental analysis and by IR spectra, which are identical with the spectra of the clusters Q_2M with M = Co, Fe, Mn, or Cr.

Finally, the reactions of compounds (III) and (IIIa) with the nickel complexes [Ni], which readily lose their ligands [$Ni(CO)_4$, $Ni(COD)_2$, and $(MeC_5H_4)_2Ni$] have been used to synthesise the clusters $[(RC_5H_4)_2Cr(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2Ni$ (R = H or Me):[39]

$$2\,(RC_5H_4)_2Cr_2(SCMe_3)_2S \xrightarrow{[Ni]} [(RC_5H_4)_2Cr_2(\mu\text{-}SCMe_3)(\mu_3\text{-}S)_2]_2Ni.$$

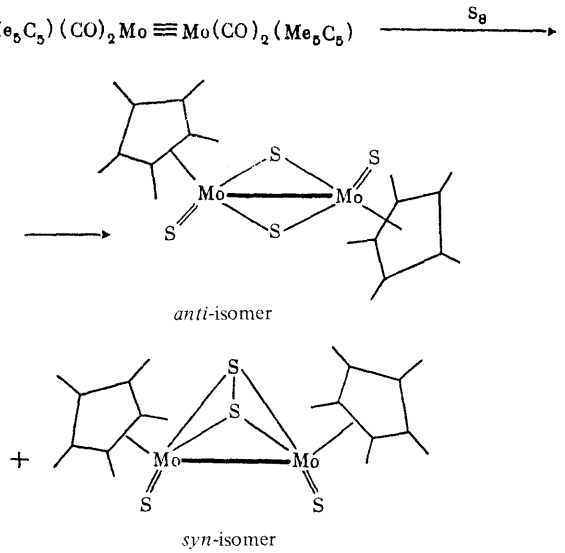
Both antiferromagnetic clusters have been isolated in the form of dark-green crystals and have been characterised by elemental analysis and IR spectra.

7. Sulphide-bridged heterometallic clusters based on $(C_5R_5)_2Mo_2S_4$ and $(C_5R_5)_2Mo_2(SH)_2(S)_2$

Dinuclear molybdenum tetrasulphide complexes exist in the form of three isomers, whose formation depends on the duration of the reaction of $(C_5Me_5)_2Mo_2(CO)_4$ with elemental sulphur. Thus the isomer $(C_5Me_5)_2Mo_2(\mu\text{-}S)_2(\mu,\eta^2\text{-}S_2)$ arises in hot toluene in the course of 17 h. It contains, apart from two sulphide bridges, the S_2 fragment coordinated at right angles to the short Mo–Mo bond (2.599 Å).[49] The analogous complex $(MeC_5H_4)_2Mo_2$ $(\mu\text{-}S)_2(\mu\text{-}S_2)$ has been described.[50] The diamagnetism of both molybdenum complexes probably indicates the presence of the Mo=Mo double bond and some shortening of the Mo–S bonds is evidence for an appreciable contribution by the additional Mo–S π-interaction.

If the reaction of $(C_5Me_5)_2Mo_2(CO)_4$ with S_8 is carried out over a period of three days, then the tetrasulphide complex described above is converted into two isomers with terminal sulphur atoms, which involves the dissociation of either the S–S bond or of the Mo–S bridge bonds. In the former case, the isomer contains Mo(V) atoms and, according to X-ray diffraction data,[51] only two sulphide bridges are present in the complex (Mo–S = 2.297 Å), while the other two sulphur atoms are terminal (Mo=S = 2.144 Å). The Mo(V) atoms then form a single Mo–Mo bond (2.905 Å). The complex has the *anti*-configuration as regards the Mo=S bonds and the C_5Me_5 rings.

The reaction via the second pathway affords a low yield of the *syn*-isomer, containing the disulphide group:



The *anti*-isomers of $(Me_nC_5H_{5-n})_2Mo_2(\mu\text{-}S)_2(S)_2$ are formed in a low yield even in the reactions of $(Me_nC_5H_{5-n})_2Mo_2(CO)_6$, where n = 0, 1, or 5, with S_8, but the main products are found to be the insoluble polymeric complexes $(Me_nC_5H_{5-n})_2Mo_2(\mu\text{-}S)_4$.[51]

The geometry of the Mo_2S_2 cores of the cyclopentadienyl[52] and methylcyclopentadienyl[51] complexes hardly differs form the geometry of the core in the pentamethylcyclodienyl analogue. The molybdenum atoms in these systems have a 16-electron environment (when account is taken of the Mo–Mo bond), which lead to a sharp shortening of the bonds with bridging sulphur atoms (to 2.297 Å) in conformity with the significant contribution of the additional Mo–S π-bonding.

The tetrahedral clusters $(C_5R_5)Mo_2(\mu_3\text{-}S)_4(Cr_2(C_5R'_5)_2$ (R = H, R′ = Me or R = Me, R′ = H), obtained by the reactions of the *anti*-isomers of $(C_5R_5)_2Mo_2S_4$ with $(C_5R'_5)_2Cr_2(CO)_4$, were described above.[27] If all the rings are methylated, then the interaction of $(C_5Me_5)_2Mo_2S_4$ with $(C_5Me_5)_2M'_2(CO)_4$ (M′ = Cr or W) gives rise to the stable paramagnetic trinuclear clusters $(C_5Me_5)_3Mo_2M'(\mu_3\text{-}S).(\mu\text{-}S)_3$.[27]

A 60-electron tetrahedral cluster, in which the $(C_5R_5)Cr$ groups have been replaced by the isoelectronic Fe(NO) groups, is formed in the reaction of $(C_5Me_5)_2Mo_2(\mu\text{-}S)_2(\mu,\eta^2\text{-}S_2)$ with $(Ph_3PNPPh_3)^+Fe.(CO)_3(NO)^-$.[53] On the other hand, the reaction of $(C_5Me_5)_2Mo_2.(\mu\text{-}S)_2(\mu,\eta^2\text{-}S_2)$ with $Fe_2(CO)_9$ at 25 °C in THF or with $Fe(CO)_5$ on UV irradiation gives rise to the tetranuclear cluster $(C_5Me_5)_2Mo_2.(\mu_3\text{-}S)_4Fe_2(CO)_4$ containing two $Fe(CO)_2$ fragments.[54] The cluster therefore has 62 electrons and the metal atoms form a "butterfly" structure with the Mo–Mo "abdomen" (2.761 Å) and the Mo_2Fe "wings" (Mo–Fe = 2.792–2.832 Å) and a non-bonded Fe...Fe distance of 3.334 Å. In addition, the trinuclear clusters $(C_5Me_5)_2.Mo_2(\mu,\eta^2\text{-}S_2)(\mu_3\text{-}S)_2Fe(CO)_2$ and $(C_5Me_5)_2Mo_2\{\mu\text{-}SC(O)S\}(\mu_3\text{-}S)_2Fe.(CO)_5$, containing the metallotriangular Mo_2Fe fragment (Mo–Mo = 2.592 and 2.574 Å and Mo–Fe = 2.777 and 2.826 Å respectively in the first and second triangular clusters) are formed. A distinctive feature of the second cluster is the insertion of the CO molecule in the disulphide bridge present in the initial dimer and in the first triangle (S–S = 2.071 Å).

The formation of the trinuclear cluster $(C_5Me_5)_2Mo_2S_4Mn(CO)_2Cp$ in the reaction of $(C_5Me_5)_2Mo_2S_4$ and $CpMn(CO)_2.THF$ has been briefly reported. It probably has the structure of an adduct with the coordination of the $CpMn(CO)_2$ fragment via one sulphide bridge, although the authors do not rule out a structure with the insertion of the Mn atom in the S–S bond.[24]

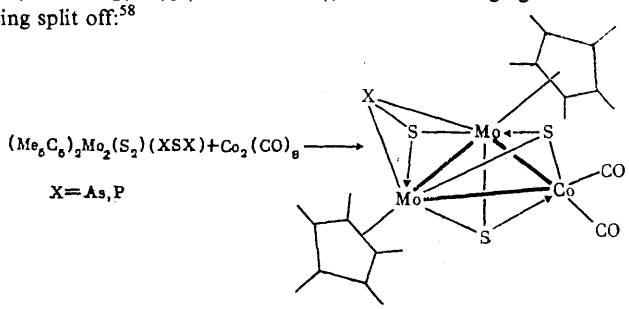
All the isomers of $(Me_nC_5H_{5-n})_2Mo_2S_4$ (n = 0, 1, or 5), including also the insoluble polymers, are converted on treatment with H_2 into the dinuclear tetrabridged complexes $(Me_nC_5H_{5-n})_2Mo_2(\mu\text{-}S)_2.(\mu\text{-}SH)_2$. These complexes are of interest because they contain two types of functional groups: MoSMo with unshared pairs in the sulphur atoms and Mo(SH)Mo with the thiol group SH.[55] The thiol groups in these complexes are readily substituted on treatment with HSR, affording $(Me_nC_5H_{5-n})_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SR)_2$ (R = Me, Et, Pr^i, or Ph). Accorinng to X-ray diffraction data, the sulphide bridges in the methyl analogue (Mo–S = 2.352 Å) alternate with the mercaptide bridges (Mo–SMe = 2.479 Å), while the Mo(IV) atoms (d^2 electronic configuration) with a 16-electron environment form the Mo=Mo double bond (2.582 Å).

The complex $(MeC_5H_4)_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2$ reacts with $Fe(CO)_5$ in the presence of Me_3NO, combining with two $Fe(CO)_3$ fragments. The cluster $(MeC_5H_4)_2\ Mo_2(\mu_3\text{-}S)_4Fe_2(CO)_6$, which has 66 electrons and the corresponding planar metallic core with a diagonal Mo–Mo bond (2.853 Å) and only two Mo–Fe bonds (2.826 Å) (the sulphide bridges are located over each Mo_2Fe fragment), is obtained. As a result, the metallic core acquires the "metallozigzag" Fe–Mo–Mo–Fe configuration[56] in contrast to the "metallobutterfly" obtained for the C_5Me_5 derivative.

The influence of the nature of the cyclopentadienyl ligands at the Mo atom is also manifested in reactions with $Co_2(CO)_8$. In the case of the $(C_5Me_5)_2Mo_2(\mu\text{-}S)_2(\mu,\eta^2\text{-}S_2)$ isomer, a 60-electron tetrahedral cluster $(C_5Me_5)_2Mo_2(\mu_3\text{-}S)_4Co_2(CO)_2$ is formed.[25] On the other hand, if one begins with $Cp_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2$, then the 62-electron cluster $Cp_2Mo_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2(CO)_4$, with a "metallobutterfly" core and containing only three sulphur atoms, is formed. As in the $Cp_2Cr_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)Co_2(CO)_4$ cluster described above, one of the sulphur atoms is tetradentate and is located between the Mo_2Co_2 wings (Mo–Mo = 2.646 Å and Mo–Co = 2.640 Å). The other two sulphur atoms are tridentate and are located under the Mo_2Co wings. Each cobalt atom is linked to two CO groups and each Mo atom is linked to the Cp ring.[57]

The $Cp_2Mo_2(\mu_3\text{-}S)_4Ni_2(CO)_2$ cluster, containing four tridentate sulphide bridges and two Ni(CO) fragments, is also of the 62-electron type. It is formed in the reaction of $Cp_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2$ with $Ni(CO)_2$ and has the "metallobutterfly" Mo_2Ni_2 core (Mo–Mo = 2.829 Å and Mo–Ni = 2.772 Å) with a non-bonded Ni...Ni distance of 2.962 Å.[57]

The insertion of the $Co(CO)_2$ fragment in the S–S bond is observed in the reaction of $(C_5Me_5)_2Mo_2(\mu,\eta^2\text{-}S_2)(\mu\text{-}XSX)$ (X = As or P) with $Co_2(CO)_8$ (toluene 25 °C), one of the bridging X atoms being split off:[58]



According to X-ray diffraction data for the As-containing derivative, the cluster has the Mo_2Co metallotriangular core (Mo–Mo = 2.610 Å and Mo–Co = 2.722–2.725 Å) with tridentate sulphide bridges located above and under the metallotriangle. The AsS μ,η^2-bridging group (As–S = 2.237 Å), which is a 5-electron donor, is located along the periphery of the cluster between the molybdenum atoms. In this situation, the cluster with the Mo_2Co core is an isoelectronic analogue of the $(C_5Me_5)_2Mo_2S_4Fe(CO)_2$ complex described above,[54] containing the 6-electron group μ,η^2-S_2 in combination with the $Fe(CO)_2$ groups having one electron less than the $Co(CO)_2$ fragment.

Among other cyclopentadienyl-containing SHMC with Group VIA metals, we may mention $\{[Cp_2Mo(SMe)_2]_2Ni\}^{2+}(BF_4^-)_2$, obtained from $Cp_2Mo(SMe)_2$ and $Ni(BF_4)_2$.[17] In contrast to the analogous niobium(IV) complex described above (d^1 electronic configuration), in the given molybdenum(IV) complex (d^2 electronic configuration) there are two electrons more. They are apparently found in the antibonding orbitals, which leads to a marked lengthening of the Mo–Ni bonds to 3.39 Å (bond order 0.5).

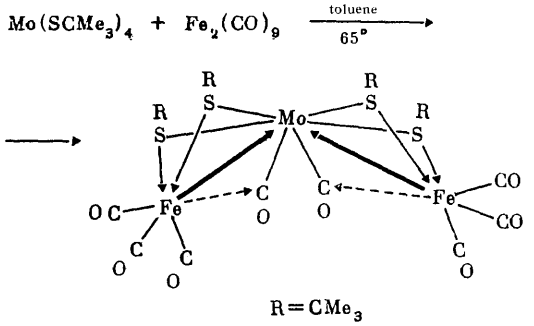
Finally, the cubane-like clusters with the $M_2Co_2(\mu_3\text{-}S)_4$ core (M = Mo or W) (Mo–Mo = 2.788 Å, Co–Co = 2.533 Å, and Mo–Co = 2.680 and 2.672 Å) have been obtained in reactions of the dinuclear molybdenum or tungsten diethyldithiocarbamate sulphides with cobalt carbonyl:[59]

$$(Et_2NCS_2)_2M_2S_4 + Co_2(CO)_8 \xrightarrow{MeCN} [(Et_2NCS_2)(MeCN)M]_2[Co(CO)]_2(\mu_3\text{-}S)_4$$
$$M = Mo, W.$$

In such a 60-electron cluster, the chelating Et_2NCS_2 group and the MeCN molecule occupy three orbitals at the M atom, donating five electrons, i.e. the entire system is similar to the $(CpMo)_2Co_2(CO)_2.(\mu_3\text{-}S)_4$ clusters described above. It has been noted that the MeCN molecule is not coordinated to the initial Mo or W dimers owing to the additional π-bonding to the sulphur atoms (the Mo–S bond length increases from 2.09 to 2.312 Å).

8. Sulphide-bridged heterometallic clusters based on $Mo(SCMe_3)_4$

The trimetallic complex $Mo(\mu\text{-}SCMe_3)_4(\mu\text{-}CO)_2Fe_2(CO)_6$ is formed in the reaction of $Mo(SCMe_3)_4$ with an excess of $Fe_2(CO)_9$. The reaction can be regarded as the addition of two $Fe(CO)_3$ fragments to pairs of SR groups at the Mo(IV) atom with an additional dative Fe–Mo interaction and the incomplete transfer of two CO groups to the molybdenum atom.[60] The molecular core is the almost linear Fe–Mo–Fe metal chain (Mo–Fe = 2.757 Å with an FeMoFe angle of 160.43°) having two bridging $SCMe_3$ groups above each Mo–Fe bond, the FeS_2Mo fragments having the "butterfly" configuration:

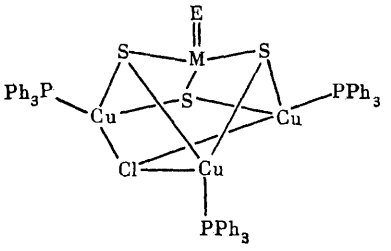


Treatment of $Fe_4S_4(SPh)_4^{2-}$ with $Mo(SCMe_3)_4$ results in transmetallation probably as a consequence of the greater strength of the Mo–Fe bonds compared with Fe–Fe. The $(Me_3CS)MoFe_3S_4.(SPh_2)^{2-}$ dianion was isolated under these conditions. It is reduced by sodium acenaphthenide in the presence of $(NBu_4)Br$ to the salt $(NBu_4)_3[(Me_3CS)MoFe_3S_4(SPh)_3]$ containing a trianion.[61] These cubane-like clusters model the active MoFeS centre of the cofactor of nitrogenase.

9. Sulphide-bridged heterometallic clusters based on the thiometallates MS_4^{2-} (M = Mo or W)

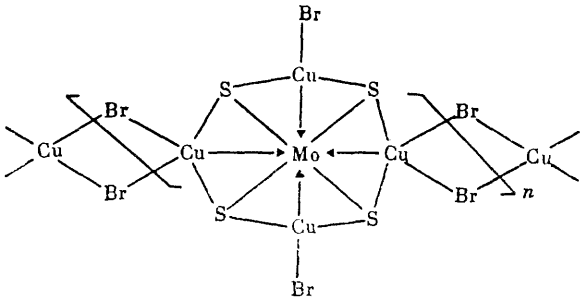
The readily available thiometallate complexes comprising Group VI transition metals, namely MS_4^{2-} (in the main, M = Mo or W), which are isolated as a rule in the form of ammonium or phosphonium salts, are extremely common starting materials for the synthesis of SHMC. Such monomeric anions contain the tetrhedral MS_4 fragment (Mo=S = 2.175 Å [62]). The highly electron-deficient character of M(VI) (d^0 electronic configuration) promotes the formation of dative M ← M′ bonds with the salts of other metals (in their absence, MS_3 and the sulphide of the heterometal are formed readily). Several reviews[63–65] have been devoted to their reactions and here we shall consider only examples of Cu- and Fe-containing complexes whose structure has been confirmed by X-ray diffraction data.

The former are of interest from the standpoint of the antagonism between copper and molybdenum in biological systems, throwing light on the nature of the Cu–Mo–S interaction.[66] The dianions MS_4^{2-} (M = Mo or W) reduce copper to Cu^+ on interaction with Cu^{2+}, forming polymers having the composition $\{[NH_4][Cu(MoS_4]\}_n$ [67] or $\{[NH_4][Cu(WS_4)]\}_n$.[68] Discrete molecules with Cu and M (Mo or W) atoms can be obtained by treating $(CN)_nCu_n(MS_4)^{m-}$ with KSPh in acetonitrile. $[PhSCu(S)_2Mo(S)_2]^{2-}$ and $[PhSCu(S)_2Mo(S)_2CuSPh]^{2-}$ were isolated under these conditions. In both cases the molybdenum atoms have a tetrahedral environment and the copper atoms have a planar trigonal environment. Furthermore, Mo ← Cu dative bonds (2.636 Å) are formed.[69] The metal chain in $Et_3PAu(S)_2.Mo(S)_2AuPEt_3$ is constructed analogously (the Mo ← Au bond length is 2.815 Å).[70] The interaction of MS_4^{2-} (or MoS_3^{2-}) with $CuCl_3$ in the presence of PPh_3 in CH_2Cl_2 results in the formation of clusters with a distorted pseudocubane core $(PPh_3)_3Cu_3S_3ClM(E)$ (M = Mo or W; E = S or O):[71]

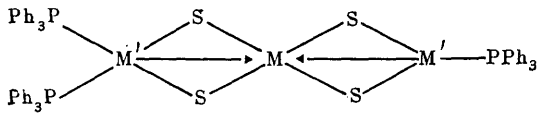


A cluster with the ratio Cu : Mo = 3 : 1 is also formed in the reaction of stoichiometric amounts of CuCl and $(Ph_4P)_2(MoS_4)$. In $(ClCu)_3.MoS_4^{2-}$, two sulphur atoms are bidentate and two are tridentate.[72,73] There is a possibility of the situation where all four sulphur atoms become tridentate. This happens in the cluster $(CuBr)_4MoS_4^{2-}$, which is a one-dimensional polymer.[74] In this polymeric cluster, two *trans*-Cu atoms have a planar-trigonal environment and two

others have a tetrahedral environment (all the metal atoms are then located in a single plane):

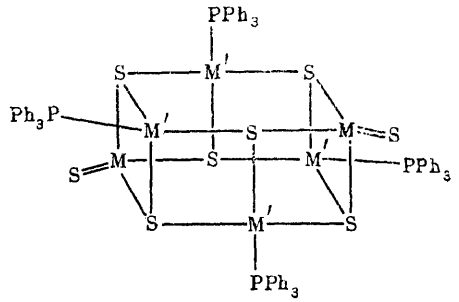


Partial cleavage of the Cu-S-M bridges has been observed[75] when the $[Cu(MS_4)]_n$ and $[Cu_2(MS_4)]_n$ polymers are treated with PPh_3. Complexes with a non-equivalent environment of the copper atoms are then formed. A cluster containing silver atoms of an analogous type has been isolated after the reaction of MS_4^{2-} with $AgNO_3$ in the presence of PPh_3 in CH_2Cl_2:[71]



M=Mo, W M′=Cu(I), Ag(I)

Finally, the bonding of each MS_4 group to other metals occurs in the complexes $(Ph_3P)_4M'_4(MS_4)_2$ (M = Mo or W; M′ = Cu or Ag):[76]

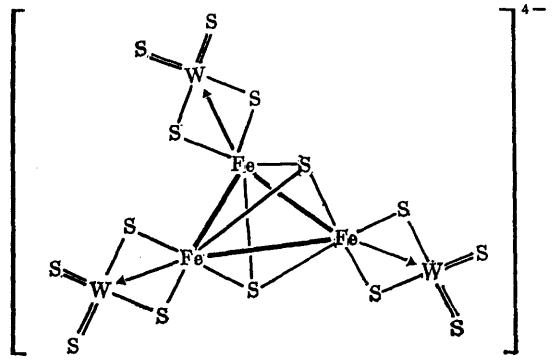


The core of this cluster is a complex polyhedron produced by the binding of two $MS_2M'_2S$ fragments.

The composition of the iron-containing complexes depends on the reactant ratio. For the $MS_4^{2-}:[M']^{2+}$ = 1:1 or 1:2 reactant ratio, the complexes $MoS_4FeCl_2^{2-}$ or $Cl_2FeS_2MoS_2FeCl_2^{2-}$, for example, were isolated,[64] in which the MoS_2 fragment chelates are the iron atom. Reactions of MS_4^{2-} (M = Mo or W) with iron carboxylates[77] and thiolates[78] take place analogously:

$$Fe(OOCMe)_2 + (Et_4N)_2(MS_4) \xrightarrow{MeCN} (MeCOO)_2FeS_2MS_2^{2-},$$
$$Fe(SPh)_4^{2-} + MS_4^{2-} \rightarrow (PhS)_2FeS_2MS_2^{2-}.$$

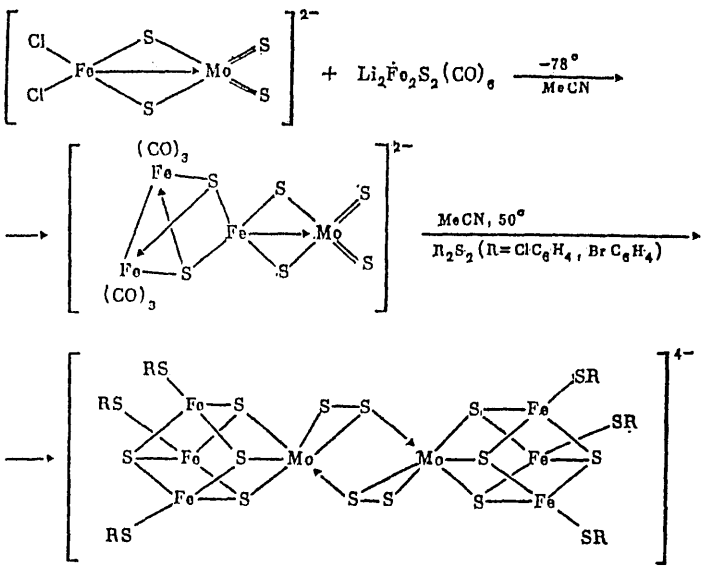
On the other hand, an excess of MS_4^{2-} reacts with various transition metal $[M']^{2+}$ salts, affording the anionic complexes $M'(MS_4)_2^{2-}$ [in particular, $TcO(MoS_4)_2^{2-}$, $(Ph_3P)_2Tc(MoS_4)_2$,[79] $Fe(MoS_4)_2^{2-}$,[80] $(FeMoS_4)_2^{3-}$,[81] $Co(MoS_4)_2^{3-}$,[82] $Co(WS_4)_2^{2-}$, $Fe(WS_4)_2^{2-}$, $Fe(WS_4)_2^{3-}$,[83] and $Fe(WS_4)_2^{4-}$], in which all the metal atoms have a tetrahedral environment made up of sulphur atoms. In the presence of an excess of PPh_4^+ and Et_4N^+ cations, the complex $Fe(WS_4)_2^{2-}$ is converted into the more stable cluster anion $Fe_3W_3S_{14}^{4-}$ with loss of some of the tungsten sulphide fragments.[84,85]



The cluster contains the triangular $Fe_3(\mu_3\text{-}S)_2$ core in which the iron atoms are linked by chelate bonds to three WS_4 fragments via sulphide bridges and have direct dative Fe → W bonds (2.774 Å).[84]

10. MoFe-containing sulphide-bridged heterometallic clusters modelling the active centre of the cofactor of nitrogenase

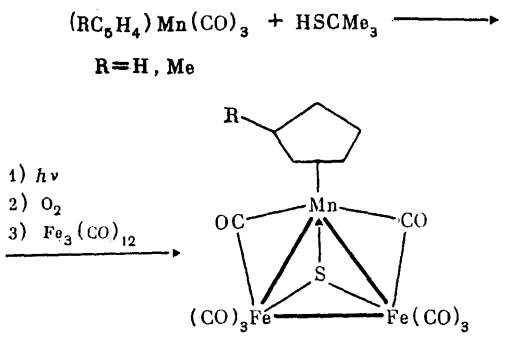
Thiometallate anions are good starting materials for the synthesis of the main types of the Mo–Fe–S clusters modelling the iron-molybdenum centre of the nitrogenase cofactor.[86-88] Such systems are obtained as a rule by the single-stage interaction of simple reactants ($FeCl_3$, NaSR, and MoS_4^{2-}) in methanol. Depending on the reaction conditions and the reactant ratio, three main types of complexes are formed: $Mo_2Fe_6S_8(\mu\text{-}S)(\mu\text{-}SR)_2(SR)_6^{3-}$, $Mo_2Fe_6S_8.(\mu\text{-}SR)_3(SR)_6^{3-}$, and $Mo_2Fe_7S_8(\mu\text{-}SR)_6(SR)_6^{n-}$ (n = 3, 4).[89-96] All these clusters have the structure of two Fe_3MoS_4 cubane-like moieties connected by bridging ligands. The mechanism of the formation of Mo–Fe–S clusters of this type is so far obscure, but it has been possible to achieve a multistage synthesis of compounds of this type from $Cl_2FeMoS_2^{2-}$ and iron carbonyl complexes:[97]



In the intermediate cluster $MoFe_3S_6(CO)_6^{3-}$, the diiron disulphide fragment (Fe–Fe = 2.491 Å) adds to the Fe atom of the initial complex via μ_3-S bridges [Fe–(μ-S) = 2.288 Å, Mo–Fe = 2.762 Å, Mo=S = 2.156 Å, and Mo–(μ-S) = 2.263 Å]. Further treatment of this cluster with the disulphide $(XC_6H_4S)_2$ (X = Cl or Br) affords a cluster with a double cubane-like core in which the molybdenum atoms are linked by two S_2 bridging groups (Mo...Mo = 3.97 Å). This cluster has also been obtained by specific synthesis in accordance with the traditional mechanism from MoS_4^{2-}, $FeCl_2$, Na_2S_2, $(XC_6H_4S)_2$, and NaOMe in methanol.

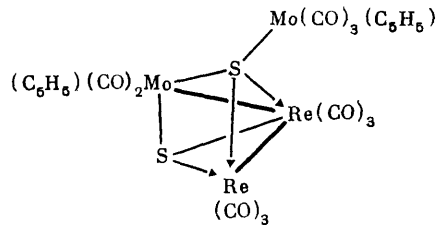
IV. Sulphur-containing group VIIA metal complexes as ligands and the clusters based on them

There are very few sulphur-containing complexes of Group VIIA metals used as cluster-forming agents. One of them is the paramagnetic complex $(C_5R_5)Mn(CO)_2SCMe_3$ (R = H or Me), which has been characterised by X-ray diffraction (for R = Me, the Mn–SR bond length is 2.187 Å).[98] It is probably in fact the cluster-forming agent in the photochemical reaction of $(RC_5H_4)Mn(CO)_3$ with $HSCMe_3$ and subsequent treatment with O_2 and $Fe_3(CO)_{12}$, which resulted in the formation of the cluster $(RC_5H_4)Mn(\mu_3\text{-S}).(\mu\text{-CO})_2Fe_2(CO)_6$ (R = H or Me):[99]



In this metallotriangular cluster (Mn–Fe = 2.660 and 2.689 Å and Fe–Fe = 2.609 Å), the sulphur atom is located above the plane of the Fe_2Mn triangle (Fe–S = 2.176 Å and Mn–S = 2.206 Å) and the sides of the triangle are linked additionally by bridging CO groups.

Another starting material for the formation of SHMC is the complex $[(CO)_4Re(\mu\text{-SSnMe}_3)]_2$.[100] Its reaction with $CpMo(CO)_3Cl$ in benzene results in the elimination of two moles of $ClSnMe_3$ and three moles of CO and the formation of a tetranuclear cluster in which the initially planar Re_2S_2 fragment is converted into a "butterfly", the electron deficiency in the partially decarbonylated rhenium atoms being compensated by the Mo–Re and Re–Re bonding:



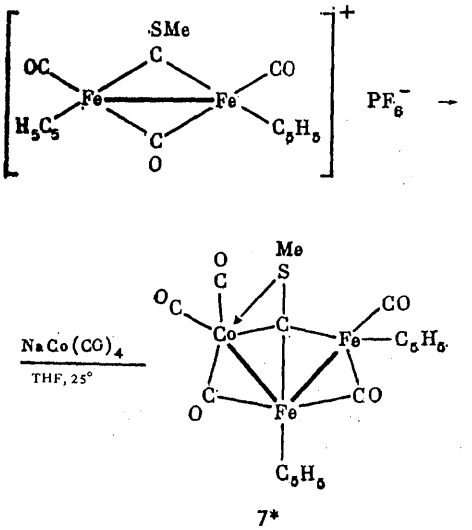
This results in the formation of the Mo–Re–Re "metal chain" (Mo–Re = 2.909 Å and Re–Re = 2.985 Å), above and under the plane of which are located tri- and tetra-dentate bridging sulphur atoms [the latter forms a σ-bond with the $Mo(CO)_3Cp$ group[101]].

A cluster containing three different metal atoms can be obtained by using $M(SAsMe_3)(CO)_3(PMe_3)_2$ (M = Mn or Re) as ligands in relation to $FeCo(\mu\text{-AsMe}_2)(CO)_7$.[102] This leads to the formation of the trinuclear cluster $(PMe_3)_2(CO)_3M(\mu\text{-SAsMe}_2)Co(CO)_3(\mu\text{-AsMe}_2).Fe(CO)_4$ containing the M–Co–Fe (M = Mn or Re) metal chain.[103]

V. Clusters based on sulphur-containing group VIII metal complexes

Among these compounds, the greatest number of SHMC have been obtained from sulphur-containing iron complexes. For example, it has been shown[104] that treatment of 1/2 of a mole of $Rh_2(CO)_4Cl_2$ with $CpFe(CO)_2SR$ leads to the formation of the trinuclear linear cluster $[Cp(CO)_2Fe]_2(\mu\text{-SR})_2Rh^+$.

A cluster with two iron atoms and a cobalt atom is formed in the reaction of the ionic complex $Cp(CO)Fe(\mu\text{-CO})(\mu\text{-CSMe})Fe(CO)Cp^+$ with $NaCo(CO)_4$ in THF at 25 °C:[105]



7*

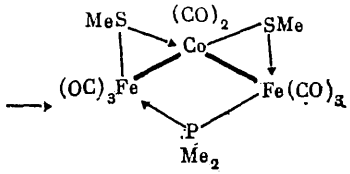
The cluster has a core consisting of a non-linear metal chain with short Fe–Co (2.500 Å) and Fe–Fe (2.537 Å) distances. The sulphur atom in this compound plays the role of a stabilising agent, building up the coordination sphere of the cobalt atom (Co–S = 2.313 Å) to an 18-electron shell.

The dinuclear thiolatoiron carbonyl complexes $Fe_2(\mu\text{-SR})_2(CO)_6$, which have already been known for about 30 years, have themselves proved to be inert in relation to other metal carbonyls [for example, $Fe_2(\mu\text{-SMe})_2(CO)_6$ does not react with $Co_2(CO)_8$ even under severe conditions].[106] However, after preliminary treatment with $HPMe_2$,

the subsequent reaction with $Co_2(CO)_8$ proceeds in accordance with the scheme[107]

$$Fe_2(SMe)_2(CO)_6 \xrightarrow{PMe_2H} Fe_2(SMe)_2(CO)_5(PMe_2H) \xrightarrow{Co_2(CO)_8}$$

$$\longrightarrow (CO)_3Fe(\mu\text{-}SMe)_2Fe(CO)_2(\mu\text{-}PMe_2)Co(CO)_3 \longrightarrow$$

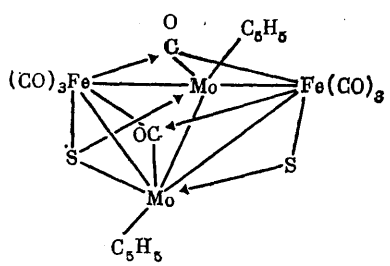


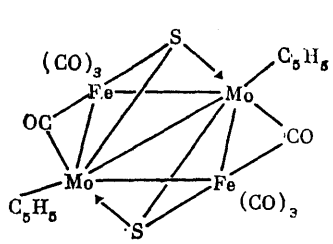
The same product has been obtained in the reaction of $Fe_2(SMe)_2(CO)_6$ with $(C_3H_5)Co(CO)_3$ in the presence of PMe_2H.[108]

The commonest starting material for the synthesis of iron-containing SHMC is the complex $S_2Fe_2(CO)_6$, first synthesised by Hieber and Gruber.[109] According to X-ray diffraction data,[110] the two iron atoms in this complex are separated by a short distance of 2.552 Å and form together with the disulphide fragment (S–S = 2.007 Å) a distorted Fe_2S_2 tetrahedron in which the angle between the planes of the Fe_2S triangles is 54°, the three Co groups at each iron atom being directed away from the S_2 group. The latter group is the site of attack by the metal-containing $M'L_n$ reagent, which donates electrons to the LUMO antibonding in relation to the S–S bond.[111,112]

On interaction of $S_2Fe_2(CO)_6$ with $[CpCr(CO)_3]_2$, the cluster $Cp_2Cr_2Fe_2(\mu_3\text{-}S)_2(\mu_3\text{-}CO)_2(CO)_6$ with the "metallobutterfly" Cr_2Fe_2 core was isolated. When the cluster is produced, the Fe–Fe bond is ruptured and the CO group at each Cr atom acquires tridentate-bridging character and is bound to two iron atoms.[113]

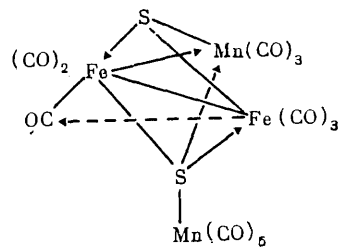
A "butterfly" cluster of analogous composition, containing molybdenum atoms, has been obtained by the reaction of $S_2Fe_2(CO)_6$ with $Cp_2Mo_2(CO)_4$.[114] Later it proved possible to isolate this isomer with a planar disposition of the four metal atoms and the bridging CO groups between the iron and molybdenum atoms:[115]





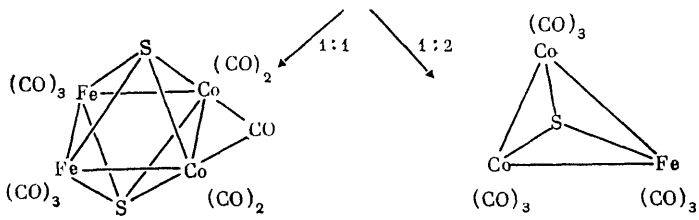
The tetranuclear clusters $Mn_2Fe_2S_2(CO)_{14}$, having a complex structure, is formed in the reaction of $S_2Fe_2(CO)_6$ with $Mn_2(CO)_{10}$. It is possible to identify in it the MnFeFe metal chain with a semibridging CO group between the iron atoms. The tetradentate bridging sulphur atom, located above the $MnFe_2$ plane, is σ-bonded to the manganese atom of the $Mn(CO)_5$ group:[116]

$$S_2Fe_2(CO)_6 + Mn_2(CO)_{10} \xrightarrow[h\nu]{THF}$$



The reaction of $S_2Fe_2(CO)_6$ with $Co_2(CO)_8$ is equimolar amounts at 20 °C gives rise to the cluster $Fe_2Co_2(\mu_4\text{-}S)_2(\mu\text{-}CO)(CO)_{10}$ with a square planar metallic core. The "capping" sulphur atoms in the cluster are involved in a tetradentate coordination and the cobalt atoms are linked in addition to the CO group.[117] The reaction of $S_2Fe_2(CO)_6$ with an excess of $Co_2(CO)_8$ at room temperature takes place with the dissociation of the S–S and Fe–Fe bonds, giving rise to the trinuclear cluster $FeCo_2(\mu_3\text{-}S)(CO)_9$.[118] The yield of the cluster increases on UV irradiation.[106] According to X-ray diffraction data, this diamagnetic 48-electron cluster has the Co_2Fe triangular metallic core with equalised M–M distances (2.550 to 2.556 Å) over which is located the tridentate sulphur atom (M–S = 2.152–2.164 Å):[118]

$$S_2Fe_2(CO)_6 + Co_2(CO)_8$$



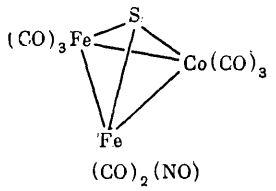
The dissociation of $S_2Fe_2(CO)_6$ into two fragments is also observed in the reaction with $[CpNi(CO)]_2$, which is isolobal in relation to $Co_2(CO)_8$. This entails the formation of the metallotriangular cluster $Cp_2Ni_2Fe(CO)_3(\mu_3\text{-}S)$.[119] According to Bogan et al.,[120] the formation of clusters with the Fe_2M_2 core is a common stage in the reactions of the dinuclear metal complexes with $S_2Fe_2(CO)_6$, which is followed by processes involving the elimination and addition of the ML or S fragments, ensuring the isolation of a wide variety of structures.

The $CpRh(\mu_3\text{-}S)_2Fe_2(CO)_6$ cluster has been obtained in the form of two isomers (a metal chain with a central or terminal rhodium atom) by treating $S_2Fe_2(CO)_6$ with $CpRh(CO)_2$ in boiling hexane.[121] Finally, trinuclear clusters without Fe–M bonds have been obtained by the reaction of $S_2Fe_2(CO)_6$ with $L_2M(C_2H_4)$ (L = PPh_3; M = Pt

or Pd).[122] The structure of the sulphide-bridged clusters $(PPh_3)_2$.$M(\mu_3\text{-}S)_2Fe_2(CO)_6$ (M = Pt or Pd) has been proposed on the basis of X-ray diffraction data for the selenium-containing analogue $(PPh_3)_2Pt(\mu_3Se)_2Fe_2(CO)_6$ (Fe–Fe = 2.533 Å and Pt–Fe = 3.45 Å).[122] A palladium-containing complex is also obtained in the reaction of $S_2Fe_2(CO)_6$ with $Pd(PPh_3)_4$ via a transmethylation reaction–the substitution of the $Fe(CO)_3$ fragment in $Fe_3(CO)_9(S)_2$ on treatment with $(PPh_3)_2PdCl_2$ and elimination of $PdCl_2$. The cluster contains no Fe...Pd bonds and the Pd atom has a square planar environment made up of phosphorus atoms (Pd–PO = 2.313 and 2.348 Å) and sulphur atoms (Pd–S = 2.305 and 2.326 Å). The PdS_2 plane is perpendicular to the Fe–Fe bond (2.504 Å).[123]

1. Reactions of iron-containing sulphide-bridged heterometallic clusters

In the reaction with THF.$Cr(CO)_5$, the $FeCo_2S(CO)_9$ cluster is capable of coordinating an additional $Cr(CO)_5$ fragment via a μ_4-sulphide bridge.[124] The mixed-ligand clusters $Fe_3(\mu_3\text{-}S)(\mu_3\text{-}ER)$.$(CO)_9$ (R = alkyl or aryl and E = P or As) react analogously with $(THF)M(CO)_5$ at 0 °C.[125] It has been shown by X-ray diffraction that the $Fe_3S(ER)$ core with ER = $PCMe_3$ remains unchanged compared with the initial cluster and the $Cr(CO)_5$ or $W(CO)_5$ fragment remains on the periphery of the molecule, adding on via a fairly long S → M bond (Cr–S = 2.428 Å and W–S = 2.547 Å).[126] The syntheses of chiral iron-containing SHMC are of special interest. Thus $Fe_2Co(CO)_9(\mu\text{-}S)^-$ has been isolated in the form of the salt with the NEt_4^+ anion on reaction of $Co_2(CO)_8$ and $Fe_3(CO)_9S^{2-}$ in CH_2Cl_2. The anion has a triangular metallic core with a "capping" sulphur atom and is converted into a neutral form on nitrosylation as a result of acidification in the presence of the nitrite ion:[127]

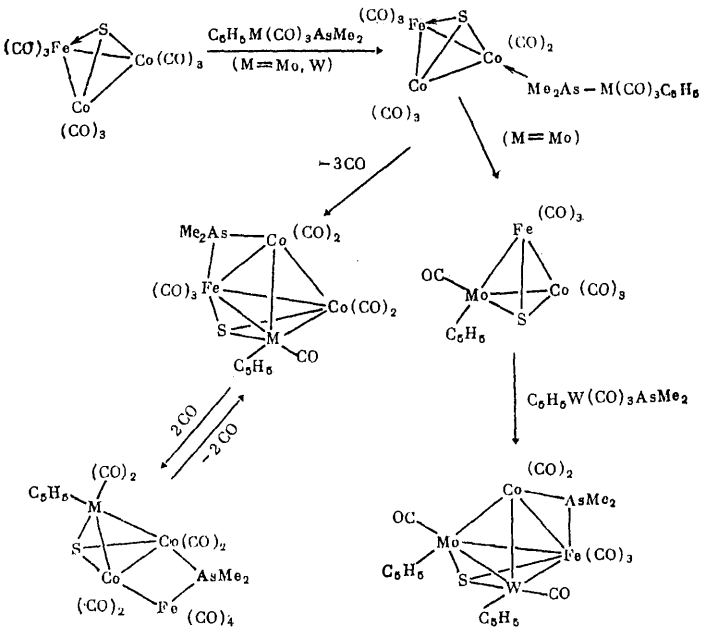


A second pathway leading to the synthesis of chiral clusters involves the formation of tetrahedra with sulphide groups at the vertices, at the base of which there is a triangle with three different metal atoms. Such clusters were first obtained[128] in 1978 by the specially developed "transmethylation" reaction of cobalt-containing clusters on treatment with dimethyl arsenide complexes of molybdenum, tungsten, and iron.[128] The cluster $CpMo(CO)_2(\mu_3\text{-}S)FeCo$.$(CO)_6$ was synthesised in this way. The substitution of one CO group at the Co atom in this cluster by the chiral ligand (*R*)-PMePrPh affords the diastereoisomers of the cluster $CpMo(CO)_2Co(CO)_2$(PMePrPh)$(\mu_3\text{-}S)Fe(CO)_3$, which were separated by crystallisation [the (–)-(*R*)-isomer with m.p. 119 °C is less soluble, while the (+)-(*S*)-isomer with m.p. 133 °C is readily soluble]. The corresponding enantiomers were then obtained by treatment with CO under conditions where phosphine was bound by methyl iodide.[129]

After transmethylation, intermediates were also isolated in which the $AsMe_2$ fragment is present as a bridging group, for example, $FeCo_2S(CO)_8$–$AsMe_2$–$MCp(CO)_3$ (M = Mo or W). The subsequent elimination of CO leads to the metallotetrahedral clusters $FeCo_2M(\mu_3\text{-}S)(\mu\text{-}AsMe_2)Cp(CO)_8$, which can in their turn combine irreversibly with two molecules of CO, the process being accompanied by the dissociation of two bonds, Fe–M and Fe–Co, whereupon the new system $CpMFeCo_2(\mu\text{-}AsMe_2)(\mu_3\text{-}S)(CO)_{10}$ (M = Mo or W) is generated.[130]

On the other hand, a cluster with four atoms of different metals was obtained for the first time with the aid of analogous reaction from the $FeCoMo(\mu_3\text{-}S)Cp(CO)_8$ cluster described above[131] (see below).

Clusters in which the iron atom has been replaced by a ruthenium atom, for example, $RuCo_2(CO)_9(\mu_3\text{-}S)$ obtained by the reaction of $Co_2(CO)_8$ with $Ru_3(CO)_{12}$ in the presence of EtSH with the reactant ratios 3 : 1 : 3.5 in an autoclave under a pressure of H_2 and CO (60 and 140 atm respectively), react similarly.[132] Treatment with the organometallic arsines $Me_3AsM(CO)_3Cp(L)$ leads to the formation of the clusters $RuCo_2(\mu_3\text{-}S)(CO)_{9-n}AsMe_2M(CO)_3Cp_n$ (M = Cr, Mo, or W; n = 1, 2), which in the case where n = 1 exists in the form of two isomers in which the ligand L is linked either to the cobalt atom or to the ruthenium atom. On heating the first isomer in cyclohexane in a CO atmosphere (T = 75–85 °C), the $Co(CO)_3$.$AsMe_2$ fragment is split off and the chiral clusters $(\mu_3\text{-}S)RuCoMCp$.$(CO)_8$ are formed. They have also been obtained by direct transmethylation in the reaction of $SRuCo_2(CO)_9$ with $[CpM(CO)_3]_2$ (M = Cr, Mo, or W).[132] The replacement of one CO group by optically active phosphines (L′) yielded the corresponding diastereoisomers $CpMoRuCo(\mu_3\text{-}S)(CO)_7L'$, in which L′ is linked to the cobalt atom:[132]

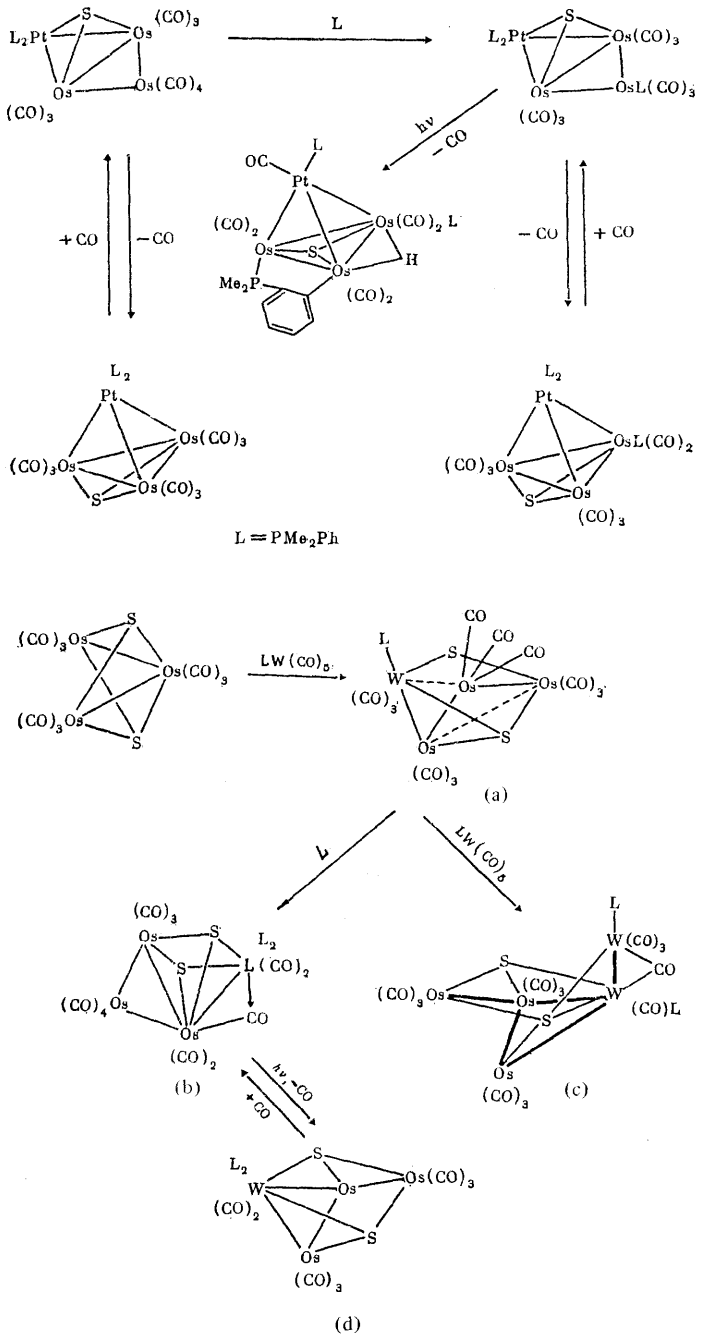


2. Sulphide-bridged heterometallic clusters based on trinuclear osmium clusters

The use of the trinuclear osmium cluster $Os_3(\mu_3\text{-}S)(CO)_{10}$ as a metal-containing ligand in the photochemical reaction with $W(CO)_6$ in hexane, affording the cluster $(CO)_9Os_3(\mu_4\text{-}S)W(CO)_5$, has been described.[133] The $W(CO)_5$ group is then located on the periphery of the molecule (W–S = 2.550 Å) and the structure of the Os_3S core hardly changes compared with the initial cluster (Os–Os = 2.804

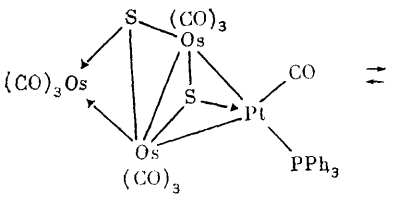
and 2.895 Å respectively). The cluster $Os_3(CO)_{10}(\mu_3\text{-}S)$ reacts readily with $Pt(C_2H_4)(PMe_2Ph)_2$ at 20 °C, forming four clusters: $PtOs_3(CO)_{10}(PMe_2Ph)_2(\mu_3\text{-}S)$, $PtOs_3(CO)_9(PMe_2Ph)_3(\mu_3\text{-}S)$, $PtOs_3(CO)_9(PMe_2Ph)_2(\mu_3\text{-}S)$, and $PtOs_3(CO)_8(PMe_2Ph)_3(\mu_3\text{-}S)$.[134] The first and second clusters with a planar metallic $PtOs_3$ core (Pt–Os = 2.768 and 2.838 Å and Os–Os = 2.869 and 2.833–2.907 Å respectively) are isoelectronic and have similar geometries, the first cluster being converted into the second on treatment with phosphine. They are readily decarbonylated, affording the third and fourth isoelectronic clusters, which contain the metallotetrahedral $PtOs_3$ core (Pt–Os = 2.740, 2.766, and 2.853 Å and Os–Os = 2.770, 2.896, and 3.064 Å) with a tridentate sulphur atom under the Os_3 triangle.

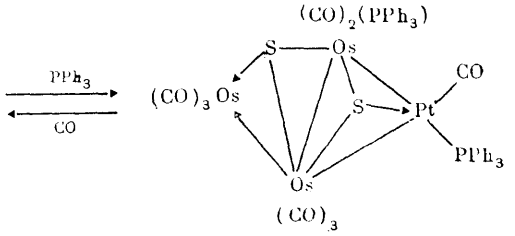
Prolonged photolysis of the second cluster leads to the formation of a cluster having a bridging hydride atom over the Os_3 triangular base of the cluster (Pt–Os = 2.684, 2.806, and 2.816 Å and Os–Os = 2.837, 2.930, and 2.972 Å). One of the phosphine ligands then becomes a bridge between two osmium atoms as a result of the formation of the Os-P and Os–C_6H_4 bonds.[134] The cluster $Os_3(CO)_9(\mu_3\text{-}S)_2$, containing two sulphide bridges, gives rise to four clusters in the formally analogous reaction with the phosphine-tungsten carbonyl complex $W(CO)_5L$ (L = PMe_2Ph); $LWOs_3(\mu_3\text{-}S)_2(CO)_{12}$ (a), $L_2WOs_3(\mu_3\text{-}S)_2(CO)_{12}$ (b), $L_2WOs_3(\mu_3\text{-}S)_2(CO)_{11}$ (c), and $(LW)_2Os_3(\mu_3\text{-}S)(\mu_4\text{-}S)(\mu\text{-}CO)(CO)_{13}$ (d):[135]



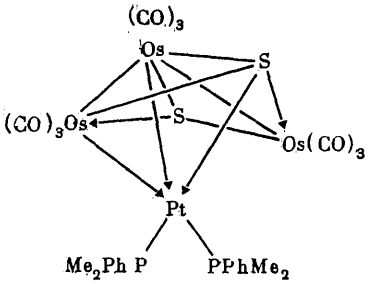
In three of them, namely (a), (c), and (d), Os_3W "metallobutterfly" core is produced to some extent with the axial Os–Os distances of 2.963, 2.923, and 2.924 Å respectively for (a), (c), and (d) and with tridentate bridging sulphur atoms located between the Os_3 and Os_2W "wings". In the 64 electron cluster (a), the two opposite M–M bonds in the "wings" are loosened under these conditions (M–Os = 3.050 and 3.054 Å). In the isoelectronic cluster (c), one WOs_2 wing contains non-equivalent W–Os bonds (2.814 and 3.016 Å), while in the second wing one Os–Os bond is missing (2.829 and 3.813 Å). Finally, in the cluster (d) the overall geometry of the "butterfly" core is close to that in (c), but the W atom is the bound to the second tungsten atom via a short bond (2.711 Å) supported by the bridging CO group, while one of the bridging sulphur atoms becomes tetradentate. In this situation, the Os–W distance (in the Os_2W wing) is shortened to 2.703 Å (the second distnce is 2.991 Å). On the basis of the analysis of the geometry of NMR data, the authors postulate the existence of the cluster (d) in two isomeric forms with short W=W and Os=W bonds. The fourth cluster (b) has a planar geometry of the rhombic Os_3W metallic core with short Os–Os (2.895 and 2.887 Å) and Os–W (3.044 Å) bonds and a long W...Os distance (3.612 Å). In this case, the sulphur atoms, remaining tridentate, bind two osmium atoms and a tungsten atom.[135]

The disulphide cluster $Os_3(CO)_9(\mu_3\text{-}S)_2$ also reacts with $Pt(PPh_3)_4$ or $Pt(C_2H_4)(PPh_3)_2$, forming the isoelectronic clusters $PtOs_3(CO)_{11-n}\cdot(PPh_3)_nX_2$ (n = 1,2), which are interconverted on treatment with phosphine or Co respectively:[136]





Both clusters contains the planar Os_3Pt metallic core with a metallotriangular Os_2Pt fragment (Os–Pt = 2.858–2.905 and 2.868–2.904 Å and Os–Os = 2.990 and 2.998 Å respectively) and one Os atom bound to Os_2Pt via a single direct Os–Os bond and one Os–S bond (Os–Os = 2.826 and 2.819 Å and Os–S = 2.399 and 2.403 Å respectively).[136] If PPh_3 in the platinum complex is replaced by PMe_2Ph, then both phosphine ligands in the Os–Pt-containing cluster $(PMe_2Ph)_2PtOs_3(\mu_3\text{-}S)(\mu_4\text{-}S)(CO)_9$ are bound to the Pt atom, and are non-equivalent:[137]



Although the platinum atom forms strong bonds only with the two neighbouring Os atoms (Os–Pt = 2.789 and 2.936 Å), the migration of Pt over all Os atoms is observed (according to NMR data) and the Pt–(μ_4-S) bond is always retained.[137]

3. Sulphide-bridged heterometallic clusters based on platinum-containing complexes

The "butterfly" Pt_2S_2 core is produced in the complex $(S)_2Pt_2L_4$ (L = PPh_3),[138] but here there are neither S–S (S...S = 3.1 Å) nor Pt–Pt bonds.[139] The platinum(II) atoms then have the traditional square planar environment made up of two sulphur atoms and two phosphorus atoms. As a result, the phosphine ligands are directed away from the sulphide bridges and do not prevent the coordination of the metal atoms to the latter.

Chelate coordination solely via the sulphide bridges without the formation of new M–M bonds has been observed when $L_4Pt_2(\mu\text{-}S)_2$ was used as the metal-containing ligand. The complex reacts with various mononuclear palladium compounds and affords, depending on the reaction conditions, SHMC containing between 3 and 6 nuclei.[139] The Scheme overleaf also indicates the products of the reactions of $L_4Pt_2(\mu\text{-}S)_2$ with mecury[139] and silver[140] compounds. According to X-ray diffraction data, the pentanuclear cluster $L_8Pt_4(\mu_3S)_4Pd^{2+}$ (L = PPh_3) contains no M–M bonds (M...M is greater than 3.15 Å). The palladium atom then has a square planar environment made up of four sulphur atoms (Pd–S = 2.348 Å and Pt–S = 2.344–2.351 Å, as a result of which all five metal atoms are located in the same plane (the average deviation is ±0.088 Å):[139]

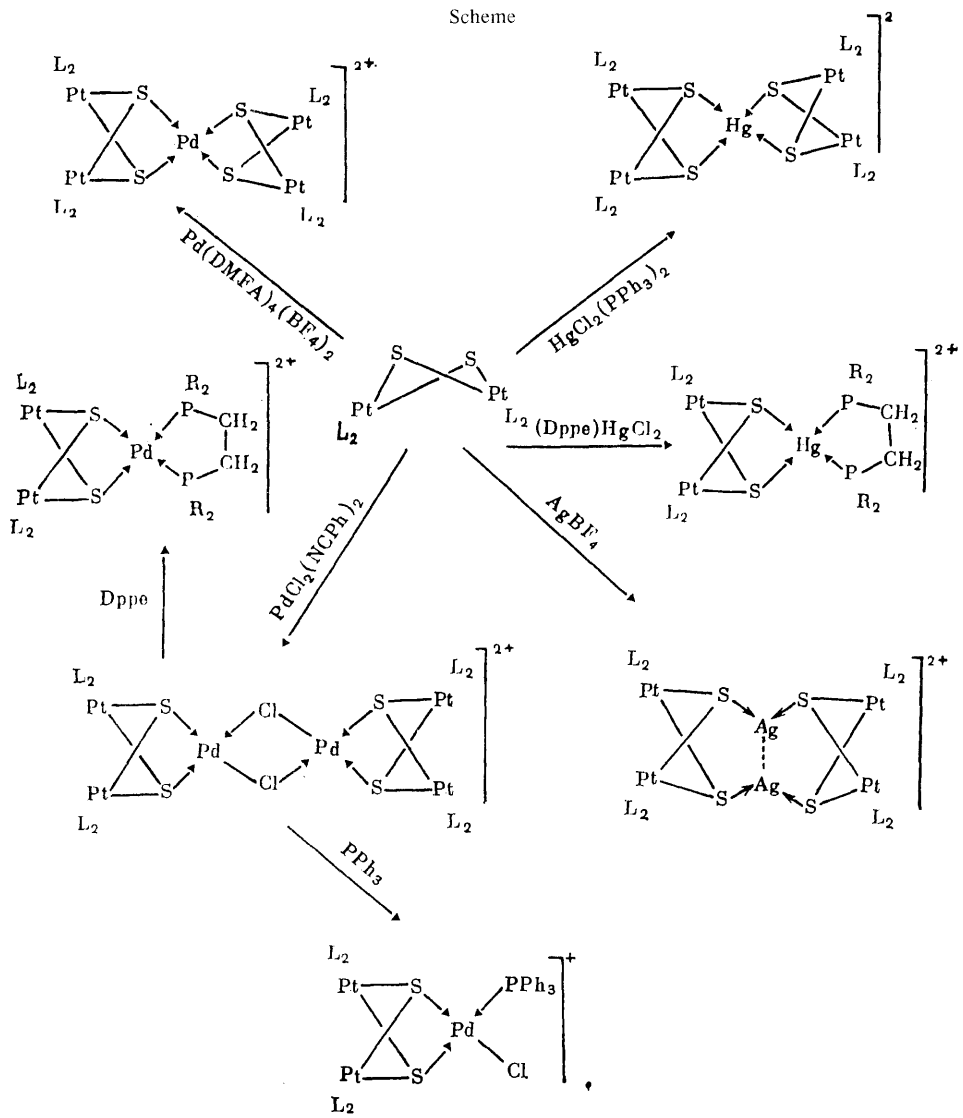
In the hexanuclear $Ag_2Pt_4(\mu_3\text{-}S)_4L_8^{2+}$, the two $L_4Pt_2S_2$ fragments (Pt...Pt = 3.278 and 3.350 Å) fragments are linked by two silver atoms (in a quare-trigonal environment made up of sulphur atoms) (Ag–S = 2.381–2.399 Å and Pt–S = 2.350–2.374 Å), which are separated by a fairly short distance (2.815 Å). The Ag...Pt distances of 3.450–3.905 Å imply the absence of bonds between these atoms.[140]

References

1. B F G Johnson (Editor) *Transition Metal Clusters*, Wiley, Chichester, 1980
2. E L Muetterties *Bull. Soc. Chim Belges*, 1975, **84** 959
3. D A Roberts, G L Geoffray *Comprehensive Organometallic Chemistry* (Edited by F G A Stone, et al.), Pergamon Press, Oxford, 1982, Vol. 6, Chapter 40, p. 763
4. W L Gladfelter, G L Geoffray *Adv. Organometal.Chem.*, 1980, **18**, 207

5. A Muller, E Dieman in *Transition Metal Chemistry—Current Problems of General, Biological and Catalytical Relevance* (Edited by Weinheim), Verlag Chemie, 1981, p. 221
6. P K Baltzer, P J Wojtowicz, M Robbins, E Lopatin *Phys. Rev.*, 1966, **151** 367
7. C K Banks, L Kammerdiner *J. Sol. State Chem.*, 1975, **15** 271
8. F G A Stone *Philos. Trans. R. Soc. London*, 1982, **308A** 87
9. S P Gubin *Pure Appl. Chem.*, 1986, **58** 567
10. H Vahrenkamp *Philos. Trans. R. Soc. London*, 1982, **308A** 17
11. R Blumhofer, H Vahrenkamp *Chem. Ber.*, 1986, **119** 683
12. Y Do, E D Simhon, R H Holm *J. Amer. Chem. Soc.*, 1983, **105** 6731
13. Y Do, E D Simhon, R H Holm *Inorg. Chem.*, 1985, **24** 4635
14. J W Lauher, R Hoffmann *J. Amer. Chem. Soc.*, 1976, **98** 1729
15. W R Duglas, M L H Green, C K Prout *J. Chem. Soc. Chem. Comun.*, 1971, 896
16. K Prout, S R Crytchley, G V Reeds *Acta Crystallogr.*, 1974, **30B** 2305
17. C M Bolinger, T D Weatherill, T B Rauchfuss, et al. *Inorg. Chem.*, 1986, **25** 634
18. C M Bolinger, T B Rauchfuss, A L Rheingold *J. Amer. Chem. Soc.*, 1983, **105** 6321
19. C M Bolinger, T B Rauchfuss, R L Rheingold *Organometallics*, 1982, **1** 1551
20. C M Bolinger, T B Rauchfuss, S R Wilson *J. Amer. Chem. Soc.*, 1982, **104** 7313
21. C M Rauchfuss, T D Weatherill, S R Wilson, J P Zebrowski *J. Amer. Chem. Soc.*, 1983, **105** 6508

Scheme



22. C T-W Chu, L F Dahl *Inorg. Chem.*, 1977, **16** 3245
23. H Brunner, J Wachter, E Guggolz, M L Ziegler *J. Amer. Chem. Soc.*, 1982, **104** 1765
24. H Brunner, H Kauermann, W Meier, J Wachter *J. Organometal. Chem.*, 1984, **263** 183
25. H Brunner, J Wachter *J. Organometal. Chem.*, 1982, **240** C41
26. H Brunner, W Meier, J Wachter, et al. *Z. Naturforsch*, 1985, **40b** 923
27. H Brunner, H Kauermann, J Wachter *J. Organometal. Chem.*, 1984, **265** 189
28. A A Pasynskii, I L Eremenko, B Orazsakhatov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 733
29. A A Pasynskii, I L Eremenko, Yu V Rakitin, et al. *J. Organometal. Chem.*, 1979, **165** 57
30. A A Pasynskii, I L Eremenko, Yu V Rakitin, et al. *J. Organometal. Chem.*, 1983, **248** 309
31. A A Pasynskii, I L Eremenko, G Sh. Gasanov, et al. *Polyhedron*, 1984, **3** 775
32. F Basolo, R G Pearson *Mechanisms of Inorganic Reactions* (Translated into Russian), 1971
33. A A Pasynskii, I L Eremenko, B Orazsakhatov, V T Kalinnikov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 1227
34. A A Pasynskii, I L Eremenko, Yu. V Rakitin, et al. *J. Organometal. Chem.*, 1981, **210** 377
35. A A Pasynskii, I L Eremenko, B Orazsakhatov, et al., *J. Organometal. Chem.*, 1981, **214** 351
36. A A Pasynskii, I L Eremenko, B Orazsakhatov, et al., *J. Organometal. Chem.*, 1981, **216** 211
37. A A Pasynskii, I L Eremenko, B Orazsakhatov, et al., *J. Organometal. Chem.*, 1981, **210** 385
38. A A Pasynskii, I L Eremenko, B Orazsakhatov, et al. *J. Organometal. Chem.*, 1984, **270** 53
39. I L Eremenko, Doctoral Thesis in Chemical Sciences, Institute of General and Inorganic Chemistry, USSR Academy of Sciences, Moscow, 1985
40. B A Bidinosti, N C McIntyre *J. Chem. Soc. Chem. Commun.*, 1967, 1
41. A A Pasynskii, I L Eremenko, O G Ellert, et al. *J. Organometal. Chem.*, 1982, **234** 315
42. A A Pasynskii, I L Eremenko, B Orazsakhatov, et al. *J. Organometal. Chem.*, 1981, **214** 367
43. I L Eremenko, A A Pasynskii, G Sh. Gasanov, et al. *J. Organometal. Chem.*, 1984, **275** 71
44. I L Eremenko, A A Pasynskii, B Orazsakhatov, et al. *Inorg. Chim. Acta*, 1983, **73** 225
45. A B Blake, A Yavari *J. Chem. Soc. Chem. Commun.*, 1982, 1247
46. A A Pasynskii, I L Eremenko, G Sh Gasanov, et al. *J. Organometal. Chem.*, 1984, **276** 349
47. I L Eremenko, A A Pasynskii, G Sh. Gasanov, et al. *J. Organometal. Chem.*, 1984, **275** 183
48. A A Pasynskii, I L Eremenko, B Orazsakhatov, et al. *J. Organometal. Chem.*, 1984, **269** 147
49. H Brunner, W Meier, J Wachter, et al. *Organometallics*, 1982, **1** 1107
50. O A Rajan, M McKenna, J Noordik, et al. *Organometallics*, 1984, **3** 831
51. M Rkowski DuBois, D L DuBois, M C VanDerveer, R Haltiwanger *Inorg. Chem.*, 1984, **20** 3064
52. H Vahrenkamp *Angew. Chem. Int. Ed. Engl.*, 1975, **14** 322
53. H Brunner, H Kauermann *Angew. Chem.*, 1983, **95** 567; *Angew. Chem. Int. Ed. Engl.*, 1983, **22** 549
54. H Brunner, N Janietz, J Wachter, et al. *Angew. Chem.*, 1985, **97** 122
55. M Rakowski DuBois, M C VanDerveer, D L DuBois, et al. *J. Amer. Chem. Soc.*, 1980, **102** 7456
56. B Cowens, J Noordik, M Rakowski DuBois *Organometallics*, 1983, **2** 931
57. M D Curtis, P D Williams *Inorg. Chem.*, 1983, **22** 2661
58. H Brunner, H Kauermann, U Klement, et al. *Angew. Chem.*, 1985, **97** 122
59. Th. R Halbert, S A Cohen, E I Stiefel *Organometallics*, 1985, **4** 1689
60. S Lu, N Okura, T Yoshida, et al. *J. Amer. Chem. Soc.*, 1983, **105** 7470
61. S Otsuka, M Kamata *Molybdenum Chemistry of Biological Significance* (Edited by W E Newton et al.), Plenum Press, New York–London, 1981, p. 229
62. M G Kanatzidis, D C Coucouvanis *Acta Crystallogr.*, 1983, **39C** 835
63. A Muller, E Diemann, R Jostas *Angew. Chem. Int. Ed. Engl.*, 1981, **20** 934
64. D C Coucouvanis *Accounts Chem. Res.*, 1981, **20** 2
65. R Coulton *Coord. Chem. Rev.*, 1985, **62** 145
66. S Sarkar, S B S Mishra *Coord. Chem. Rev.*, 1984, **59** 239
67. W P Binnic, M J Redman, W J Mallic *Inorg. Chem.*, 1970, **9** 1449
68. A Muller, R Menge *Z. Anorg. Chem.*, 1972, **393** 259
69. S R Acott, C D Garner, J R Nicholson, W Clegg *J. Chem. Soc., Dalton Trans.*, 1983, 713
70. E M Kinsch, D W Stephan *Inorg. Chim. Acta*, 1985, **96** L87
71. A Muller, H Bogge, U Schimanskii *Inorg. Chim. Acta*, 1983, **69** 5
72. W Clegg, C D Garner, J R Nicholson *Acta Crystallogr.*, 1983, **39C** 552
73. C Potwin, J M Manoli, M Salis, F Secheresse *Inorg. Chim. Acta*, 1984, **83** L19
74. J R Nicholson, A C Flood, C D Garner, W Clegg *J. Chem. Soc. Chem. Comm.*, 1983, 1179
75. A Muller, H Bogge, U Schimanski *Inorg. Chim. Acta*, 1980, **45** L249
76. A Muller, A M Dommrose, C Romer, et al. *Angew. Chem.*, 1981, **93** 1119
77. B Zhuang, J W McDonald, W E Newton *Inorg. Chim. Acta*, 1983, **77** L221
78. D Coucouvanis, P Stremple, E D Simhimon, et al. *Inorg. Chem.*, 1983, **22** 293
79. J G H DuPreez, T I A Gerber *Inorg. Chim. Acta*, 1985, **110** 59
80. A Muller, S Sarkar *Angew. Chem.*, 1977, **89** 748
81. D Coucouvanis, E D Simhon, N C Baenziger *J. Amer. Chem. Soc.*, 1980, **102** 6644
82. W-H Pan, D C Johnston, S McKenna, et al. *Inorg. Chim. Acta*, 1985, **97** L17
83. A Muller, N Mohan, H Bogge *Z. Naturforsch.*, 1978, **33B** 978
84. A Muller, W Hellman, H Bogge, et al. *Angew. Chem. Int. Ed. Engl.*, 1982, **21 860**
85. A Muller, E Dieman, R Jostas, H Bogge *Angew. Chem.*, 1981, **93** 957
86. R H Holm *Chem. Soc. Rev.*, 1981, **10** 455
87. B A Averill *Structure and Bonding*, Springer Verlag, Berlin, 1983, Vol. 53, p. 59
88. F A Schultz, S F Gheller, B K Burgess, et al. *J. Amer. Chem. Soc.*, 1985, **107** 5364

89. T E Wolff, J M Berg, C Warrick, et al. *J. Amer. Chem. Soc.*, 1978, **100**, 4630
90. T E Wolff, J M Berg, K O Hodgson, *J. Amer. Chem. Soc.*, 1979, **101** 4140
91. T E Wolff, J M Berg, P P Power, et al. *J. Amer. Chem. Soc.*, 1979, **101** 5454
92. T E Wolff, P P Power, R B Frankel, R H Holm *J. Amer. Chem. Soc.*, 1980, **102** 4694
93. G Christon, C D Garner, F E Mabbs, T J King *J. Chem. Soc. Chem. Commun.*, 1978, 740
94. S R Acott, G Christon, F E Mabbs, et al. *Inorg. Chim. Acta*, 1979, **35** L337
95. G Christon, C D Garner, F E Mabbs, M G B Drew *J. Chem. Soc. Chem. Commun.*, 1979, 91
96. T E Wolff, J M Berg, P P Power, et al. *Inorg. Chem.*, 1980, **19** 430
97. J A Kovacs, J K Bashkin, R H Holm *J. Amer. Chem. Soc.*, 1985, **107** 1784
98. A Winter, G Huttner, L Zsolnai, et al. *Angew. Chem.*, 1984, **96** 986
99. A Winter, L Zsolnai, G Huttner *J. Amer. Chem. Soc.*, 1984, **269** C29
100. H Vahrenkamp *Chem. Ber.*, 1970, **103** 3580
101. F J Vergmini, H Vahrenkamp, L F Dahl, *J. Amer. Chem. Soc.*, 1971, **93** 6326
102. A Muller, H Vahrenkamp *Chem. Ber.*, 1983, **116** 2322
103. R Kury, H Vahrenkamp *J. Chem. Res.*, 1982 **(S)31** M(0417)
104. R J Haines, R Mason, J A Zubieta, C R Nolte *J. Chem. Soc., Chem. Commun.*, 1972, 990
105. N C Schroeder, J W Richardson, S-L Wang, et al. *Organometallics*, 1985, **4** 1226
106. D Seyferth, R S Henderson *J. Organometal. Chem.*, 1981, **204** 333
107. E Keller, H Vahrenkamp *Chem. Ber.*, 1981, **114** 1111
108. M I Bruce *J. Organometal. Chem.*, 1983, **257** 417
109. W Hieber, J Gruber *Z. Anorg. Chem.*, 1958, **296** 91
110. C H Wei, L F Dahl *Inorg. Chem.*, 1965, **4** 1
111. B K Teo, M B Hall, R F Fenske, L F Dahl *Inorg. Chem.*, 1975, **14** 3103
112. R L Dekock, E F Baerends, R Hengelmolen *Organometallics*, 1984, **3** 288
113. P Braunstein, A Tiripicchio, M Tiripicchio-Camellini, E Sappa *Inorg. Chem.*, 1981, **20** 3586
114. P Braunstein, J M Jud, A Tiripicchio, et al. *Angew. Chem.*, 1982, **94** 318
115. P D Williams, M D Curtis, D N Duffy, W D Butler *Organometallics, 1982*, **2** 165
116. D Seyferth, R S Henderson, J P Fackler, A M Mazany *J. Organometal. Chem.*, 1981, **213** C21
117. H Vahrenkamp, E J Wuoherer *Angew. Chem. Int. Ed. Engl.*, 1981, **20** 373
118. D L Stevenson, C H Wei, L F Dahl *J. Amer. Chem. Soc.*, 1971, **93** 6027
119. P Braunstein, E Sappa, A Tiripicchio, M Tiripicchio-Camellini *Inorg. Chim. Acta*, 1980, **45** L191
120. L E Bogan, T B Rauchfuss, A L Rheingold *J. Amer. Chem. Soc.*, 1985, **107** 3843
121. D A Lesch, T B Rauchfuss *Inorg. Chem.*, 1983, **22** 1854
122. V W Day, D A Lesch, T B Rauchfuss *J. Amer. Chem. Soc.*, 1982, **104** 1290
123. I L Eremenko, B Orazsakhatov, A S Abdullaev, et al. *Zhur. Vses. Khim. Obshch. im. Mendeleeva*, 1987, **32** 109
124. E Richter, H Vahrenkamp *Angew. Chem. Int. Ed. Engl.*, 1978, **17** 444
125. A Winter, I Jibril, G Huttner *J. Organometal. Chem.*, 1983, **247** 259
126. J P Fackler, A M Mazany, D Seyferth, et al. *Inorg. Chim. Acta*, 1984, **82** 31
127. L Marko *J. Organometal. Chem.*, 1981, **213** 271
128. F Richter, H Vahrenkamp *Angew. Chem. Int. Ed. Engl.*, 1978, **17** 864
129. F Richter, H Vahrenkamp *Angew. Chem.*, 1980, **92** 66
130. F Richter, H Vahrenkamp *Organometallics*, 1982, **1** 756
131. F Richter, H Vahrenkamp *Angew. Chem.*, 1979, **91** 566; *Angew. Chem. Int. Ed. Engl.*, 1979, **18** 531
132. E Roland, H Vahrenkamp *Chem. Ber.*, 1984, **117** 1039
133. R D Adams, I T Horvath, S Wang, *Inorg. Chem.*, 1985, **24** 1728
134. R D Adams, T S A Hor *Inorg. Chem.*, 1984, **23** 4723
135. R D Adams, I T Horvath, P Mathur *J. Amer. Chem. Soc.*, 1984, **106** 6296
136. R D Adams, T S A Hor, I T Horvath *Inorg. Chem.*, 1984, **23** 4733
137. R D Adams, S Wang *Inorg. Chem.*, 1985, **24** 4449
138. R Ugo, G LaMonica, S Cenini, et al. *J. Chem. Soc. A.*, 1971, 522
139. C F Briant, T S A Hor, N D Nowells, D M P Mingos *J. Chem. Soc., Chem. Commun.*, 1983, 1118
140. C E Briant, T S A Hor, N D Nowells, et al. *J. Organometal. Chem.*, 1983, **256** C15

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Application of thermoscanning methods using gas detectors in the quantitative assessment of the results of separation in thin layer chromatography

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ABSTRACT. The review deals with the application of gas detectors in combination with the thermoscanning of adsorption layers in thin layer chromatography for the recording of the results of the separation. Attention is concentrated on a combined method, based on the use of cylindrical thin layer chromatography and a flame-ionisation detector; which fulfills two functions simultaneously: thermoscanning of the adsorption layer with separated organic compounds and detection of the thermoscanning products. The prospects for the development of the method are discussed. The biology includes 179 references.

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I. Introduction

Thin layer chromatography (TLC) is one of the most effective and economical methods in liquid chromatography. At the present time optical scanning methods are most widely used in TLC practice for the quantitative and qualitative assessment of the results of the separation.[1,2] However, the application of these methods is limited, firstly, by the possibility of analysing only the compounds which absorb radiation or fluoresce in parts of the spectrum which are not too inconvenient for measurement and, secondly, by the need for laborious calibration which is usually associated with the high individual selectivity of the method. Therefore, for a series of compounds (lipids, carbohydrates, many polymers of practical importance, etc.), it is necessary to employ in many instances detectors of other types.

Gas detectors, for example the flame-ionisation detector (FID), the katharometer, etc., are used widely and successfully in gas chromatography; they are universal and highly sensitive, especially the FID. Their use for the scanning of TLC plates is therefore undoubtedly a promising application in the development of quantitative TLC methods. However, for analysis with the aid of gas detectors, it is first necessary to achieve transfer of the organic substances in the chromatographic bands from the adsorbed state to the gas phase. This stage is usually based on evaporation, oxidation, or thermal degradation of the substances and can be combined with the detection proper. For example, if the FID is used, then the high temperature of the flame usually ensures the quantitative conversion of the compound analysed into volatile chemical forms.

The characteristic features (and certain fundamental limitations) of this method consist in the fact that the process described above must be performed within a very narrow range to increase the resolving power, especially in the assessment of high performance chromatograms. The evaporation (degradation) band width must apparently be not more than 0.1–0.3 of the width of the chromatographic band. However, firstly, the practical application of the TLC–gas detectors (TLC–GD) method has shown that there exist many problems of practical importance for which a high resolving capacity is not required and, secondly, the possibilities of modern experimental techniques as regards a significant improvement of sensitivity are far from being exhausted.

The problem of detection is one of the central problems in TLC on the successful solution of which many investigators are working. As mentioned in a review devoted to the prospects of TLC,[3] the development of effective and universal detection methods is very important.

II. General characteristics of the thermoscanning method

Fig. 1 presents two main schemes used at present for the quantitative assessment of thin layer chromatograms by the thermoscanning method with subsequent (*a*) and simultaneous (*b*) detection.

In scheme (*a*), a furnace heated to 600–700 °C is moved over the reaction *3* containing the absorption layer with the separated components. In order to increase the temperature gradient, a cooling unit is placed in front of the furnace. As the chromatographic band is heated, the volatile evaporation-degradation products are transferred continuously with the stream of carrier gas (inert or oxidising) to the detector *5* (FID, katharometer, or a detector of another type). According to some investigators, the quantitative characteristics of the detection can be improved if the volatile products are oxidised on copper oxides to CO_2 with subsequent hydrogenation on a nickel catalyst.

A version of the method in which the TLC plate is placed within a rectangular reactor *3* was first proposed by Cotgreave and Lynes,[4] while the method using an adsorption layer deposited on the

inner walls of the reactor tube was developed by a number of investigators.[5-7]

An FID, the size of the flame of which is significantly greater than that normally used in gas chromatography, is employed in scheme (*b*) for the scanning of a cylindrical adsorption layer deposited on the lateral surface of a rod. The FID then fulfills simultaneously the function of a furnace (thermodegrader) and a detector. The method involving the thermoscanning of a cylindrical adsorption layer using an FID was first proposed by Padley.[8,9] A version of this procedure is used most widely nowadays in chromatographic practice.[10]

We shall consider these two groups of methods in greater detail.

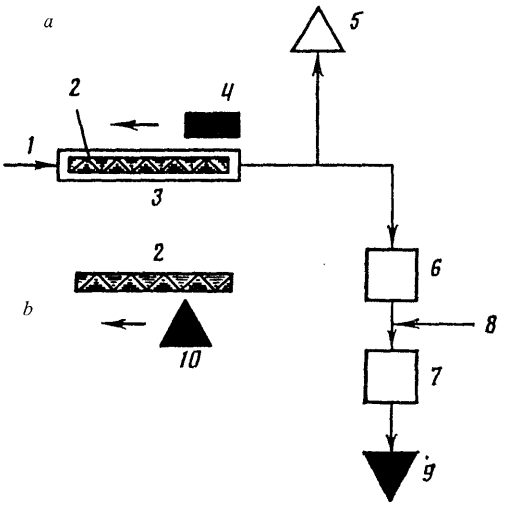


Figure 1. Generalised thermoscanning schemes in TLC: *a*, scheme with separated thermoscanning and detection devices; *b*, scheme for scanning with a thermodetector; *1*, stream of inert gas or oxidant (air); *2*, thin layer chromatogram; *3*, reactor; *4*, scanning furnace; *5*, universal detector (for example, a katharometer or an FID); *6*, reactor with oxidant; *7*, catalytic reactor; *8*, stream of hydrogen; *9*, highly sensitive universal detector; *10*, thermodetector (FID).

III. The thermoscanning method with subsequent detection of the thermoscanning products

The existing versions of this method (Fig. 1*a*) differ in a series of principal characteristics: (1) the position of the adsorption layer relative to the reactor walls; (2) the type of carrier gas used; (3) the function of the gas stream in the reactor; (4) the type of detector used (Table 1). It is noteworthy that Table 1 does not include TLC methods involving the thermoscanning and detection of radioactive compounds,[6,11] in particular, those containing isotopes with soft radiation whose detection in the gas phase is preferable.

The TLC-GD method was first described by Cotgreave and Lynes.[4] The TLC plate (150 × 12 mm, silica gel as the adsorbent on a quartz support) was placed in a heated tube with a rectangular cross-section. The authors[4] justifiably narrowed the limits of applicability of the method developed, indicating only the possibility of analysing compounds evaporated from the adsorption layer and disregarding the possibility of their thermal degradation. However, overall, this study demonstrated the possibility, in principal, of a new aspect of quantitative TLC—thermoscanning of the adsorption layer.

Table 1. Characteristics of the method for the thermoscanning of the adsorption layer with subsequent detection.

Characteristic of method	Characteristics of the application of method	
Form of adsorption component of thin layer	traditional (layer on a rectangular plate) (Ref.4)	tubular (Refs.5-7)
Linkage between adsorption layer and reactor	support not linked to the reactor; quartz support (plate) (Ref.4)	adsorption layer deposited on the inner walls of tubular reactor; reactor plays the role of support (Refs.5-7)
Function of gas stream through reactor	carrier gas transports volatile products to detector (Refs.4-7); the carrier gas is also a reactant, for example, an oxidant, which helps to convert the adsorbed compounds into volatile products	
Type of detector used	gas detector employed, for example, in gas chromatography (thermal conductivity detector, FID) (Refs.4-7)	

It is notable that the development of this method for liquid chromatography with a capillary column has been proposed.[12,13] The mobile phase was used in an amount sufficient for the separation of dyes without their elution from the sorbent (Al_2O_3) layer. The free part of the column, without the sorbent, was filled with an inert friable material and CuO to ensure the completion of the combustion of the dyes. The carrier gas (air) passed through the column to the katharometer. The electric furnace, heated to 650–700 °C at a rate of 1 cm min^{-1}, was moved onto the column in opposition to the stream of air; the CO_2 formed on combustion of the components was recorded by the detector (Fig. 2). This method can be used not only for liquid chromatography, but also, for example, for tubular TLC.

An interesting version of the TLC-GD procedure is the method of tubular TLC in which the inner walls of the tubes serve as the support for the fixed layer of the active sorbent.[5-7] After the separation (and the volatilisation of the mobile phase), the tube is thermoscanned and the products pass through the detector in the stream of carrier gas. Thus the tube fulfills the function of a solid carrier for the sorption layer and of a device for the formation of the gas stream.

In the apparatus for tubular TLC (Fig. 1*a*), one can use a katharometer. For this purpose, the substances separated are oxidised (by the oxygen present in the carrier gas and by the CuO in the adsorbent layer), the resulting water is collected in a trap, and CO_2 is detected.[7] The detector signal is proportional to the carbon content in the chromatographic band. When an FID is used in the TLC-GD method, the sensitivity of the detection of, for example, lipids, is close to the sensitivity of the analysis by column chromatography. It is notable that the separation of, in particular, shark liver oil is the same in both of the above versions, but polar lipids have been detected solely by the TLC-GD method.[7]

A detection system for the thermoscanning of the adsorption layer deposited on the inner walls of the tube has also been described by Mukherjee et al.[14] A quartz or Pyrex tube with a silica gel layer passes through three zones after the separation of, for example,

neutral lipids and bile acids and the removal of the organic eluent—a cooling unit, the pyrolytic furnace, and a thermostat, which prevents the condensation and adsorption of the pyrolysis products.

We may note that, in the method considered, the inner diameter of the reactor tube must be sufficiently large to ensure the rise of the mobile phase solely via the adsorption layer and not via the tube. This creates certain difficulties when an attempt is made to increase the temperature gradient and hence the resolving capacity of the method, which is nowadays used extremely rarely.

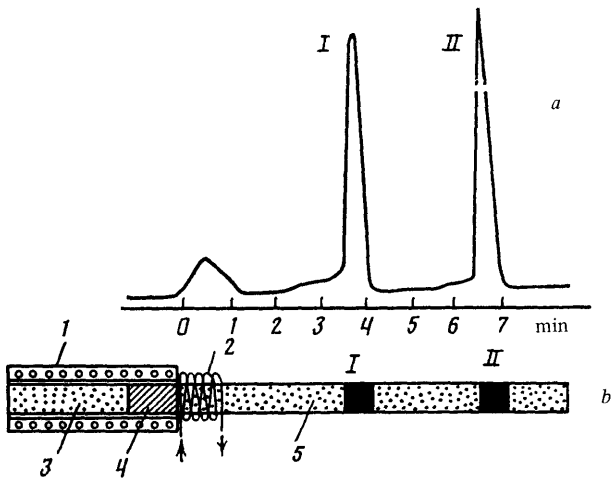


Figure 2. Schematic illustration of the thermoscanning of a capillary column for liquid chromatography (*b*) in the chromatogram (*a*) for azobenzene (I) and sudan red (II) separated on a column with Al_2O_3;[13] *1*, electric furnace; *2*, water-cooled quartz coil; *3*, part of the column filled with solid carrier (Spherochrom); *4*, part of the column filled with CuO; *5*, separating section of the column filled with Al_2O_3.

Fig. 3 illustrates schematically the scanning device of the "Iatroscan" apparatus.[18] The FID signal is known[19,20] to be directly proportional to the rate at which the organic substance enters the flame and, in the case under consideration (for a constant rate of movement of the rod), also to the concentration of the substance in the chromatographic band. In the "Iatroscan" apparatus, ten rods are fixed in a frame which moves in accordance with a definite programme, rod after rod being scanned automatically. The scanning time of a single rod is 30 s and the hydrogen flow rate is 160 ml min^{-1}. The results of the separation on a cylindrical thin layer are recorded by a pen recorder in the form of the usual chromatogram and in the integral form.

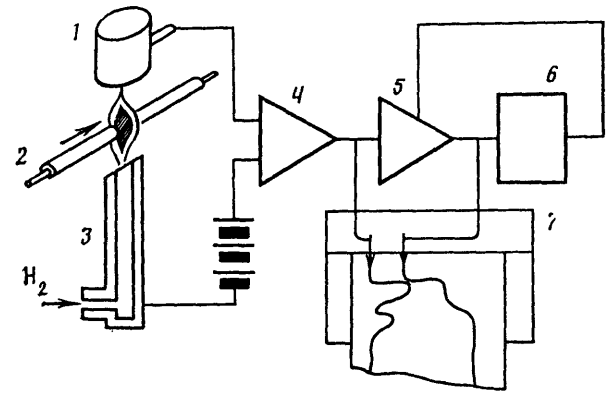


Figure 3. Schematic illustration of a device with an FID for the scanning of a rod with an adsorption layer containing the separated bands:[18] *1*, collector electrode; *2*, chromarod; *3*, burner; *4*, current amplifier; *5*, and *6*, signal integration units; *7*, two-channel pen recorder.

IV. A method for the thermoscanning of a cylindrical adsorption layer with simultaneous detection

The method for scanning a thin adsorption layer with the aid of an FID, described in 1967 [8] (Fig. 1*b*), is simpler than the methods described above in which the thermoscanning and detection stages are separated. An entirely satisfactory separation of glycerides has been achieved using a quartz rod 0.5 mm in diameter and 200 mm long with deposited silica gel. It was shown that the disposition of the rod in the flame and the rate of its movement relative to the flame influence the sensitivity of detection.

A scanning method using an FID was described in 1970.[15] The chromium–nickel alloy strip (215 mm long, 3 mm wide, and 0.1 mm thick) on which a silica gel layer 0.3–0.4 mm thick had been deposited, was used as the chromatographic system. Despite the entirely satisfactory analytical results, this system has not come to be widely used in chromatographic practice.

The development and investigation of repeatedly used rods with an adsorption layer, carried out by Okumura and Kadono[16,17] were very important for the application of Padley's method. This system, which was subsequently modified somewhat, is widely used in practice.

Since a cylindrical adsorption layer is used in this method as the chromatographic system, which is of fundamental importance for this variety of TLC, it is useful to call this version cylindrical TLC (CTLC) and to designate the above combined method as a whole by CTLC-FID.

The first three stages in this method are usual for transitional TLC: the deposition of the sample on the adsorption layer, its separation in a stream of an ascending mobile phase, and the removal of the mobile phase (at an elevated temperature). The preliminary rod activation stage with the aid of FID and the last stage involving the scanning of the rod with the separated bands by the same detector have no analogues in traditional TLC.

At the present time the CTLC-FID method has come to be most widely used in analytical practice compared with other thermoscanning methods. In our view, this can be explained by the following causes: (1) the scanning apparatus and the analytical method are distinguished by simplicity (the FID fulfills simultaneously the thermoscanning and detection functions); (2) the FID is characterised by a wide linear dynamic range, a high sensitivity, and universality also as regards organic compounds (hydrocarbons, lipids, etc.), to which the widely used optical detection methods are almost applicable; (3) the availability of commercial rods of the "Chromarod"

brand and equipment manufactured by the Japanese Company Iatron Laboratories;[18] (4) the high productivity of the method (about 10 analyses in 10 min) by virtue of the high scanning rate.

Since the CTLC-FID method differs from traditional TLC as regards the form of the adsorption layer and the type of scanning and detection, it is necessary to examine the features of this method both in chromatographic separation and in quantitative analysis.

1. Characteristic features of the chromatographic separation by the CTLC method

The widely used cylindrical open chromatographic system (chromarod) consists of a quartz rod on the surface of which a porous layer of silica gel or Al_2O_3 is deposited (Fig. 4). The geometrical parameters of the chromarod are as follows: length 152 mm, diameter 0.9 mm, length of an adsorption layer 120 mm, thickness of adsorption layer 75 μm. After thermoscanning, the rod is automatically activated by the FID, is cleaned, and becomes suitable for re-use. One rod can be used for 100 analyses.

Three types of rods are being manufactured at the present time: chromarod SI, chromarod SII, and chromarod A (since 1987 also chromarod SIII). The first two types of rods are based on silica gel, the particle diameters of which are 10 and 5 μm respectively, chromarod SII being characterised by a higher resolving power. The adsorption layer on chromarod A is obtained from Al_2O_3 particles 10 μm in diameter and is normally employed for the separation of compounds which are unstable on silica gel and also of certain stereoisomers. The adsorption layers on the rods are obtained by sintering the adsorbent particles in the presence of a small amount of readily fusible glass particles added as a binder. The cylindrical shape of the adsorption layer has definite advantages. In this system there are no edge effects disturbing the movement of the eluent front and observed in many cases on the usual rectangular TLC plates. The width of the adsorption layer is small amounting to πd = 2.8 mm (d = 0.9 mm is the diameter of the adsorption layer) and the possible disturbances of the eluent front show a tendency towards "self-healing". For separation the small size of the adsorption system needs only small amounts of the mobile phase, which is frequently extremely expensive.

Further reduction of the rod diameter is justified, which would apparently make it possible (1) to increase the resolving power in the detection of the separated bands by virtue of the increase in the temperature gradient on the rod during scanning, (2) to reduce the uncontrollable losses of the substances analysed during detection, (3) to increase the rate of detection, and (4) to reduce the amount of eluent consumed.

The sample is deposited and separated by the procedure of traditional TLC,[21,22] although, in our view, it would be more justifiable to use special apparatus taking into account the geometry of the rods. The samples (with a volume not exceeding 1 μl) are deposited on the adsorption layer of the rod at a distance of 1–2 cm from its end and the syringe or an applicator of another type must not touch the adsorption layer. The deposited samples on rods fixed in cassettes, which can contain up to 10 rods, are separated in small rectangular chambers for 15–40 min. After the separation, the rods are dried to remove the mobile phase: at a temperature above 100 °C, this takes several minutes. For example, 3 min is sufficient to evaporate a mixture of chloroform, benzene, and formic acid at 130 °C.[23] For labile compounds, the drying can be carried out at low temperatures in a stream of an inert gas or *in vacuo*.

The removal of the mobile phase before scanning is an important stage, since even its traces create an appreciable background and reduce the sensitivity of the detection. Therefore, in our view, it is useful to use as mobile phases substances to which the FID is almost insensitive: water,[19,24] carbon disulphide,[25] ammonia,[26,27] formamide,[25] formic acid,[24] and certain other substances. It is possible and desirable to employ also combinations of these compounds.

It is likewise useful to point out the possibilities of the use of chemically selective inorganic phases in CTLC. Thus organic acids and their methyl esters or triglycerides have been separated on chromarods impregnated with a silver nitrate solution as a function of the degree of unsaturation and isomerisation of the molecules.[28–30] It has been noted[30] that the rods employed are not washed entirely free of silver nitrate even after they have been kept for a long time in aqua regia. The possibility of reusing the rods with silver nitrate has been investigated also in another study.[31]

Another example of the employment of a chemically selective phase is provided by the separation of the glycerides on rods impregnated with a 3% solution of boric acid.[32]

Single separation in CTLC is the simplest but not the only method of chromatographic analysis. The application of repeated elution using several mobile phase systems to improve the separation of samples with a complex composition has been described. For example, a clear separation of the main groups of hydrocarbons present in the residue from the vacuum distillation of petroleum using three consecutive elutions over definite distances has been achieved on a chromarod.[33]

The repeated elution procedure with intermediate scanning of part of the rod is important and methodologically elegant. Thus, in the analysis of blood serum lipids,[34,35] neutral lipids were initially

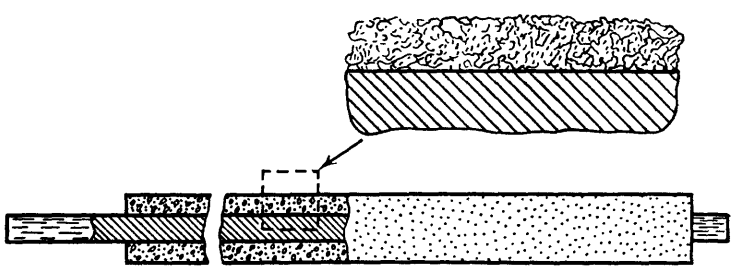


Figure 4. Schematic illustration of the chromarod.[18]

separated and scanned with the aid of an FID and the phospholipids remaining at the start were then separated using a more polar eluent and were also thermoscanned. This version has no direct analogue in traditional TLC and can apparently be regarded as a version of the two-dimensional separation.

It is necessary to differentiate an important application of the CTLC-FID method for the quantitative analysis of components, including impurity components, which cannot be determined by the traditional TLC. The lipid components of the crab have been determined[36] using for the analysis the extract from the part of the TLC plate, which, according to optical scanning data (after the corresponding derivatives have been obtained), did not contain even traces of any compounds. The CTLC-FID method can be used successfully for the analysis of fractions separated by column chromatography and of extracts obtained from sorbent specimens from definite sections of the TLC plate.[10,37]

The combination of the separation on a traditional TLC plate with subsequent separation of individual bands by the CTLC-FID method can also be regarded as one version of the two-dimensional separation.

The moving transporter system proposed earlier[38] is of interest for the analysis of components which cannot be determined by an optical detector especially when packed capillary columns are used in liquid chromatography. A chromarod can apparently be used as such a transporter.

In our view, the CTLC-FID method is promising, since it makes it possible to analyse complex objects rapidly and with a resolving capacity which is sufficient for many practical purposes. It is therefore useful to compare both the versions of chromatography realised in this method as well as those which have not yet been used.

Table 2. Classification of the chromatographic systems used in TLC on the basis of the state of aggregation of the mobile and stationary phases.

Chromatographic system	TLC	
(Mobile phase) [stationary phase]	traditional, on plates	cylindrical, on rods
(Liquid) [solid]		
Traditional, direct phase (non-polar or polar liquid) [polar solid]	is used	is used
Reversed phase (polar liquid) [non-polar solid]	is used	is possible
(Liquid) [liquid–solid]		
Traditional, direct phase (non-polar liquid) [polar liquid–solid]	is used	is possible and desirable
Reversed phase (polar liquid) [non-polar liquid–solid]	is used	is possible

Table 2 presents a classification of various chromatographic systems in traditional and cylindrical TLC. In fact, only one chromatographic system is used in CTLC: (liquid) [polar solid]. The application of other types of chromatography, especially the reversed phase chromatography, is likely to be extremely promising in the future. Here there is apparently a possibility of two approaches: firstly, to obtain the grafted phase each time on the adsorption layer (by standard grafting methods in the gas or liquid phases) and, secondly, to obtain rods with a coating of a carbon adsorbent which will probably also have to be renewed after each use of the rod.

Comparison of the traditional TLC and CTLC in terms of the types of chromatographic processes suggests that at the present time only adsorption is used in CTLC. The employment of partition chromatography will permit, in our view, a significant expansion of the number of parameters for the selection of the optimum solution. The only additional requirement is the use of a volatile compound or substance to which the FID is almost insensitive to the stationary phase.

By using an adsorbent with a known and controllable porosity, it is undoubtedly possible to achieve exclusion CTLC.

Fundamentally new possibilities arise when electromigration methods on cylindrical rods are resorted to. The application of ion exchange to the separation of inorganic and organic ions is also extremely promising. In this version of CTLC, it is desirable to employ optical detectors, for example, the flame-photometric detector, together with the FID.

Table 3 compares the known and possible methods of elution in traditional and cylindrical TLC. In our view, among the elution methods which have not been used in CTLC hitherto, descending and centrifugal elution, whose application would permit an acceleration of the separation process, is of interest.

Table 3. Elution methods in traditional and cylindrical TLC.

Elution method	TLC	
	traditional, on a plate	cylindrical, on a rod
Ascending	is used	is used
Descending	is used	is desirable
Horizontal	is used	is possible
Continuous	is used	is possible
Radial and circular	is used	–
Repeated	is used	is used
Stepwise	is used	is used
Stepwise with intermediate detection of some of the separated compounds and their removal from adsorption layer	is desirable	is used
Two-dimensional	is used	–
Centrifugal	is used	is desirable
Gradient	is used	is desirable

Table 4. Combination of CTLC with other analytical physicochemical methods.

Analytical method	Combination with CTLC
Thin layer chromatography	is used (Refs.10, 36)
Column liquid chromatography	has been proposed (Ref.10)
Gas chromatography	is possible
Mass spectrometry	is used (Ref.10)
Spectroscopic methods	is desirable
Electrochemical methods	is possible

Hybrid methods (see, for example, Zolotov[39]) based on the joint employment of two and more methods, have been increasingly introduced into analytical chemistry and chromatography in recent years. It is therefore of interest to analyse the possibility of combining different methods with CTLC (Table 4).

Thus, it follows from the analysis of Tables 2–4, that the CTLC method has wide prospects for development and the majority of the known separation principles in liquid chromatography can apparently be used successfully in this procedure also.

An important aspect of any analytical method is the estimation of the reliability and reproducibility of the results obtained. We shall now consider the quantitative aspects of the CTLC-FID method.

2. Quantitative aspects of the CTLC-FID method

In the FID method considered, the FID is not used under the normal conditions for which it has been designed.[40,41] Thus the coefficients of sensitivity of this type of detector with respect to lipids differ for the CTLC-FID method from the coefficients for gas chromatography.[42] The main characteristics of the quantitative analysis by the CTLC-FID method are influenced not only by the FID operating conditions (the rod passes through the flame whose dimensions are comparable to those of the rod), but also by the unusual conditions in the detection of organic compounds adsorbed on the porous layer of the rod. The transport of these compounds (or their degradation products) to the hydrogen flame is hindered by the limited mass exchange and also by the high scanning rate (about 4 mm s^{-1}). The adsorbed involatile compounds must be initially subjected to thermal degradation which complicates detection and undoubtedly influences the accuracy of the quantitative determination. It has been noted[43] that, in order to obtain the full signal due to the chromatographic bands of certain substances, repeated scanning of the rod with the summation of the results of all the scans is essential. With increase in the size of the molecule of the substance analysed, the number of scans increases.

In order to avoid repeated scanning, it has been suggested[44] that the rod be rotated through 180°, which improves the contact between the flame and the adsorbed substance.

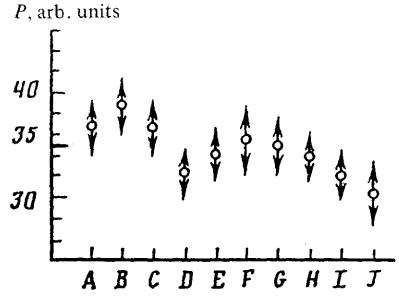


Figure 5. The areas of the peak (P, arbitrary units) of octadecanoic acid for 10 chromarods S (from A to J);[45] sample size 10 μg; the sample deposited on the rod was not eluted and the measurements on each rod were performed ten times.

The reproducibility of the analytical properties of the adsorbent and hence of the results of the quantitative analysis constitutes an extremely important problem in the adsorption chromatogaphy in general and in CTLC in particular. It has been shown[45] that the quantitative results of repeated analysis for chromarods S are different and that this applies both to the average peak area (the points on Fig. 5) and to its standard deviation (arrows). Mares et al.[46] suggest that the reproducibility of the method can be increased in the future by a preliminary selection of the rods (see, for example, Hirayama and Morita[47]).

The large standard deviation is explained by some investigators in terms of the differences in the properties of the rods,[48] while according to others it is due to the inadequate reproducibility of the detection process.[49] Some workers[48,50–53] have concluded that the results of the quantitative determinations by the CTLC-FID method are unfortunately characterised by a low accuracy, although it is sufficient for the solution of many practical problems.

The study[54] in which it has been suggested that the rods with a silica gel layer be impregnated beforehand with a 5% $CuSO_4$ solution appears important in connection with the foregoing. It has been shown that, in the determination of lipids, the base line of the detector is improved and the scatter of the results from rod to rod is diminished. However, it has to be said that the impregnation with copper sulphate shortens the useful life of the rods.[55]

The reproducibility of the results improves with increase in the scanning rates from 3.2 to 4.2 mm s^{-1}.[56] It is of interest that impregnation with copper sulphate alters the relative sensitivities for different substances. For example, the sensitivity with respect to methyl haptanoate increases relative to triglycerides.

The choice of the quantitative determination method is important. Many investigations have been devoted to the analysis of lipids—one of the most important practical applications of the CTLC-FID method.[10,57–61]

It has been shown,[18] in relation to the analysis of glycerides and free acids, that, when the relative and not the absolute peak area is used for the calculations, the "individuality" of the rod is not manifested quite so sharply.

It has been confirmed experimentally that the application of the internal standard method permits, in contrast to the absolute calibration, a significant improvement of the reproducibility of the results of the method. Despite the fact that the use of an internal standard reduces the scatter of the results when one rod is replaced by another,[51,52,62] it is difficult to obtain accurate quantitative analytical results because the relative sensitivity depends on the sample size,[62–64] the ratio of the concentrations of the substance analysed and the internal standard,[65] the scanning rate,[61,66] and whether a biological object or an artificial mixture is analysed.[46]

It has been stated[63] that the CTLC-FID method using an internal standard can yield an approximate result in the study of the lipid composition of marine organisms and deposits as well as sea water, whose determination had been attempted earlier:[67,68] for a <2–3 μg sample, the relative sensitivity coefficients change appreciably and to different extents for lipids of different classes.

The calibration plots for lipids are not linear and cannot always be extrapolated to the zero point.[62,64,69–72] For lipids, aliphatic hydrocarbons, esters, ketones, free aliphatic acids, triglycerides, free alcohols, and free sterols, present in sea water, the calibration plots are described by different equations:[73] for example, $y = 0.07 + 4.19x$ for polar lipids, while $y = -0.72 + 1.39x + 0.09x^2$ for free sterols and, in order to attain an accuracy of the quantitative analysis better than to within 10 rel.%, it is essential to carry out many measurements (see also Tanaka et al.[74]).

The multifactorial experiment on the analysis of triglyceride mixtures of different composition, differing in the acidities of the components, on 10 chromarods S showed[56] that the previous history of the rod, the mixture composition, and the acid composition of the triglyceride are very important for quantitative analysis, the relative sensitivity (with an ester as the standard) gradually diminishing as a function of time. It has also been established that the sensitivity

coefficients for single and mixed triglyceride specimens are not the same[56] and yet the majority of investigators use coefficients obtained by calibration with respect to individual compounds for the analysis of biological objects.[46,52,61,72,74-76]

It is noteworthy that, in the analysis of hydrocarbons, the results obtained by the CTLC-FID method are stable as a function of time. Thus, in the determination of the composition of petroleum on chromarod SII, random oscillations in the absolute values of the signal were observed in the course of 5 days, although they were different for different groups of hydrocarbons.[77]

Thus the nature of the substance influences the error of the measurement. It may be that the scanning of each band or separate groups of bands can be usefully carried out separately under optimum conditions for each band.

Studies designed to improve not only the accuracy of the quantitative analysis but also the sensitivity of the method are of great interest. The size of the sample analysed influences significantly the standard deviation of the signal and it must be greater than 1 μg in order to obtain reproducible results.[46]

It has been shown that the sensitivity of the Iatroscan apparatus in the determination of lipids (combined with a satisfactory accuracy and reproducibility) is a maximum for a hydrogen flow rate >200 ml min^{-1}, a distance between the rod and the detector burner nozzle not greater than 0.8 mm, when the vibration air pump is replaced by a compressor, and when new rods are washed with concentrated nitric acid.[78] The above measures led to an increase in sensitivity by a factor of ~ 2 and to a decrease in background by a factor of ~ 5; the standard deviations of the signal were then 5–15 rel.%. It was possible to determine 0.05 μg of each lipid in a small sample volume (0.2 μl). According to the data in Ref. 18, the sensitivity of the CTLC-FID method is fairly high: the detection limit is about 0.07 μg m^{-1}. Different procedures are used to increase the sensitivity: mounting of the ion collector at a distance of ~ 1.7 mm about the rod,[79] the focussing of the band of the test substance on the rod,[69] and chemical treatment of the rods, for example with iodine vapour, to intensity the FID signal in the analysis of unsaturated lipids.[80]

Comparison with the traditional methods for the solution of the same problem is important for the estimation of the quantitative aspect of the new method. Mares et al.[46] compared the accuracies of the analysis of human blood plasma lipids by the CTLC-FID and gas chromatographic methods. The reproducibility of the former method proved significantly lower, but one must agree with the above authors,[46] who assume that further development of the CTLC-FID method will permit an improvement in this important parameter.

We may note the following important advantages of the CTLC method compared with gas chromatography: (1) the possibility of using involatile and thermally labile compounds for analysis; (2) an unusual selectivity which is frequently difficult to achieve in gas chromatography—for example, group separation of hydrocarbons, phospholipids, etc. is possible; (3) high rate of detection (1 scan in ~ 30 s).

The results of the determination of malthenes and asphaltenes in heavy petroleums by the CTLC-FID method agree well with data obtained by the traditional IP 143 method of the Institute of Petroleum (London).[81] Both methods are characterised by virtually the same reproducibility, but the CTLC-FID method is less laborious: the time required for the analysis of 9 specimens is about 30 min (excluding the time consumed in the weighing and dissolution of the specimens).

In the determination of the group compositions of heavy hydrocarbons, the data obtained by the CTLC-FID method and the standard ASTM D2007 method differ significantly, which is associated with the sharp difference between the fractions actually isolated by the ASTM method and the declared fractions.[33]

When the CTLC-FID method is used to analyse heavy petroleum and coal processing products, a disadvantage of high performance column chromatography, namely the loss of appreciable proportions (from 5 to 15%) of the specimen analysed, is eliminated.[44]

It has been shown[82] that the CTLC-FID method yields reliable quantitative results in the determination of polycyclic aromatic hydrocarbons, in contrast to methods such as liquid–liquid extraction, liquid column chromatography, and gas chromatography.

In conclusion, it must be emphasised that, despite many critical comments concerning the quantitative characteristics of the CTLC-FID method, numerous studies indicate a positive aspect of its practical application for the quantitative analysis of a wide variety of objects—ranging from petroleum to biologically active compounds.

There is no doubt that the further perfection of the apparatus will permit a significant improvement in the quantitative characteristics of this promising method.

3. Practical applications of the CTLC-FID method

The CTLC-FID method is widely used in various branches of science, industry, medicine, protection of the environment, etc. It is of special interest for the study of objects in which the optical detection methods, widely used in liquid chromatography (column chromatography and TLC), are almost inapplicable and the preparation of the corresponding derivatives is complicated or undesirable. We shall quote certain examples of the practical employment of the CTLC-FID method.

(a) Lipids. Tanaka et al.[74] investigated the separation of complex lipid mixtures. The products of the methanolysis of sphingoglycolipid were fully separated on chromarod SII using two consecutive elutions.

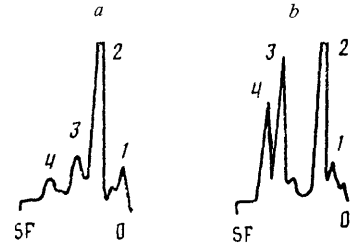


Figure 6. Chromatography of rat brain phospholipids;[83] chromarod S with copper sulphate; eluent: chloroform–methanol–water (68.5:29:2.5) without (*a*) and with (*b*) addition of 0.5% of formic acid; *1*, sphingomyelin; *2*, phosphatidylcholine; *3*, phosphatidylethanolamine; *4*, diphosphatidylglycerol; 0, start; SF, solvent front.

The separation of rat brain phospholipids has been demonstrated[83] on rods impregnated with copper sulphate (Fig. 6*a*). As in the author's previous studies using non-impregnated rods,[75,84] the eluent was a mixture of chloroform with methanol and water. The addition

of formic acid decreased the spreading of the bands of certain compounds (peaks *3* and *4* on Fig.6 *b*) and reduced the peak at the start.

Analysis of lipids is of definite interest also in connection with the diagnosis of certain diseases. For example, a sharp qualitative change in the lipid content of the amniotic fluid of pregnant women occurs in the case of illness.[51,85,86] The determination of lipids by the CTLC-FID method is used in pharamaceutical and clinical studies, in toxicological analysis, and in the analysis of food.[87-89] Data on the quantitative determination of lipids and their derivatives by the CTLC-FID method have been surveyed.[90] Apart from the investigations mentioned here and in the preceding Sections, other studies of lipid objects must be indicated: blood plasma,[91-94] blood serum,[91,92,95] human gums,[96] yeast,[97] micro-organisms,[98] vegetable oils,[99,100,133] as well as glycerides and fatty acids,[95,99,101-117] phospholipids,[118-120] and lipids of other classes.[121-129]

It is notable that the use of computers has expanded in chromatographic practice. Thus the application of computers in the Iatroscan apparatus for the analysis of lipids of biological origin has been described.[130]

In conclusion we may mention that the determination of lipids in various specimens is at present the most thoroughly developed field of the practical application of the CTLC-FID method and its use in this field alone undoubtedly justifies the development of this method.

(b) Petroleum and hydrocarbon fuel. The application of the CTLC-FID method in the determination of the group composition of heavy fuel was first described by Suzuki and Takeuchi.[131,132] The study of Yamamoto and Kawanobe[134] was devoted to a method for the rapid determination of asphaltenes in heavy oils and of the composition of these oils. The method for the determination of malthenes and asphaltenes on rods with a silica gel layer has been successfully tested on 16 specimens of bitumen, heavy petroleums, and synthetic fuels.[81] Components insoluble in benzene were removed before the analysis.

The liquid products of the hydrogenation of coal from Japanese deposits were resolved into the following fractions: saturated, polycyclic aromatic, and heteroaromatic compounds, tars, and asphaltenes.[135]

Other examples of the use of the CTLC-FID method in the analysis of hydrocarbon raw materials and products should also be mentioned.[136-143] It has been concluded[33] that the CTLC-FID method ensures the rapid determination of the group composition of high-boiling fractions of petroleum, heavy oils, and liquid coal processing products and preliminary deasphaltisation is not required.

Thus the determination of hydrocarbons of different classes is an important practical application of the method considered.

(c) The monitoring of the environment and analysis of physicologically active objects. The possibilities and advantages of the CTLC-FID method in the determination of polycyclic aromatic hydrocarbons extracted from filters for the selection of contaminated air samples have been demonstrated.[82] The determination of the composition of the particles present in the exhaust from diesel engines has been described.[144] The method made it possible to analyse involatile organic compounds with $T_b \geqslant 300$ °C (the limit of the determination is ~ 0.03 μg).

Numerous studies have been devoted to the analysis of biological objects and medicinal drugs: psychotropic preparations,[145,146] alkaloids,[17,124] aminoacids, vitamins, pesticides, corticosteroids, cardiac glucosides and genins,[17] oestrogens, progestins and androgens,[17,124] saccharides,[147] antibiotics,[148] bile acids,[149-151] aglucones,[152] and glycyrrhizin.[153]

Here one may also indicate the following objects analysed: surfactants (quaternary ammonium chlorides, oleates, and sulphonates,[45] olefin sulphates,[149] and other surfactants[154-156]), sulphanilic acid and sulphonamides,[17] phthalates,[157] ginseng saponins,[158] perfumes,[159] peony extracts,[160] food products,[161-163] leather articles,[164] and cosmetics.[165]

The examples quoted in this section indicate the possibility of the effective application of the CTLC-FID method also in those fields which are important for human health.

(d) Applications in other fields. The distribution of liquid rubbers in terms of "functionality" has been investigated.[166] αω-Polybutadienols have been separated by the CTLC method into three fractions: a fraction without functional groups and fractions with one and two functional groups. Comparison of two scanning methods—the optical and FID methods—showed that the results of the optical method are too high by 30–50%.

The CTLC-FID method has been used successfully to investigate the radiation-induced graft copolymerisation of styrene on cellulose.[167] Homopolystyrene and homopolyacrylonitrile have been determined.[168] The analysis of polymers has also been described in another communication.[169] The composition of industrial emulsions and its variation during use have been studied.[170]

One of the examples of the employment of the CTLC-FID method in the study of the kinetics of the formation of an ester has been described.[171] Ethyl benzoate and benzoic acid have been determined on chromarod SII. Chemical reactions have also been investigated in other studies.[70,172-174]

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Analysis of the data described in this review permits the conclusion that a new promising aspect of TLC and of the scanning field has been established, namely CTLC-FID. The practical application of this combined method is particularly useful primarily for compounds whose detection by optical methods is unsatisfactory. Numerous communications, and reviews published in recent years[175-178] as well as the monograph by the Czechoslovak scientist Ranny[179] are an indication of the great and continuing interest in the CTLC-FID method.

The method has good prospects, some of which have been noted in the present review. In the course of the further development of the method, it will be desirable to concentrate attention to the following promising aspects: (1) the development of new methods of improving the resolving power of thermoscanning detection; (2) the application of new detection methods, for example flame-photometric methods; (3) use of other versions of chromatography apart from the familiar liquid–solid version.

References

1. J Touchstone et al. (Editors) *Densitometry in Thin Layer Chromatography*, Wiley Intersci., New York, 1979
2. A Zlatkis et al. (Editors) *High Performance Thin Layer Chromatography*, Elsevier, Amsterdam; Bad Durkeim, Institute of Chromatography, 1977
3. E Stahl *J. Chromatogr.*, 1979, **165** 59
4. T Cotgreave, A J Lynes *J. Chromatogr.*, 1967, **30** 117

5. H P Kaufman, K D Mukherjee *Fette, Seifen, Anstrichmittel.*, 1969, **71** 11
6. E Haahti, R Vihko, I Jaakonmaki, R S Evans *J. Chromatogr. Sci.*, 1970, **8** 370
7. H K Mangold, K D Mukherjee *J. Chromatogr. Sci.*, 1975, **13** 393
8. F B Padley *Chem. Ind. (London)*, 1967, 592
9. F B Padley *J. Chromatogr.*, 1969, **39** 37
10. R G Ackman *Methods in Enzymology. Flame Ionization Detection Applied to Thin Layer Chromatography on Coated Quartz Rods* (Edited by J M Lowenstein), Vol. 72, *Lipids*, Part D, Acad. Press, New York, 1981, p. 205
11. K D Mukherjee, H K Mangold *J. Chromatogr.*, 1973, **82** 121
12. V G Berezkin, V S Kruglikova, USSR P. 342 128; *Byul. Izobret*, 1972, (19)
13. V G Berezkin, V S Kruglikova, L N Kolomiets *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 1396
14. K D Mukherjee, H Spaans, E Haahti *J. Chromatogr.*, 1971, **61** 317
15. J J Szakasits, P V Peurifoy, L A Woods *Anal. Chem.*, 1970, **42** 351
16. T Okumura *J. Chromatogr.*, 1980, **184** 37
17. T Okumura, T Kadono, A Iso'o *J. Chromatogr.*, 1975, **108** 329
18. Iatroscan TH-10. TLC/FID Analyzer, Iatron Laboratories, Tokyo, 1981
19. R Komers, M Krejci *Laboratory Handbook of Chromatographic and Applied Methods* (Edited by O Mikes), Ellis Horwood, Chichester, 1979
20. S Dal Nogare, R S Juvet, Jr. *Gas–Liquid Chromatography. Theory and Practice* (Translated into Russian), Izd. Nedra, Leningrad, 1966, p. 242
21. J G Kirchner *Thin Layer Chromatography*, Wiley Intersci., New York, 1978
22. M Sarsunova et al. (Editors) *Chromatographia na Tenkych Vrstvach vo Farmacii a v Klinickej Biochemii, Vydatelstve 'Osveta'*, Bratislava, 1977.
23. E Gantois, F Mordret, N Le Barbanchon *Rev. Fr. Corps Gras.*, 1977, **24** 167
24. A Nonaka *Anal. Chem.*, 1973, **45** 483
25. V G Berezkin, B A Rudenko, T P Popova, et al. *J Chromatogr.*, 1977, **130** 318
26. H A Saroff, A Karmen, J W Healy *J. Chromatogr.*, 1962, **9** 122
27. V G Berezkin, L A Shkolina *J. Chromatogr.*, 1976, **119** 33
28. T Itoh, H Waki, H Kaneko *Agric. Biol. Chem.*, 1975, **39** 2365
29. M Tanaka, T Itoh, H Kaneko *Yukagaku*, 1976, **25** 263
30. M H Jee, A S Ritchie *J. Chromatogr.* 1986, **370** 214
31. J-L Sebedio, R E Farquarson, R G Ackman *Lipids*, 1985, **20** 555
32. M Tanaka, T Itoh, H Kaneko *Lipids*, 1980, **15** 872
33. J E Ray, K M Oliver, J C Wainwright *The Application of the Iatroscan TLC Technique to the Analysis of Fossil Fuels. Petroanalysis-81, IP Symp., London, 1981*, Heyden and Son, London, 1981
34. *Iatroscan TH-10 Analyser. Instruction Manual*, Newman-Howells Associates Limited, Winchester
35. R G Ackman *Chem. Ind. (London)*, 1981, 715
36. R G Ackman, D Nash, J McLachlan, *Proc. N. S. Inst. Sci.*, 1979, Vol. 29, p. 501
37. M Ranny *Chem. Listy*, 1982, **76** 1121
38. E Haahti *Acta Chem. Scand.*, 1963, **17** 2565
39. Yu A Zolotov *Ocherki Analiticheskoi Khimii* (An Outline of Analytical Chemistry), Izd. Khimiya, Moscow, 1977
40. I G McWilliam, Australian P. 224 504, 1957
41. J Harley, W Nel, V Pretorius *Nature*, 1985, **181** 177
42. J-L Sebedio, R G Ackman *J. Chromatogr. Sci.*, 1981, **19** 552
43. M W Rigler, R L Leffert, J S Patton *J. Chromatogr.*, 1983, **277** 321
44. M L Selucky *Anal. Chem.*, 1983, **55** 141
45. T Fujii, R Tanaka, K Sasai, T Tanaka *Microquantitative Analysis of Surface Agents Using Iatroscan TH-10*, Paper presented at the XIV Annual Meeting of the Japan Oil Chemists' Society, Tokyo, 1975
46. P Mares, M Ranny, J Sedlacek, J Skorepa *J. Chromatogr.*, 1983, **275** 285
47. P Hirayama, K Morita *Agric. Biol. Chem.*, 1980, **44** 2217
48. G L Mills, C E Taylaur, A L Miller *Clin. Chim. Acta, 1979*, **93** 173
49. E W Hammond *J. Chromatogr.*, 1981, **203** 397
50. D Vandamme, V Blaton, H Peeters *J. Chromatogr.*, 1978, **145** 151
51. A M Ponthieu, N Porchet, J C Fruchart, et al. *Clin. Chem.*, 1979, **25** 31
52. P Van Tornout, R Vercaemst, H Caster, et al. *J. Chromatogr.*, 1979, **164** 222
53. W W Christie, M L Hunter *J Chromatogr.*, 1979, **171** 517
54. T N B Kaimal, N C Shantha *J. Chromatogr.*, 1984, **288** 177
55. T Itoh, M Tanaka, H Kaneko *J. Am. Oil Chem. Soc.*, 1979, **56** 191A
56. J K G Kramer, B K Thompson, E R Farnworth *J. Chromatogr.*, 1986, **355** 221
57. S Ishii *Med. Technol. (Tokyo)*, 1980, **8** 1196
58. M Tanaka, T Itoh, H Kaneko *Yukagaku*, 1976, **25** 263
59. J K G Kramer, R C Fouchard, E R Farnworth *J. Chromatogr.*, 1980, **198** 279
60. D Vandamme, G Vankerckhoven, R Vercaemst, et al. *Clin. Chim. Acta*, 1978, **89** 231
61. D M Bradley, C R Richards, N S T Thomas *Clin. Chim. Acta*, 1979, **92** 293
62. E R Farnworth, B K Thompson, J K G Kramer *J. Chromatogr.*, 1982, **240** 463
63. J K Volkman, D A Everitt, D I Allen *J. Chromatogr.*, 1986, **356** 147
64. J K Kaitaranta, N Nicolaides *J. Chromatogr.*, 1981, **205** 339
65. T Tatara, I Fujii, T Kawase, M Minagawa *Lipids*, 1983, **18** 732
66. M Ranny, J Sedlacek, E Mares, et al. *Seifen Oele Fette Wachse*, 1983, **109** 219
67. R B Kellogg, J S Patton *Mar. Biol.*, 1983, **75** 137
68. H R Harvey, M D Richardson, J S Patton *Deep-Sea Res.*, 1984, **31** 403
69. H R Harvey, J S Patton *Anal. Biochem.*, 1981, **116** 312
70. M Ranny, M Zbirovsky, M Blahova, et al. *J. Chromatogr.*, 1982, **247** 327
71. B Petersson *J. Chromatogr.*, 1982, **242** 313
72. M Foot, M T Clandinin *J. Chromatogr.*, 1982, **241** 428
73. R F Delmas, C C Parrish, R G Ackman *Anal. Chem.*, 1984, **56** 1272
74. M Tanaka, K Takase, T Itoh, et al. *J. Chromatogr.*, 1984, **284** 433
75. J K G Kramer, E R Farnworth, B K Thompson *Lipids*, 1985, **20** 536
76. C Sipos, R G Ackman *J. Chromatogr. Sci.*, 1978, **16** 443

77. *Optimising Reproducibility with the Iatroscan TLC/FID Analyser. Iatroscan TH-10 Instrument Application,* No. 1, Iatron Laboratories, Tokyo
78. T Terabayashi, T Ogawa, V Kawanishi, et al. *J. Chromatogr.,* 1986, **367** 280
79. P L Patterson *Lipids,* 1985, **20** 503
80. A K Banerjee, W M Ratnayake, R G Ackman *J. Chromatogr.,* 1985, **319** 215
81. M A Poirier, A E George *J. Chromatogr. Sci.,* 1983, **21** 331
82. H Boden, R Roussel *International Environment and Safety News,* 1983, 7
83. J K G Kramer, R C Fouchard, E R Farnworth *J. Chromatogr.,* 1986, **351** 571
84. J K G Kramer *Lipids,* 1980, **15** 651
85. K Tokuno, K Mitani, H Tanaka, et al. *Rinsho Kensa,* 1983, **27** 322
86. J C Fruchart, A Pothien, N Porchet, et al. *Ann. Biol.Clin.,* 1978, **36** 149
87. R T Crane, S C Goheen, E C Larkin, G A Rao *Lipids,* 1983, **18** 74
88. C C Parrish, R G Ackman *Lipids,* 1985, **20** 521
89. I Zeman, M Ranny, L Winterova *J. Chromatogr.,* 1986, **354** 282
90. H Kaneko *Yukagaku,* 1983, **32** 565
91. T Kawai, S Hasunuma, E Nakano, et al. *Jap. J. Clin. Pathol.,* 1971, **19** 293
92. E Nakano, I Sakurabayashi, S Hasunuma, et al. *Jap. J. Clin. Pathol.,* 1972, **20** 186
93. N Shishido, T Isobe, I Horii, K Udaka *J. Toxicol. Sci.,* 1976, **1** 94
94. I Horii, N Shishido, K Udaka *J. Toxicol. Sci.,* 1976, **1** 95
95. K Ueda, K Ito, T Tejima, et al. *Japan. J. Med. Technol.,* 1975, **19** 639
96. S Murai, J Obata, K Ito, et al. *Nippon Shishubyo Gakkai Kaishi,* 1976, **18** 340
97. J Kaneko, M Hosohara, M Tanaka, T Itoh *Lipids,* 1976, **11** 837
98. M Tanaka, T Itoh, H Kaneko *Yukagaku,* 1977, **26** 454
99. F Mordret, A Prevot, N Le Barbanchon, C Barbati *Rev. Fr. Corps Gras.,* 1977, **24** 467
100. J C Fruchart, A Ponthieu, N Porchet, et al. *Ann. Biol. Clin.,* 1978, **36** 176
101. E Gantois, F Mordret, N Le Barnachon *Rev. Fr. Corps Gras.,* 1977, **24** 167
102. K Hiramatsu, H Nozaki, S Arimori *J. Chromatogr.,* 1980, **182** 301
103. T Furuya, T Nagumo, T Itoh, H Kaneko *Agric. Biol. Chem.,* 1980, **44** 517
104. K Hiramatsu, H Nozaki, S Arimori *Nippon Naika Gakkai Zasshi,* 1980, **69** 454
105. J K G Kramer, R C Fouchard, E R Farnworth *J. Chromatogr.,* 1980, **198** 279
106. J K Kaitaranta *J. Sci. Food Agric.,* 1980, **31** 1303
107. S M Innis, M T Clandinin *J. Chromatogr.,* 1981, **205** 490
108. J K Kaitaranta, P J Ke *J. Am. Oil Chem. Soc.,* 1981, 710
109. T G Redgrave, F Jeffery *Lipids,* 1981, **16** 626
110. R G Ackman *Fette, Seifen, Anstrichmittel,* 1980, **82** 351
111. J K Kaitaranta, R G Ackman *Comp. Biochem. Physiol.,* 1981, **69B** 725
112. T Kobayashi, K Kubota *Chemosphere,* 1980, **9** 777
113. K Hiramatsu, S Arimori *J. Chromatogr.,* 1982, **227** 423
114. J-L Sebedio, T E Farquarson, R G Ackman *Lipids,* 1982, **17** 469
115. Y Takemoto *Kawasaki Medical J.,* 1981, **7** 195
116. T Naganuma, Y Uzuka, K Tanaka *Agric. Biol. Chem.,* 1982, **46** 1213
117. *Analysis of Glyceride Isomers by Boric Acid-impregnated Chromarods. Iatroscan TH-10. Instrument Application,* No.2, Iatron Laboratories, Tokyo
118. A K Banerjee, W M N Ratnayake, R G Ackman *Lipids,* 1985, **20** 121
119. J R Hazel *Lipids,* 1985, **20** 516
120. M Blahova, M Ranny, J Sedlacek *Acta Univ. Carol. Med.,* 1986, **32**(1–2)
121. *Analysis of Serum Lipid by the Iatroscan. Iatroscan TH-10. Instrument Application,* No.4, Iatron Laboratories, Tokyo
122. *Analysis of Lipids by Iatroscan Data. Iatroscan TH-10. Instrument Application,* No.5, Iatron Laboratories, Tokyo
123. *Analysis of Triglycerides Molecular Species by Silver Nitrate-impregnated Chromarods. Iatroscan TH-10. Instrument Application,* No.6, Iatron Laboratories, Tokyo
124. T Okumura, T Kadono *Jap. Anal.,* 1973, **22** 980
125. S Ando *Comprehensive Experimental Methodology of Biochemistry* (Edited by T Yamakawa et al.) Japan Biochem. Soc., Tokyo, 1974, p. 58
126. M Tanaka, T Itoh, H Kaneko *Yukagaku,* 1979, **28** 96
127. K Deguchi, S Kawashima, H Ichio, N Ueta *J. Biochem. (Tokyo),* 1979, **85** 1519
128. M Tokunaga, S Ando, N Ueda *Proc. Jap. Conf. Biochem. Lipids,* 1973, Vol. 15, p. 195
129. M Ranny, J Sedlacek, P Svec *J. Planar Chromatogr.,* 1988, **1** 35
130. R D Knapp, B C Sherrill, Lipoprotein Lipid Quantitation by Iatroscan. Lecture at the 75th Annual Meeting of the AOCS, Dallas, 1984 *J. Amer. Oil Chem. Soc.,* 1984, **61** 4
131. Y Suzuki, T Takeuchi *XXI Annual Meeting of the Japan Society for Analytical Chemistry. Abstracts of Papers,* 1972, No.47
132. Y Suzuki, T Takeuchi *Bunseki Kagaku,* 1972, **21** 47
133. R G Ackman, A D Woyewoda *J. Chromatogr. Sci.,* 1979, **17** 514
134. Y Yamamoto, T Kawanobe *J. Jap. Petrol. Inst.,* 1984, **27** 269, 373
135. S Yokoyama, J Umematsu, K Inoue, T Katoh, Y Sanada *Proceedings of the International Conference on Coal Science, Düsseldorf, 1981* Verlag Gluckauf GmbH, Essen, 1981, p. 465
136. M A Porier, P Rahimi, S M Ahmed *J. Chromatogr. Sci.,* 1984, **22** 116
137. Y Yamamoto, Y Ohno *J. Jap. Petrol. Inst. (Sekiyu Gakkaishi),* 1985, **28** 493
138. Y Yamamoto, H Akutsu *J. Jap. Petrol. Inst. (Sekiyu Gakkaishi),* 1986, **29** 38
139. R Yoshida, T Miyazawa, T Yoshida, et al. *Fuel,* 1986, **65** 421
140. B Sol, E Romero, L Carbognani, et al. *Revista Technica Intevep.,* 1984, **4** 127
141. D T Kaschani *Erdöl und Kohle, Erdgas, Petrochem.,* 1986, **39** 241
142. L L Leazar *J. Chromatogr. Sci.,* 1986, **24** 340
143. Leming Ling, Lefeng Zhang *Sepu.,* 1986, **4** 146
144. A Obuchi, H Aoyama, A Ohi, H Ohuchi *J. Chromatogr.,* 1984, **288** 187
145. M Ono, M Shimamine, K Takanashi *Eisei Shikensho Hokoku,* 1978, **96** 67

146. T Yamaguchi, H Kaneshima, T Tamagishi *Eisei Kagaku*, 1975, **21** 286
147. K Capek, T Vydra, J Capkova, et al. *Collect. Czech. Chem. Commun.*, 1985, **50**, 1093
148. S Tomio, K Hiroyasu, O Michinori *Hokkaidoritsu Eisei Kenkyu Shoho*, 1983, **33** 131
149. A Uji *Yakugaku Zasshi*, 1975, **95** 214
150. T Masui, N Fujishima *Kanzo*, 1979, **20** 976, 1299
151. R Beke, G A De Weerdt, F Barbier *J. Chromatogr.*, 1980, **193** 504
152. W K Lee, B K Kim, H J Kim *J. Pharm. Soc. Korea*, 1977, **21** 163
153. T Namba, M Yoshizaki, T Tomimori, et al. *Yakugaku Zasshi*, 1975, **95** 809
154. H Read *Proceedings of the IIIrd International Symposium on Instrumental High Performance Thin-Layer Chromatography, Bad Durkheim, Institute for Chromatography*, Wurzburg, West Germany, 1985, p. 157
155. Y Ando, M Hayshi *Yakugaku*, 1982, **31** 372
156. O Cozzoli *Riv. Ital. Sostanze Grasse*, 1980, **57** 136
157. H Keneshima, H Ogawa, T Yamagishi, et al. *Hokkaidoritsu Eisei Kenkyu Shoho*, 1974, **24** 64
158. T Namba, M Yoshizaki, T Tomimori, et al. *Yakugaku Zasshi*, 1974, **94** 252
159. F Bindler, P Laugel, M Hasselman *Dtsch. Lebensm.-Rundsch.*, 1979, **75** 111
160. M Yoshizaki, T Tomimori, S Yoshioka, T Namba *Yakugaku Zasshi*, 1977, **97** 916
161. R Linko, R Viorela, J K Kaitaranta *J. Sci. Agric. Soc. Finland*, 1980, **52** 423
162. J K Kaitaranta *J. Food Technol.*, 1982, **17** 87
163. R J Morris, M J McCartney *J. Exp. Mar. Biol. Ecol.*, 1983, **67** 149
164. J Poré *J. Soc. Leather Technol. Chem.*, 1982, **66**(3) 41
165. J Poré, I Rasori *Parfums, Cosmet, Aromes*, 1982, **46** 31
166. T I Min, T Miyamoto, H Inagaki *Rubber Chemistry and Technology*, 1977, **50**(1) 63
167. T I Min, H Inagaki *Polymer*, 1980, **21** 309
168. T I Min *Polimo (Korean)*, 1978, **2** 146
169. T Min, A Klein, M S El-Aasser, J W Vanderhoff *Organic Coatings and Applied Polymer Science Proceedings*, 1982, Vol. 46, p. 314
170. J P Houis, E Assimacopoules, I Rasori, J Poré *Rev. Fr. Corps Gras.*, 1980, **27**(2) 61
171. *Treating of Reaction in Organic Synthesis Experiment by Iatroscan. Iatroscan TH-10. Instrument Application*, No.3, Iatron Laboratories, Tokyo
172. M Toyomizu, K Hanaoka, T Nakamura *Bull. Jap. Soc. Sci. Fisheries*, 1980, **46** 1011
173. T Miyamoto, I Yamamoto *Agric. Biol. Chem.*, 1980, **44** 2581
174. Y Kondo *Carbohydrate Research*, 1982, **103** 154
175. S Forbes *Anal. Proc. (London)*, 1981, **18** 19
176. H O Ranger *J. Liquid Chromatogr.*, 1981, **4** 2175
177. T Itoh, M Tanaka, H Kaneko *Thin Layer Chromatography: Quantitative Environmental and Clinical Applications*, Wiley Intersci., New York, 1981, p. 536
178. K D Mukherjee *Quantitative Thin-Layer Chromatography and Its Industrial Applications* (Edited by L R Treiber), Marcel Dekker, New York–Basel, 1987, p. 97
179. M Ranny *Thin-Layer Chromatography with Flame Ionization Detection*, D Reidel Publishing Company, Dordrecht–Boston–Lancaster–Tokyo, 1987, 198 pp

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Organic compounds of silicon with non-standard types of coordination

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ABSTRACT. The structures of organosilicon compounds in which the coordination number of silicon is other than 4 are examined. Derivatives of pentacoordinate silicon, in which silicon has a trigonal-bipyramidal geometry, have been most thoroughly investigated among them. Appreciably much less information is available about the unstable derivatives of tricoordinate silicon, whose structure is close to being planar. Examples of compounds in which the coordination number of silicon is greater than five are also examined. Attention is concentrated on the geometry of compounds with an increased coordination number of silicon atoms as intermediates in chemical reactions.
The bibliography includes 111 references.

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I. Introduction

The main advances in the chemistry of organosilicon compounds (OSC) are associated with studies on derivatives of traditional tetrahedral silicon. This is why the commonest valence and coordination state of silicon is in fact mainly considered in the structural chemistry of OSC.[1,2] However, compounds in which the coordination number of silicon is higher (in the first place silatranes[3,4]) have been synthesised comparatively recently and have now ceased to be unique, while in the last 5–7 years it has been possible to obtain compounds with multiple bonds at the silicon atom.[5–10] The structures of these new OSC have been investigated in fair detail (see, for example, the relevant reviews[1–6]), but so far there has been no general survey of these investigations. The aim of the present review is the examination of the structural features of all the known OSC with a non-tetrahedral coordination of the silicon atom or a coordination which differs appreciably from the tetrahedral. Attention is concentrated on compounds with a silicon–carbon bond, but certain new interesting compounds without such bonds are also considered.

The review does not claim to cover all the structural data on OSC with a non-tetrahedral silicon atom. Preference is given to X-ray diffraction studies (the most reliable method for the investigation of new structures), new results, and the authors' own data.

II. Tricoordinate silicon compounds

1. Silaethylenes

The available data on the structures of compounds with Si=C double bonds (silaethylenes) are summarised in Table 1. Their Si=C bond lengths are in the range close to the length (1.69–1.73 Å) predicted by MO calculations for sterically unhindered silaethylenes.[11] The molecule of compound (I) with the shortest Si=C bond [1.702(5) Å] has a virtually planar core $C_2Si=CSi_2$ (Fig. 1), the sum of the valence angles at each of the atoms Si(1) and C(1) being 360°. The torsional distortion (twisting) relative to the Si=C bond is only 1.6°. The deviations of the valence angles at the unsaturated Si(1) and C(1) centres from the standard values for the sp^2 hybridisation can be fairly well accounted for by the steric strain introduced by the $SiMe_3$ and especially $SiMe(Bu_t)_2$ groups at the C(1) atom.[8]

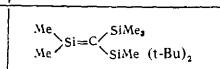
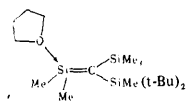
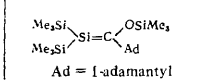
The differences between the Si=C bond lengths and the torsional distortions in the silaethylenes (I)–(III) are probably caused by the greater size of the substituents and also by their electronegativity [the $OSiMe_3$ group in compound (III)]. Since the silaethylene (I) contains less bulky and not unduly electronegative substituents, its Si=C bond length [1.702(5) Å] can be regarded as characteristic of the silaethylene $R_2Si=CR_2$ with moderately large substituents.

The most interesting feature of the silaethylene tetrahydrofuranate (II) molecule is the presence in it of a significantly planar bond system at the sp^2-hybridised C(1) atom, which forms a double bond with the tetracoordinate Si(1) atom which is involved in an unusual coordination (Fig. 2). The sum of the valence angles of the C(1) atom is 358.8° and the atom is displaced from the Si(1)Si(2)Si(3) plane by only 0.11 Å. Large valence angles at the C(1) atom are probably caused by the steric interaction between the substituents. The largest Si(1)C(1)Si(3) angle, which is 126.7(3)°, is due to the extremely bulky $Si(3)MeBu_2$ group whose Si(3)–C(8) and Si(3)–C(12) bonds are in the *gauche*-conformation relative to the Si(1)–C(1) bond.

The coordination involving the Si(1) atom does not correspond to the ideal tetrahedral geometry, which can be difficult to explain by steric hindrance. The C(1)Si(1)C(2) and C(1)Si(1)C(3) angles, which are respectively 119.7° and 124.1(3)°, unexpectedly differ little from 120°, the usual value of the angle in the sp^2-hybridisation. The C(2)Si(1)C(3) = 104.9(3)° angle is appreciably smaller than the tetrahedral value. The angles at the oxygen atom in the THF

molecule can be divided into two groups: the OSi(1)C(1) = 107.9(2)° angle is much greater than the OSi(1)C(2) = 97.9° and OSi(1)C(3) = 96.5(2)° angles. The Si(1)–O = 1.878(4) Å distance is much greater than the Si–O bond lengths characteristic of the dicoordinate O atom in siloxanes (1.68 Å) [12–15] and the bonds involving a tricoordinate O atom aluminosiloxanes (1.66–1.76 Å),[16] although in the latter the O atom is incorporated in some cases in a strained four-membered Al_2O_2 ring.

Table 1. The principal geometrical parameters of molecules with Si=C double bonds.

No. of compound	Compound	Molecular symmetry	r(Si=C), Å	τ*, deg	Refs.
(I)		C_1	1.702 (5)	1.6	[8]
(II)		C_1	1.747 (5)	22.4	[9]
(III)	 Ad = 1-adamantyl	C_1	1.764 (3)	14.6	[10]

*τ = angle of twist about the Si=C double bond.

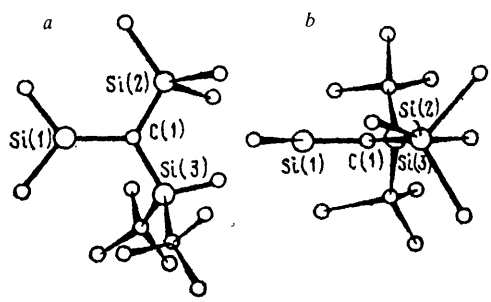
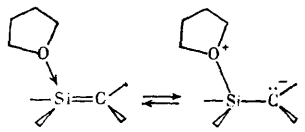


Figure 1. The structure of the molecule of compound (I): projection onto the Si_3C plane (*a*) and onto a surface perpendicular to the plane of the π-system of the C(1)=Si(1) double bond (*b*).[8]

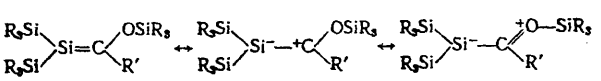
The Si(1)–C(2) and Si(1)–C(3) bond lengths [1.850 and 1.858(5) Å respectively] are somewhat greater than the C(1)–Si(2) and C(1)–Si(3) bond lengths [1.853 and 1.836(5) Å] and are much smaller than the Si–Me bond lengths in silyl groups [1.879 Å to 1.907(6) Å]. The Si(3)–C(Bu_t) [Si(3)–C(8) and Si(3)–C(12)] bonds are even longer [1.939 and 1.927(6) Å], which may be caused by steric strain.[9] The usual geometry of compound (II) can be explained by equilibrium between the forms (A) and (B):[9]



The canonical form (A) corresponds to the formation of an adduct with THF, as a consequence of which the Si atom acquires ten electrons, which requires the participation of *d* orbitals in the bonding. It is important to emphasise that the presence of an excess Si–O bond in compound (II) does not induce a sharp increase in the length of the Si=C bond, which remains shorter than, for example, in the silaethylene (III), with bulky substituents (Table 1). The second canonical form (B) presupposes charge separation between the atoms in the 1- and 3-positions as a consequence of the formation of the covalent Si–O bond, as happens in the phosphorus ylides $R_3P^+-\dot{C}R_2^-$. The increased Si–O bond length in the molecule of compound (II) agrees with a relatively low stability of the adduct (A), in which suitable *d* orbitals of the Si atom can overlap with the donor orbitals of the O atom and the approximately tetrahedral form (albeit distorted) coordination of the Si(1) atom agrees with the zwitter-ionic form (B).

The conformation of the molecule of compound (II) is apparently determined by the steric interactions of the substituents at the Si(1) and C(1) atoms. In particular, the twisting around the double bond [the C(3)Si(1)C(1)Si(3) angle is 22.4°] is probably caused by the minimisation of the steric interactions between the methyl groups at Si(1) and the t-butyl groups at the Si(3) atom. According to ^{1}H NMR data, both Me groups at the Si(1) atom in the molecule of compound (II) in solution in THF at 30 °C are equivalent.[9] This is a powerful argument in support of form (B), the ylide type of bonding in which presupposes free rotation about the Si(1)–C(1) bond.

The high stability of the silaethylene (III) can be explained partly by steric causes (bulky substituents, especially the adamantyl substituent, prevent dimerisation and other reactions) and partly by the electronic influence of the substituents Me_3SiO and Me_3Si at the double bonded C and Si atoms respectively. As a consequence of the inductive effect of the substituents and the existence of resonance forms, the polarisation of the double bond is found to be much smaller than would have been expected from the difference between the electronegativities of the Si and C atoms:



Quantum-chemical calculations confirm the stabilising influence of the silyl group at the Si atom and of the siloxy-group at the C atom on the Si=C double bond (as a consequence of electronic effects).[9]

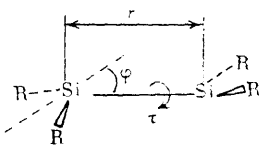
2. Disilenes

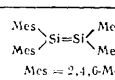
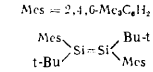
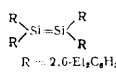
The first stable disilene, investigated by X-ray diffraction, proved to be tetramesityldisilene (IV),[17] synthesised by the photolysis of the polysilane precursor.[17] The Si–Si = 2.160(1) Å distance in the molecule of compound (IV) is shorter by 0.19–0.20 Å than in tetramesityldisilane,[19] which is consistent with the presence of a double bond in compound (IV).

It follows from the X-ray diffraction data for the heteroethylenes M_2R_4 that, with increase in the atomic number of the M atom, there arises a tendency towards an increase in the pyramidal form of

its coordination {the sum of the valence angles of the M atom is 360° in C_2Ph_4, 355.3° in compound (IV), 348.5° in $Ge_2[CH(SiMe_3)_2]_4$, and 342° in $Sn_2[CH(SiMe_3)_2]_4$} and towards the shortening of the M–M bond compared with the standard $M(sp^3)-M(sp^3)$ bond lengths adopted in the diamond-like modification of M [C(12%) > Si(8%) > Ge(4%) > Sn(2%)].[20]

Table 2. The principal geometrical parameters of molecules with Si=Si double bonds



No. of compound	Compound	Molecular symmetry	r, Å	τ, deg	φ^*, deg	Refs.
(IV)	 Mes = 2,4,6-$Me_3C_6H_2$	C_2	2.160 (1)	6.5	15	[17]
(V)		C_i	2.143 (1)	0	0	[21]
(VI)	 R = 2,6-$Et_2C_6H_3$	C_i	2.15	0	10	[5]

*φ = angle between the plane and the Si=Si bond.

Both these features indicate the presence of a large, albeit smaller than in alkenes, π-contribution to the Si–Si bond in disilenes.[21] These conclusions agree with the results of a large number of theoretical studies in which the energy of the π-bond in the Si_2H_4 model disilene was estimated as approximately 30 kcal mol^{-1},[22,23] which is smaller by a factor of approximately two than the π-bond energy in ethylene.

The weaker π-interaction in disilenes compared with alkenes is usually attributed to the less effective overlap of the 3*p* orbitals of the Si atoms.[21] The overlap of 4*p* or 5*p* orbitals of Ge or Sn analogues of olefins should be even weaker. The distinctly antipyramidal structure of distannenes probably arises as a consequence of the ineffectiveness of the $p_\pi-p_\pi$ bonding: the Sn–Sn distance in tetrakis(trimethylsilyl)distannene agrees with the length of a single Sn–Sn bond in hexaphenyldistannane.[21]

As can be seen from Table 2, the molecules of the three disilenes listed in it are characterised by very similar Si=Si bond lengths, but differ significantly in the deformability of the central fragment. According to the results of *ab initio* calculations, disilenes are appreciably more susceptible to deformations than alkenes and the differences between the molecular geometries of the environments of the Si=Si double bonds in compounds (IV)–(VI) can be explained by packing effects.[21] It is therefore entirely possible that other conformations of compounds (IV)–(VI) predominate in solution rather than in the solid phase. According to calculations of the structure of the Si_2H_4 molecule in the ground state, its potential energy level is described by a low-slope surface with two minima corresponding to antipyramidal and planar geometries, the first form being more stable than the second by ~0.5 kcal mol^{-1}.[21]

Quantum-chemical calculation[24] of the energies of the M_2H_4 molecules (M = C, Si, or Ge) as a function of the pyramidalisation angle φ showed that "for ethylene this function is a parabola with a minimum at φ = 0°, for disilene it is a U-shaped curve with low-slope bottom, indicating a contribution by a structure with a large angle φ, while for digermene the curve has a maximum at φ = 0° and a minimum at φ = ±40°. The latter can be regarded as an indication of the possibility of an intermediate structure with a single Ge–Ge bond and the resonance of the unshared electron pair, which corresponds to the angle φ ≃ 55°".[25]

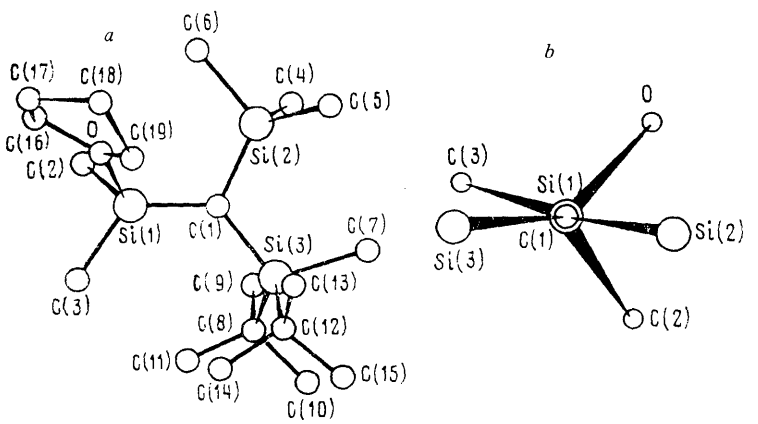
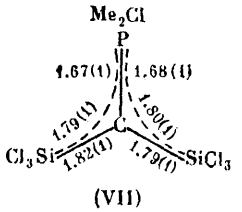


Figure 2. The structure of the molecule of compound (II): projection onto the Si_3C plane (*a*) and view along the C(1)=Si(1) bond (*b*).[10]

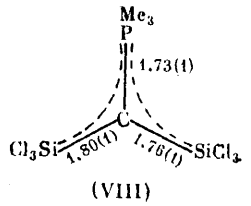
III. Compounds of tetracoordinate silicon with an appreciably distorted structure

1. Disilaphosphorane ylides

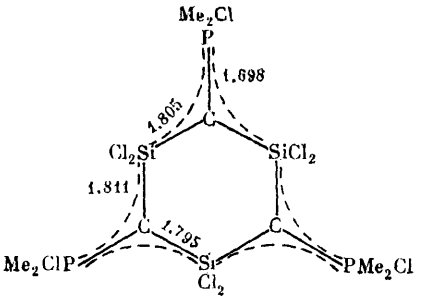
An unexpected feature of the disilaphosphorane ylides (VII)–(IX) [26]



(VII)



(VIII)



(IX)

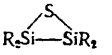
proved to be appreciably smaller lengths of the Si–C (1.76–1.82 Å) and P–C (1.67–1.73 Å) bonds involving central planar-trigonal C atoms compared with the standard Si–C (1.84–1.87 Å) [12–15] and P–C (1.78–1.82 Å) distance.[27] This indicates an increased order of the ylide bonds for what is actually an undistorted tetrahedral coordination of the Si and P atoms. Using the equations $n_i = (d_1/d_i)^5$ (d_1 is the length of the bond whose order is $n = 1$, assumed to be equal to the sum of the covalent radii with a Shomaker–Stevenson correction for the difference between the electronegativities),[28,29] the authors[26] calculated the approximate orders n_i of the shortened bonds Si–C and P–C. For all three structures (VII)–(IX), the average sum of the bond orders involving the ylide carbon atoms is ~4 and that for the Si and P atoms is ~4.33. Thus the orders of the shortened Si–C and P–C bonds are close to one another and amount to $n \simeq 1.33$. Consequently, the intensification of the interaction of the ylide C atoms with the surrounding Si and P atoms is caused not by the weakening of the interaction of the latter with the peripheral substituents [for example the Si–Cl distances in the molecules of compounds (VII)–(IX) have the usual values of 2.024–2.098 Å] but are caused by additional $p_\pi - d_\pi$ bonding.[26]

The concept of the $p_\pi - d_\pi$ interaction has also been used to explain the shortening of the Si–C bonds with participation of the carbanionic C atom [to 1.799(2) and 1.816(4) Å] in the dimeric organolithium-silicon compound $[Li^+C^-(SiMe_2OMe)_3]_2$.[30]

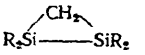
2. Small rings

Many organosilicon compounds containing small three-, four-, and five-membered Si-heterocycles are known in which the valence angles at the Si atoms are much smaller than the standard values. In these systems, the Si atom retains a distorted tetrahedral coordination and the lengths of the bonds involving it usually have the normal values characteristic of unstrained rings. However, in certain cases, for example in cyclodisiloxanes $(R_2SiO)_2$ and cyclodisilathiiranes $R_2Si-SiR_2-S$, the molecular geometry is less trivial and the presence in these compounds of some kind of coordination of the Si atom other than the distorted tetrahedral coordination may be postulated.

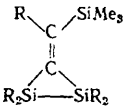
The small length of the Si–Si bond proved to be an unexpected structural feature of the 1,1,2,2-tetramesityl-1,2-disilathiiran (X) molecule.[31] It is 2.289(2) Å, which is smaller by 0.05 Å than the typical Si–Si bond length in disilane derivatives (2.34 Å).[1]



(X): R = mesityl



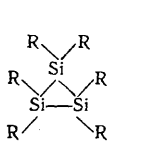
(XI): R = 2,6-dimethylphenyl



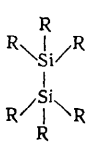
(XII): R = mesityl

The Si–Si distance in disilacyclopropane (XI) is even smaller (2.272 Å),[32] while the corresponding bond in the molecule of compound (XII) (2.327 Å) [33] has almost the normal length. In all three compounds (X)–(XII), the disposition of the second Si atom and of the exocyclic C atoms around the first Si atom of the three-membered ring is almost planar.[31] For example, in compound (X) the sum of the two CSiSi valence angles and of the CSiC angle around both Si atoms is 357.4(4)°. The corresponding values in compound (XI) are 357.4(2)° and 357.7(1)°, while in compound (XII) it is 356.6°. These structural features show that in all three molecules the hybridisation of the Si atom is of the sp^2-p-type rather than the sp^3-type. The interaction of the Si atom with the S and C atoms of the three-membered rings then takes place mainly via the 3p orbital of silicon. Furthermore, the small length of the Si–Si bond in compounds (X)–(XII) suggests that there is some overlap of the 3p orbitals of the neighbouring Si atoms leading to the π interaction between them and hence to an increase in the Si–Si bond order ($n > 1$).[31]

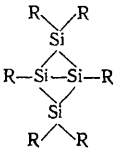
A small length of the Si–Si bond is not characteristic of all compounds containing a three-membered ring: thus in hexakis(2,6-dimethylphenyl)cyclotrisilane (C_1 symmetry) [34] and especially in hexa(t-butyl)cyclotrisilane [35] (XIII) (D_3 symmetry), the Si–Si bond lengths are greater than the normal values [2.407(4) and 2.511(3) Å respectively]. The greater length of the Si–Si bond [2.511(3) Å] in the cyclotrisilane (XIII) molecule containing more bulky substituents is striking.



(XIII): R = Bu-t



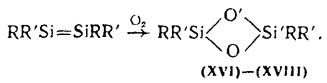
(XIV): R = Bu-t



(XV): R = 2,6-$Et_2C_6H_3$

An appreciable increase in the length of the Si–Si bond to 2.697 Å has been observed in the sterically greatly hindered acyclic molecule of compound (XIV); the Pauling order of this bond is $n = 0.45$.[36] The variability of the Si–Si bond length is as a rule explained by the characteristic features of the steric structure of the molecules. Thus in the bicyclosilane (XV) [37] the central Si–Si bridge bond is somewhat lengthened (it is readily ruptured by oxygen and chlorine; furthermore, the bicyclic system undergoes rapid inversion), while the peripheral bonds are on the whole somewhat shortened.

1,3-Cyclodisiloxanes (Table 3) are formed when the corresponding disilenes are oxidised in air:[38,39]



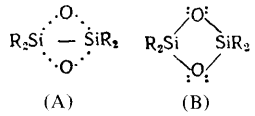
(XVI)–(XVIII)

A characteristic feature of these structures is the small transannular Si...Si distance: it amounts to 2.349(1) Å in compound (XVIII), i. e. it is the same as the length of a single Si–Si bond (2.34 to 2.35 Å),[38] it is somewhat shorter in compound (XVI) 2.306(3) Å, while in compound (XVII) it is somewhat longer (2.396 Å) than the normal Si–Si bond. The transannular O...O distances in compounds (XVI)–(XVIII) are also smaller than twice the van der Waals radius of the oxygen atom (3.40 Å).[40] The Si–O bond lengths in cyclodisiloxanes are somewhat greater than in cyclosiloxanes with a larger ring (1.61–1.65 Å).[1,2] Their SiOSi angles are forced to assume values reduced to 86.2(3)° in compound (XVI), 91.13(7)° in compound (XVII), and 89.7° and 89.4° in compound (XVIII) (in cyclosiloxane the SiOSi valence angles are usually 130–150° [1,2]).

Table 3. The principal geometrical parameters of 1,3-cyclodisiloxanes $(RMeSiO)_2$.[38,39]

Compound	R	Molecular symmetry	Interatomic distances, Å				OSiO' angle, deg	SiOSi angle, deg
			Si...Si	O...O	Si–O	Si–O'		
(XVI)	Me	C_2	2.306 (3)	2.480 (8)	1.721 (4)	1.658 (4)	95.5 (1)	86.2 (2)
(XVII)	t-Bu	C_i	2.396 (1)	2.349 (3)	1.676 (2)	1.679 (2)	88.87 (7)	91.13 (7)
(XVIII)	$(Me_3Si)_2N$	C_1	2.349 (1)	2.358 (4)	1.663	1.668	90.2	89.7
					1.667 (3)	1.672 (3)	89.8 (1)	89.4 (1)

There exist two alternative points of view on the structure of cyclodisiloxanes.[38,39] According to the first, there is a σ-bond between the Si atoms and the Si–O bonds are therefore electron-deficient [structure (A)]; according to the second, there is strong repulsion between the O atoms, which forces the Si atoms to approach one another, but there is no bond between them [structure (B)].



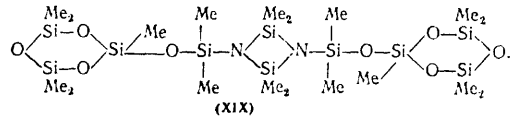
(A) (B)

If the first point of view is adopted, then the addition of oxygen to disilenes during the oxidation reaction induces the dissociation not only of the π-component of the Si=Si double bonds but also of the σ-component.[38] The first calculation by the MNDO method for the model H_4SiO_2 molecule failed to confirm the presence of a bond between the Si atoms but, as pointed out by Fink and co-workers,[38,39] this question has not yet been finally resolved.

In order to explain the structure of cyclodisiloxanes, the model of the bonding in cyclobutadiene is also used.[39] There is a 3*p* orbital (of the π-type) on the silicon atom, which is characterised by a smaller electron density than the 2*p* orbital of the O atom and the diagonal antibonding interactions of the O atoms are therefore stronger than those of the Si atoms, which leads to the rhombic distortion observed in the cyclodisiloxane molecules, for example, in compound (XVI). The differences between the SiOSi angles and the Si...Si distances in the molecules of compounds (XVI)–(XVIII) are a result of the operation of packing forces or steric factors.

The distortions observed in cyclodisiloxanes are characteristic also of cyclodisilthianes, for example of $(Me_2SiS)_2$,[41] in which the SiSSi angle, amounting to 82.41(6)°, is even smaller than in $(Me_2SiO)_2$ [86.2(2)°], because the van der Waals angle of the sulphur is even greater than that of the oxygen atom.

On the other hand, in the cyclodisilazanes $(R_2SiNR)_2$ the SiNSi angles are always greater than 90°—for example, in compound (XIX) this angle is 91.3(1)°:[42]



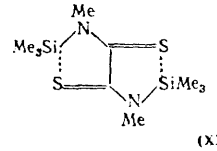
(XIX)

The stretching of the cyclodisilazanes rings in the opposite direction (along the Si...Si diagonal) may be caused by the tendency towards an increase in the valence angles at the N atoms as a result of the movement of the unshared electron pairs of the N atoms away from one another. This is associated with the fact that the Si–N bond lengths in cyclodisilazanes (1.71–1.75 Å) are somewhat greater than the Si–O bond lengths in cyclodisiloxanes [1.663(3)–1.721(4) Å—see Table 3].[39]

IV. Compounds of pentacoordinate silicon

1. Dibenzochalcogensilonins

The additional intramolecular Si ← Si interaction was first observed in the molecule of compound (XX), where the Si...S distances are 3.718 and 3.719 Å (for two symmetrically independent molecules).[43]

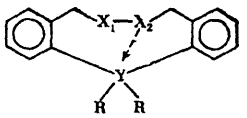


(XX)

A stronger intramolecular transannular Si ← S interaction has been observed in dibenzochalcogensilonins (Table 4). The Si...S and Si...Se distances in compounds (XXI)–(XXIII) are smaller than the sums of the corresponding van der Waals radii by 0.4–0.5 Å. The intermolecular secondary (donor–acceptor) bonds in the $H_3SiSSiH_3$ and $H_3SiSeSiH_3$ crystals are characterised by approximately the same Si...S and Si...Se distances (3.55 and 3.60 Å respectively).[48] The energy of this interaction is low.

Analysis of the conformations of the heterocycles considered using the foldability parameters[47] showed that they all have a form intermediate between the twisted double boat and double boat conformations. However, the disposition of the heteroatoms along the perimeter of the rings of this form common to them depends on the transannular donor–acceptor interaction between the silicon and chalcogen atoms: the ring in which such interaction takes place

differs from that where it does not by the shift of the X_1, X_2, and Y atoms by two positions:



It is of interest that the dihedral angle between the phenylene rings is actually the same in all the compounds (XXI)–(XXIII) of this series (97–99°). Despite this, the overall form of the molecule depends greatly on the presence of the donor–acceptor bond (between the silicon and chalcogen): if this bond is absent, the molecule has the approximate C_2 symmetry; if it is present, the molecule becomes asymmetric (Fig. 3).

Table 4. The transannular Si ← S interactions in the molecules of dibenzochalcogensilonins

Compound	$X_1 = X_2$	Y	R	Interatomic distances, Å		Σ*	$X_2 \rightarrow Y$ interaction	Refs.
				$X_1 \ldots Y$	$X_2 \ldots Y$			
(XXI)	S	Si	Ph	4.193	3.372	3.90	present	[44]
(XXII)	S	Si	Me	4.190	3.438	3.90	»	[45]
(XXIII)	Se	Si	Ph	4.382	3.608	4.00	»	[46]
(XXIV)	Se	Si	Me	4.322	4.228	4.00	absent	[47]
(XXV)	Se	Ge	Me	4.327	4.216	4.10	»	[46]

*Σ = sum of van der Waals radii.

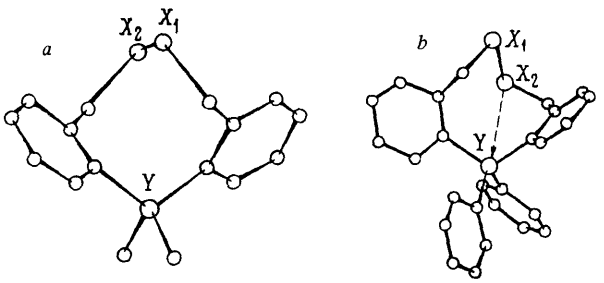


Figure 3. General view of the molecules of the (XXI)–(XXV) series in the presence (*b*) and absence (*a*) of the $X_2 \rightarrow$ Si donor–acceptor bond.[44–47]

Comparison of the lengths of the donor–acceptor bonds in compounds (XXI)–(XXIII) leads to the following conclusions: (1) the X → Si interaction is greatly intensified on passing from X = Se to X = S; (2) the replacement of the methyl groups at the Si and Ge atoms by phenyl groups also strengthens the donor–acceptor bonds; (3) the Ge atom has the same electron-accepting properties (as regards strength) as the Si atom. The replacement of the methyl groups by phenyl groups has different effects in the (XXI)–(XXII) and (XXIV)–(XXIII) pairs: in the latter case, such replacement leads to the appearance of a donor–acceptor bond, while in the former the corresponding $X_2 \ldots$ Si distance is shortened by only 0.06 Å.

Furthermore, in the structure of compound (XXII), where the S...S intermolecular distance is only 3.456 Å (twice the van der Waals radius of the S atom is 3.60 Å [40]), there is a possibility of a more complex Si ← S...S → Si intermolecular interaction.[44]

2. The (dimethylamino)silane pentamer and the chloro(dimethylamino)silane dimer

One of the first pieces of evidence for the quinary coordination of the Si atom was provided by an X-ray diffraction study of (dimethylamino)silane (XXVI), whose structure in the crystalline state proved to be pentameric (Fig. 4), while in the gas phase its molecules are monomeric.[49] This made it possible to explain the anomalously high melting point of compound (XXVI) (again 276 K) compared with other compounds $Me_{3-n}N(SiH_3)_n$ (n = 0–3),[50] which are monomeric in the solid state.[51] The crystal structure of compound (XXVI) is discussed here on the basis of a more accurate reinvestigation by X-ray diffraction.[51]

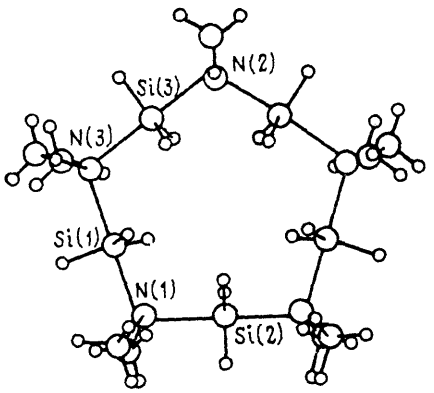


Figure 4. The structure of the (dimethylamino)silane pentamer (XXVI).[51] The molecule has the C_s symmetry.

In the crystal, the molecule of compound (XXVI) occupies a special position on the symmetry plane and has an extremely unusual structure: the N atoms are located at the vertices of a regular pentagon, while the Si atoms are in the centres of its sides, being slightly displaced from the centre of the ring. The average planes of the two crystallographically independent halves of the pentamer molecule intersect the Si(2)...N(2) line, forming a dihedral angle of 170.5°.

Whereas in the gas phase the "isolated" Me_2NSiH_3 molecule is characterised by a pyramidal geometry of the N atom and a tetrahedral geometry of the Si atom or Si–N and N–C bond lengths of 1.712(3) and 1.459(3) Å respectively,[21] in the crystalline state, the Si atoms are involved in a trigonal-bipyramidal coordination, while the N atoms are involved in a tetrahedral coordination; the average interatomic Si–N and N–C distances then increase to 1.976(4) and 1.476(4) Å respectively. Thus the Si–N distances in the pentamer, corresponding to a pentacoordinate Si atom, are

greater by 0.26 Å than the corresponding distance in the monomeric molecule in the gas phase with a tetrahedral coordination of Si. On the other hand, the N–C distances increase by only 0.02 Å when the coordination of N changes from pyramidal to tetrahedral.

We may note yet again that the silicon atom in the structure of this pentacoordinate derivative has a rigorously trigonal-bipyramidal geometry and is located precisely in the plane of the three equatorial H atoms, while both axial Si–N bonds have the same lengths. Thus the Si atom in this compound has the [3 + 2] coordination.

The distortions of the geometry of the tetrahedral molecules as a consequence of the interaction of their central atoms with a relatively close nucleophile can be described as the initial stages of S_N2 nucleophilic substitution reactions whose transition states or intermediates have a trigonal-bipyramidal geometry.[51–53] In this context, the dimethylsilylamine pentamer can be regarded as a "frozen" ensemble of five molecules of a fully symmetrical intermediate.

The vibrational spectra of chloro(dimethylamino)silane (XXVII) in the gaseous and solid states differ sharply, especially in the region of stretching vibrations of the Si–N bond (600–900 cm^{-1}).[54] According to electron diffraction data, compound (XXVII) is monomeric in the gas phase and contains a tetrahedral Si atom (Fig. 5*a*). The Si–N and Si–Cl bond lengths, which are 1.689(4) and 2.070(2) Å respectively, are close to those found in related compounds. The coordination of the N atom is slightly pyramidal and the ClSiN and CNC planes are almost perpendicular to one another.

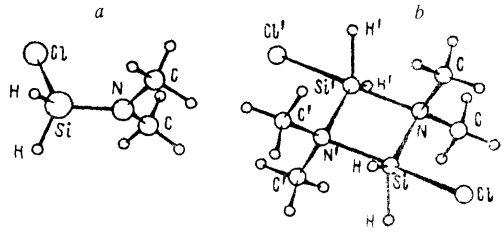
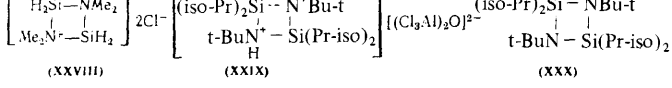


Figure 5. The structure of chloro(dimethylamino)silane (XXVII) in the gas (*a*) and solid (*b*) phases.[54]

The crystal structure of compound (XXVII) includes discrete dimers (Fig. 5*b*) [54] having the C_{2h} crystallographic symmetry: the symmetry plane coincides with the plane of the Si_2N_2 ring. In this ring, the two opposite Si–N distances are 1.81(1) Å, while the other two Si–N distances are much greater [2.05(1) Å]. Consequently the dimer can be described as a species produced by the association of two strongly interacting monomeric molecules. This interaction is manifested by a strong distortion of the tetrahedral coordination of the Si atom in the dimer. The N–Si–Cl angle in the dimer [96.1(5)°] is much smaller than the angle of 113.0(6)° in the monomer, which entails the possibility of the formation of a coordinate bond between the Si and N atoms. The N...Si–C angle is 179.0(4)°, i.e. it is in fact linear and the Si atom acquires a trigonal-bipyramidal coordination, although the N...Si–Cl line, passing through the axial N and Cl atoms, is not rigorously perpendicular to the equatorial plane in which the N atom and the two H atoms linked to the Si atom are located. The axial (and not equatorial) position of the Cl atom creates conditions for the formation of a hypervalent bond, listed by Tandura et al.,[3] and, in particular, it corresponds to the tendency by the most electro-negative substituents to occupy axial positions in a trigonal-bipyramidal molecule. The Si...N coordination interaction leads to an appreciable lengthening of the Si–Cl and Si–N bonds in the crystal (by 0.16 and 0.12 Å respectively) compared with the gas phase, the S–Cl bond being in the *trans*-position relative to the Si–N coordinate bond, while the Si–N′ bond is almost perpendicular to it. The Si–Cl bond length approaches the Si–Cl bond lengths in other derivatives of pentacoordinate (2.148–2.307 Å) or hexacoordinate Si (2.199–2.392 Å).[55] The Si–N...Si = 97.0(6)° angle proved to be intermediate between linear and tetrahedral angles.

It has been suggested[54] that the dimer (XXVII) be regarded as a "frozen" intermediate in an S_N2 reaction, which reduces to attack by the Si atom on the N atom. The Cl atom behaves as the leaving group and the tentative reaction "product" [compound (XXVIII)] represents the ionic form of the dimer with Si–N bonds of equal length:



The equalisation of the Si–N distances in the $(SiN)_2^{2+}$ ring has demonstrated by an X-ray diffraction study of the salt (XXIX).[56] It is of interest that these distances in compound (XXIX) (the average value is 1.792 Å) are appreciably greater than in the usual silazanes, for example, in compound (XXX) (1.747 Å).[56]

3. Silatranes

Silatranes constitute the most thoroughly investigated class of pentacoordinate silicon derivatives, including also the structural aspect (see, for example, the relevant reviews[1–4]). The transannular Si ← N interaction in silatranes with participation of the Si atom involved in a trigonal-bipyramidal coordination has been explained by the participation of the *d* orbitals of the silicon atom in bonding (see, for example, Tandura et al.[3]) and the hypervalent interaction in the N → Si–R fragment.[3,57] It has also been considered from the standpoint of the interaction of Lewis acids and bases.[4]

The strength of the transannular Si ← N bond depends on the structure of the silatranes, in the first place on the electron-accepting properties of the axial substituents at the Si atom. The enhancement of the electron-accepting properties (for any of the three explanations mentioned above) should strengthen the Si ← N bond.

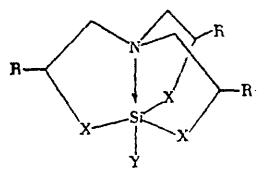
Since there are many reviews on the structure of silatranes (see, for example, Refs. 1–4), we concentrated attention here on the very latest (predominantly our own) results.

The structures of two silatranes in which the Si atom is linked to four O atoms have been determined: 1-(*m*-chlorophenoxy)silatrane (XXXI) [58] and 1-(t-butoxy)silatrane (XXXII).[59] By virtue of the greater electron-accepting capacity of the *m*-chlorophenoxy-group, the Si ← N distance in the silatrane (XXXI) [2.079(2) Å] is appreciably smaller than in compound (XXXII) [2.189(4) Å], where it is actually identical with the Si ← N distance in the α-modification of 1-phenylsilatrane (XXXIII).[60] On the other hand, the axial Si–O distance in compound (XXXI) is greater than in compound (XXXII) [1.690(2) and 1.659(4) Å respectively]. Since, judging from

the interatomic distances, the axial bond orders in compound (XXXI) are closer to one another than in compound (XXXII), the shift of the Si atom (Δ_{Si}) from the plane of the three equatorial O atoms in the silatrane (XXXI) is smaller than in compound (XXXII) [0.136(1) and 0.201(2) Å respectively]. The shift of the N atom from the plane of the three C atoms linked to it (Δ_N) is, on the other hand, smaller in compound (XXXII) than in compound (XXXI) [0.371(4) and 0.407(2) Å respectively], although the decrease in Δ_N is less distinct than the increase in Δ_{Si}. The values of Δ_{Si} and Δ_N observed in compound (XXXII) agree well with those calculated from the empirical equations[59]

$$\Delta_{Si} = 0.479 d_{Si-N} - 0.840 = 0.206 Å,$$
$$\Delta_N = -0.385 d_{Si-N} + 1.200 = 0.357 Å.$$

The replacement of the equatorial O atoms in 1-phenylsilatrane by NH groups [transition to 1-phenyltriazasilatrane (XXXIV)] does not actually affect the transannular interaction: the Si—N = 2.132(4) Å bond length in the silatrane (XXXIV) [60] is the same as the corresponding bond length in the γ-modification of compound (XXXIII) [61] and is somewhat smaller than in two other (α and β) modifications of this compound [2.193(5) Å [62] and 2.156(4) Å [63] respectively]:



(XXXIII): X = O, Y = Ph, R = H;
(XXXIV): X = NH, Y = Ph, R = H;
(XXXV): X = O, Y = C_6H_4Me-*p*, R = H;
(XXXVI): X = O, Y = C_6H_4Me-*p*, R = Me.

(XXXIII) – (XXXVI)

On the other hand, the Si—C(Ph) bond length in compound (XXXIV), which is 1.922(5) Å, is greater than in the α-, β-, and γ-modifications of compound (XXXIII) [1.882(6), 1.908(4), and 1.894(5) Å respectively]. The displacement of the Si atom from the plane of the three equatorial atoms towards the phenyl group in compound (XXXIV) is greater (0.24 Å) than in the α-, β-, and γ-forms of compound (XXXIII) (0.20, 0.20, and 0.18 Å respectively), which leads, for approximately the same Si ← N distances, to an appreciable shift of the axial N atoms from the plane of the three C atoms linked to it towards the Si atom (0.42 Å against 0.34, 0.38, and 0.39 Å).

The somewhat different parameters characterising the transannular interaction in the α, β-, and γ-modifications of compound (XXXIII) indicate their lability, a possible dependence on the packing effects, and the necessity of using in the interpretation the data for a large number of compounds.

The lengths of the equatorial Si—N bonds in compound (XXXIV) [1.731–1.756(4) Å] are close to the upper limit of the range of the Si—N distances in silazanes[64] and agree with the length of the equatorial bond [1.746(2) Å] in 1-(trichlorosilyl)-1,2,3,4-tetrahydro-1,10-phenanthroline (see subsection 5), which contains a pentacoordinate Si atom. Such increase in the lengths of the equatorial bonds in compounds (XXXIV) is analogous to a slight increase in the lengths of the equatorial Si—O bonds characteristic of "oxygen" silatranes [thus they amount to 1.656, 1.657, and 1.656 Å in the α-, β-, and γ-modifications of compound (XXXIII) respectively], whereas the range 1.61–1.65 Å is typical for the tetrahedral silicon derivatives $(RO)_nSiR_{4-n}$ with $n > 1$.[2]

The Si ← N transannular interaction is weakened when methyl groups are introduced in the 3-, 7-, and 10-positions of the silatrane nucleus: the Si—N distances in two symmetrically independent molecules of 1-(*p*-tolyl)silatrane (XXXV) are 2.171 and 2.167(1) Å, while the corresponding distance in 3,7,10-trimethyl-1-(*p*-tolyl)-silatrane (XXXVI) is 2.236(3) Å.[65] This effect is explained both by the electron-donating influence of the CH_3 group (which reduces the electron-accepting effect of the equatorial O atoms) and by the conformational difference between the five-membered chelate rings in the silatranes (XXXIV) and (XXXV) caused by them.

The breakdown of the C_3 symmetry of the silatrane ring, induced by the different directions of the deviation of the C_β atoms (and hence of the methyl groups attached to them) from the planes of the remaining atoms of the five-membered rings, observed for the first time in compound (XXXVI), is also remarkable.[65,66]

Naturally the introduction of C atoms in the equatorial positions relative to the Si atom (transition to tricarbasilatranes) weakens the transannular Si ← N interactions. Thus the Si...N distance in the $[Si(CH_2CH_2CH_2)_3N]_2O$ molecule[67] is 2.477(5) Å, which indicates a weak Si ← N coordination (a formal bond order of 0.35). The coordination of the Si atom in this compound is intermediate between tetrahedral and trigonal-bipyramidal (the difference between the sums of the equatorial and apical valence angles is 40.2°). The NSiO and SiOSi valence angles are 180° (C_{3i} intrinsic symmetry of the molecule).

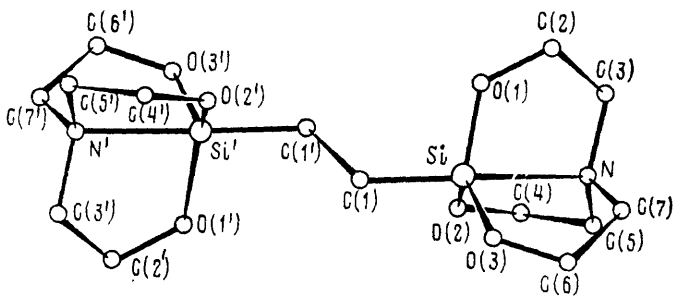


Figure 6. The structure of the centrosymmetrical molecule of compound (XXXVII).[64]

The linking of the two silatranyl groups in 1,2-bis(1-silatranyl)-ethane (XXXVII) by the CH_2CH_2 bridge is hardly reflected in their geometry. The length of the Si ← N transannular bond [2.230(5) Å] and the shift of the Si atom from the plane of the equatorial O atoms (Δ_{Si} = 0.24 Å) of the centrosymmetric molecule of compound (XXXVII) (Fig. 6) [64] are close to those observed in 1-ethylsilatrane, which are respectively 2.21(1) and 0.23 Å.[68] Thus there is virtually no mutual influence of the silatranyl groups in compound (XXXVII). On the other hand, the presence of the methylene bridge ensures this influence to some extent. The Ge ← N bond length and Δ_{Ge} in bis(1-germatranyl)methane [69] are greater than in 1-ethylgermatrane by 0.05 and 0.08 Å respectively.

In the series of onium derivatives of the type $[RCH_2Si(OCH_2CH_2)_3N]^+I^-$ [R = Me_2S^+ (XXXVIII),[70] Me_3N^+ (XXXIX),[71] and Ph_3P^+ (XL) [72]], the lengths of the transannular

Si ← N bonds, correlated with electron-accepting properties of the substituent R, are respectively 2.046(2) Å in compound (XXXVIII), 2.08(1) Å in compound (XXXIX), and 2.07 and 2.12(1) Å in compound (XL) (in the last case there are two independent molecules). In fact, the l_{Si-N} distance in compound (XXXIX) for example, should be 2.08(2) Å according to the equation $l_{Si-N} = 2.20(1) - 0.063(6)\sigma_X^*$ [71] (σ_X^* is the Taft inductive constant) for $\sigma^*_{Me_3NCH_2} = 1.90$, which agrees with X-ray diffraction data.[71] Among all the onium compounds considered, intramolecular steric hindrance has been observed only in the molecule of compound (XXXIX). Thus the SiCR angles in these compounds have the following values: 114.4(1)° in compound (XXXVIII), 121.2(9)° in compound (XXXIX), and 113.6° and 115.3(6)° in compound (XL).

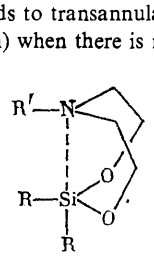
Among the silatranes whose structures have been investigated, the shortest Si ← N distance (l = 2.023 Å) has been noted in 1-chlorosilatrane, although, according to the correlation equations used to predict the values of l from the Taft inductive constant σ^* [73] and the average electronegativity of the substituent in the 1-position,[4] this distance in 1-fluorosilatrane (XLI) should be even smaller (2.007 and 1.927 Å respectively).[74] However, according to X-ray diffraction data, the Si ← N distance in compound (XLI) proved to be 2.042(1) Å, which is somewhat greater than in 1-chlorosilatrane.

Since the mechanism of the interaction of the N and Si atoms in silatranes still remains controversial, the experimental (X-ray diffraction) study of the distribution of electron density in the region of the Si ← N bond assumes special importance.[74] Two maps of the deformation electron density in the planes passing through the Si ← N and Si–F bonds are presented in Fig. 7. In the region between N and Si atoms, there is a distinct maximum with a height of 0.4 eÅ^{-3} actually on the lines connecting them, its distances from the Si and N atoms corresponding approximately to the ratio of the covalent radii. The reliability of this experimental manifestation of the hypervalent Si ← N interaction is confirmed by the presence of a comparable maximum on the line corresponding to the Si–F covalent bond.

A precision X-ray diffraction study made it possible to investigate also the distribution of deformation electron density in the chloromethylsilatrane crystal.[75] The peak corresponding to the unshared electron pair of the N atom is separated from it in the direction towards the Si atom by 0.7 Å, which is greater than the distances usually observed between the N atom and the peaks due to its unshared electron pairs (0.40–0.42 Å). This finding can be interpreted as confirmation of the transannular Si ← N interaction.

4. 1,3-Dioxa-6-aza-2-silacyclo-octanes

Depending on the electronic and steric properties of the substituents at the Si and N atoms in 1,3-dioxa-6-aza-2-silacyclo-octanes, the Si...N distance varies from 2.30 Å (for R = Ph and R′ = H), which corresponds to transannular interaction, to 3.19 Å (for R = Me and R′ = Ph) when there is no such interaction.[76]



As the Si...N interaction intensifies, the coordination of the Si atom deviates increasingly from the tetrahedral and there is an increase in the contribution of the "crown" conformation to the shape of the eight-membered ring.[76] The replacement of the N atom in the molecules considered, where R = Ph and R′ = H, by the O atom (transition to 1,3,6-trioxa-2-silacyclo-octane) weakens appreciably the transannular interaction. The corresponding Si...O distance is 2.976(5) Å, which is smaller by only 0.5 Å than the sum of the van der Waals radii of Si and O.[40,44–47] As a result of the Si ← O interaction, the eight-membered ring in 1,3,6-trioxa-2-silacyclo-octane assumes the unfavourable crown conformation.[77]

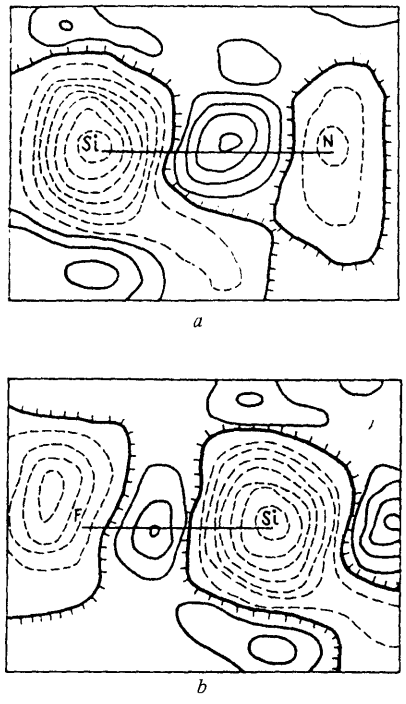


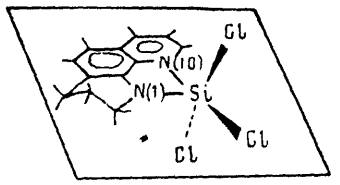
Figure 7. The distribution of deformation electron density in the Si(1)O(2)N(5) (*a*) and Si(1)O(2)F (*b*) planes in the molecule of compound (XLI) in the crystalline state. The isolines are drawn at 0.1 e Å^{-3} intervals, the dashed lines correspond to negative values of the density, and the "spiked" line corresponds to zero density.[74]

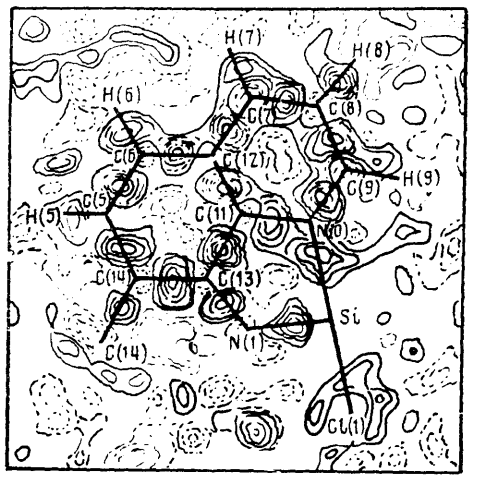
5. 1-(Trichlorosilyl)-1,2,3,4-tetrahydro-1,10-phenanthroline

In order to elucidate the electronic nature of the sharp difference between the lengths of the axial (donor–acceptor) and equatorial (covalent) Si–N bonds involving the pentacoordinate Si atom in the 1-(trichlorosilyl)-1,2,3,4-tetrahydro-1,10-phenanthroline (XLII) molecule (Fig. 8) [1.979(2) and 1.746(2) Å respectively], a precise X-ray diffraction study has been made of the distribution of electron density in a crystal of compound (XLII).[78]

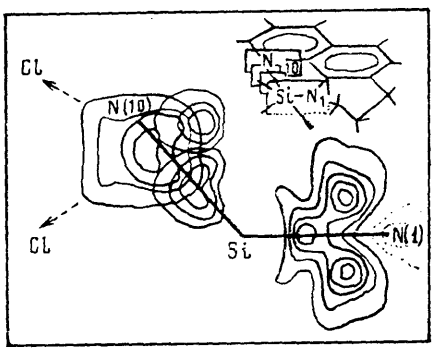
The molecule of compound (XLII) is located in a crystallographic plane with symmetry *m*, while the Si atom is involved in a trigonal-bipyramidal coordination with the N(10) and Cl(1) atoms in the axial positions. Fig. 8*a* shows that the unshared electron pair of the pyridine N(10) atom is highly polarised by the neighbouring Si atom. The maximum deformation electron density between these atoms is separated from the N(10) atom by a distance of ~0.7 Å, is

highly distorted, and decreases more gently in the direction of the Si atom than in the direction of the N(10) atom. On the other hand, the electron density maximum on the Si–N(1) bond decreases much faster in the direction of the Si atom than the N(1) atom and is located at a distance of ~1 Å from the latter. A similarity is observed in the character of the distribution of electron density of the unshared electron pair of the N(10) atom and of the pyridine nitrogen atom in the structure of 2-amino-5-chloropyridine involved in the formation of the intermolecular N–H...N bond.[79]





a



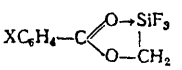
b

Figure 8. Distribution of deformation electron density in the molecule of compound (XLII) in the crystalline state: *a*, section by the crystallographic plane *m* through the molecule as shown at the top of the figure (two C atoms of the tetrahydropyridine ring are arranged above and below this plane); *b*, sections perpendicular to the Si–N(10) bond (on the left) and the section along the Si–N(1) bond (on the right). The isolines are drawn at 0.1 e Å^{-3} intervals.[78]

It is believed[78] that the donor–acceptor N(10) → Si bond in compound (XLII) is formed by the unshared electron pair of the pyridine N(10) atom and is highly polarised by the Si atom. This interaction can increase the barrier to the rotation of the $SiCl_3$ group about the Si–N(1) bond. Furthermore, the unshared electron pair of the amine N(1) atom of the saturated heterocycle is displaced towards the Si atom and towards the Si–N(1) bond (Fig. 8*b*). Such anisotropic distribution of electron density between the Si and N(1) atoms can also increase the barrier to rotation about the Si–N(1) bond, which has been confirmed by NMR data for solutions.[78]

6. (Aroyloxymethyl)trifluorosilanes

The length of the Si ← O bond in (aroyloxymethyl)trifluorosilanes (XLIII)–(XLVII) varies in the range from 1.95(2) to 2.08(2) Å:[72,80,81]



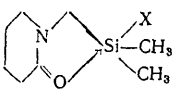
(XLIII)–(XLVII)

(XLIII): X = 4-H,
(XLIV): 4-F,
(XLV): 4-Cl,
(XLVI): 4-Br,
(XLVII): 2-Cl.

It amounts to 2.029(2) Å in the structure of compound (XLV), which has been established most precisely. The length of the Si–F axial bond in compounds (XLIII)–(XLVII) is greater than that of the equatorial bonds by ~0.03 Å and reaches 1.59(2)–1.61(1) Å, which agrees with the concept of the three-centre hypervalent F–Si ← O bond. The introduction of the Cl atom in the *ortho*-position of the benzene ring [compound (XLVII)] increases the angle between the plane of the ring and the average plane of the five-membered ring, resulting from the cyclisation via the Si ← O bond, from 5–7° to 17.5°.[81]

7. *N*-(Halogenodimethylsilylmethyl)lactams

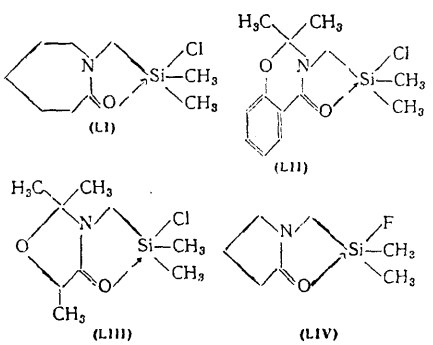
Compounds (XLVIII)–(L) constitute a new class of derivatives of pentacoordinate silicon. Measurements of the electrical conductivities of solutions and analysis of IR spectra showed that the Si ← O interaction weakens with decrease in the atomic number of the halogen X in the sequence I → Br → Cl:[57,82]



(XLVIII)–(L)

(XLVIII): X = I,
(XLIX): X = Br,
(L): X = Cl.

The authors of the present review carried out an X-ray diffraction study of compounds (XLVIII)–(L) and the related compounds (LI)–(LIV), differing in the structure of the lactam fragment:[82]

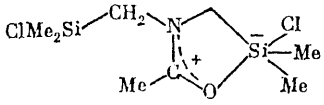


The Si atom has in fact an undistorted trigonal-bipyramidal [3 + 2]-coordination in the chloro-derivatives (L)–(LII) and an appreciably distorted, almost tetrahedral [4 + 1]-coordination in the iodo-derivative (XLVIII), the bromo-derivative (XLIX), the fluoro-derivative (LIV), and the chloro-derivative (LIII) with a modified bicyclic lactam system (Table 5).

The axial positions at the Si atoms are occupied in all the structures investigated by the O and X atoms and the equatorial positions are occupied by three C atoms. The Si–O distance in the axial O–Si–X fragments varies within very wide limits [from 1.749(2) Å in the iodo-derivative (XLVIII), which is close to the Si–O distances in compounds of tetrahedral silicon, for example, 1.690(5) Å in the 2,2′-dimethyl-5,10-dioxoanthra-[1,2-*e*]-1′,4′,2′-dioxasilin,[83] to 2.316–2.461(8) Å in the fluoro-derivative (LIV)]. The character of the lactam ring and the nature of the substituent also have a strong influence on the Si ← O interaction: the Si ← O distance in the chloro-derivatives varies from 1.954(2) Å in compound (L) to 2.425(4) Å in compound (LIII).[82,84]

It has been found that the stronger the Si ← O interaction, the weaker the Si–X interaction. Thus the Si–I distance in compound (XLVIII) is smaller by only 0.3 Å than the sum of the van der Waals radii of the Si and I atoms (4.08 Å [85]); on the other hand, in compound (LIV) the Si–F = 1.652 Å distance is close to the length of the Si–F covalent bond (1.55 Å) in derivatives of tetrahedral silicon.[37]

An increase in the size of the lactam ring [to the seven-membered ring in compound (LIII)] and the fusion with the latter of the benzene ring [as in compound (LII)] hardly influence the structure of the axial fragment. Thus the Si–O distances, amounting to 1.950(2) Å in compound (LII) and 1.989(4) Å in compound (LIII), differ little from the distance of 1.954(2) Å in compound (L). On the other hand, according to Onan et al,[86] the length of the Si–O bond in the related structure (LV), where there is no lactam ring, is appreciably smaller [1.918(3) Å] than in the lactam chloro-analogue (L) with a six-membered lactam ring [1.954(2) Å].



The replacement of the I atom by Br, Cl, and F in the series of compounds (XLVIII)–(L) and (LIV) entails, as it were, a "migration" of the Si atom along the O...X line from the O atom to the X atom relative to the plane of the three equatorial C atoms (Fig. 9). It is remarkable that in this migration the distance from the carbonyl O atom to the equatorial plane remains almost unaltered [2.097 Å in compound (XLVIII) and 2.109 Å in compound (LIII)].

The crystal of compound (LIV) (with a weak Si ← O interaction) is made up of four symmetrically independent molecules whose different environments lead to a difference between the geometrical parameters of the axial O–Si–F fragment. In particular, the Si ← O bond length changes appreciably, from 2.316 to 2.461(8) Å, although the Si–F bond length remains actually unaltered.

We may note yet again the unusual nature of the structure of compound (LIII). In contrast to the structures of compounds (L)–(LII), the Si–Cl distance in compound (LIII) is close to values typical for derivatives of tetrahedral silicon, while the Si ← O distance approaches the values observed in the fluoro-derivative

Table 5. The principal geometrical parameters of the molecules of *N*-(halogenodimethylsilylmethyl)lactams.

Compound	*l*, Å	*r*, Å	Δ*l*, %	Δ*r*, %	ω, deg	Δ, Å	n_0	n_X
(XLVIII)	1.749 (2)	3.734 (1)	7.3	51.8	161.90 (7)	0.348 (1)	0.82	0.12
(XLIX)	1.800 (4)	3.122 (2)	10.4	41.3	162.6 (6)	0.218 (2)	0.71	0.18
(L)	1.954 (2)	2.307 (2)	19.9	13.3	171.16 (5)	−0.058 (2)	0.46	0.55
(LI)	1.950 (2)	2.315 (1)	19.6	13.7	171.70 (7)	−0.055 (1)	0.47	0.53
(LII)*	1.989	2.313	22.0***	13.4***	172.06	−0.074 (1)	0.43	0.55
	1.990 (2)	2.305 (2)			170.67 (9)	−0.060 (1)		
(LIII)	2.425 (4)	2.148 (2)e	48.8	5.5	171.8 (1)	−0.451 (1)	0.16	0.79
(LIV)**	2.316	1.656	46.9***	6.6	172.8***	−0.238	0.17	0.73
	2.350	1.665				−0.305		
	2.451	1.658				−0.302		
	2.461 (8)	1.630 (7)				−0.297 (3)		

Note. Notation adopted: *l* is the Si–O bond length, *r* the Si–X bond length, Δ*l* and Δ*r* are the increments in *l* and *r* relative to the lengths of the covalent bonds of tetrahedral Si,[13,83] ω is the axial OSiX angle, Δ the shift of the Si atom from the equatorial plane in the direction towards the O atom, and n_0 and n_X are the Si–O and Si–X bond orders calculated as described by Allmann.[28]

* Data for two independent molecules are quoted.

** Data for four independent molecules are quoted.

*** The average value for independent molecules is quoted.

(LIV). It may be that this is caused by the conjugation of the unshared electron pair of the ether oxygen atom with the π-electron density of the carbonyl bond. A decrease in the size of the lactam ring [or its absence as in the structure (LIV)] is less significant.

A very large and concerted change in the lengths and orders of the O–Si and Si–X bonds is observed in compounds (XLVIII)–(LIV). It is also accompanied by the "inversion" of the coordination polyhedron of the Si atom, which makes it possible to regard the geometry of these compounds as a component part of the model of the hypothetical S_N2 reaction at the Si atom.

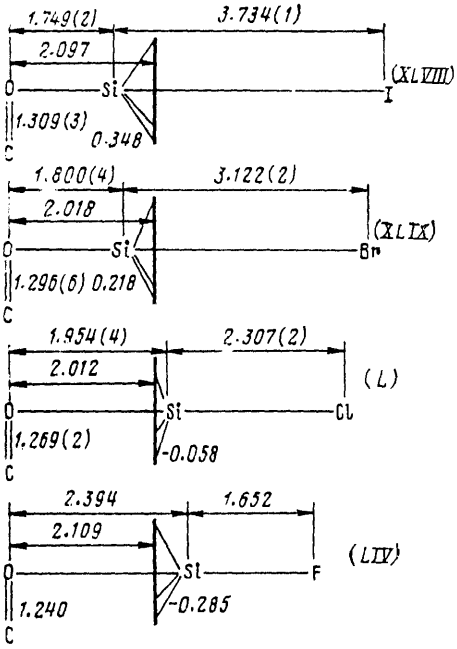
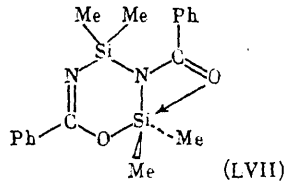


Figure 9. Variation of the coordination of the silicon atom as a function of the nature of the axial halogen atom in *N*-(halogenodimethylsilylmethyl)lactams. The plane of three equatorial C atoms is indicated by a bold line. The deviations of the Si atom from this plane and the lengths of the C=O carbonyl bond, diminishing in succession with intensification of the Si–O interaction, are indicated.[57,82]

strength.[88] The weak additional Si...O interaction in compound (LVII) is accompanied by an appreciable deviation of the O_a–Si...O_a angle from 180°, which amounts to 161°.



(LVII)

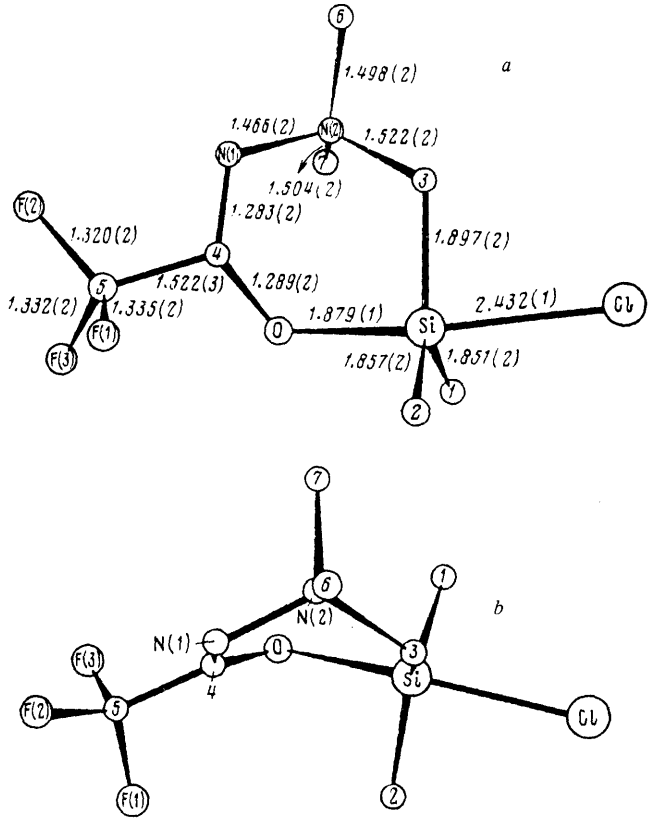


Figure 10. The structure of the molecule of compound (LVI): *a*, projection onto the average plane; *b*, projection onto the plane perpendicular to the average plane and passing through the N(1) and C(3) atoms.[87]

8. (O–Si)-Chloro-[1-(1,1-dimethyl-2-trifluoroacetylhydrazonium)methyl]dimethylsilane

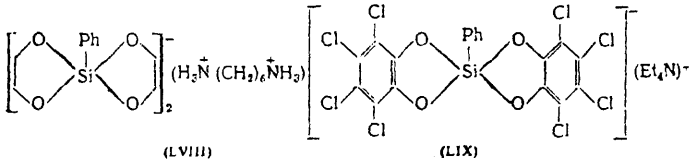
(O–Si)-Chloro-[1-(1,1-dimethyl-2-trifluoroacetylhydrazonium)-methyl]dimethylsilane (LVI) (Fig. 10) is the first example of a pentacoordinate silicon derivative in which the "additional" (coordinate) Si ← O bond is part of a six-membered, and not a five-membered, chelate ring.[87] Admittedly, in the molecule of compound (LVII) the pentacoordinate Si atom is also incorporated in a six-membered heterocycle, but in this case the additional O → Si interaction with the carbonyl group is very weak [the Si...O distance is 2.613(2) Å] and the endocyclic (second axial) Si–O bond is close to the usual covalent bond as regards length [1.670(2) Å] and

The coordination of the Si atom in compound (LVI), namely the [3 + 2]-coordination, is close to its coordination in the pentacoordinate silicon derivatives, examined above, with an axial O–Si–X fragment, where the O–Si bond is incorporated in a five-membered ring. The shift of the Si atom from the equatorial plane (in the direction towards the Cl atom) is very small [Δ_{Si} = 0.078(1) Å]. The lengthening of the Si–Cl axial bond [2.432(1) Å] relative to the "normal" Si–Cl = 2.048(1) Å bond in the H_3SiCl molecule[89] is somewhat greater than the increase in the

length of the Si–O = 1.879(1) Å axial bond relative to the Si–O = 1.68 Å "normal" bond in the molecule of 2′,2′-dimethyl-5,10-dioxoanthra[1,2-*e*]-1′,4′,2′-dioxasilin.[83] The O–Si–Cl angle is 172.20(5)°. However, despite the similarity of the coordination of the Si atom in compound (LVI) and in the lactam derivatives (L) and (LV), the Si ← O interaction in compound (LVI) is somewhat stronger, which may be caused by the greater electron density in the conjugated N⋯C⋯O fragment in compound (LVI).

9. Phenyl spirosilicates

The change in the coordination geometry of the Si atom in the cyclic anionic phenyl spirosilicates of type (LVIII) and (LIX) from that of a square pyramid (SP) to that of a trigonal bipyramid (TBP) makes it possible to trace the hypothetical path followed in the ligand rearrangement of the Berry pseudorotation type:[90]



(LVIII) (LIX)

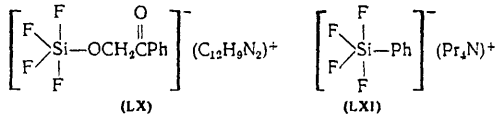
The coordination polyhedron of the Si atom in both phenyl spirosilicates, (LVIII) and (LIX), represents a distorted SP, although the structure of the latter is much closer to the ideal geometry.[91] This is indicated best by the *trans*-basal 1-Si-5 (θ_{15}) and 2-Si-4 (θ_{24}) angles which are closer to one another in compound (LIX) [152.9° and 147.3(2)°] than in compound (LVIII) [159.2° and 143.6(1)°] (Fig. 11). The Si–O bond lengths in these compounds also indicate that the coordination polyhedron of the Si atom in compound (LIX) is closer to the ideal SP. If the structure of compound (LVIII) is described as a TBP, then the average lengths of the axial and equatorial Si–O bonds should be 1.748(3) and 1.701(3) Å respectively. The corresponding values for the spirosilicate (LIX) are 1.756(6) and 1.752(6) Å, i.e. they are identical within the limits of the error of the determination. In compound (LIX), the four atoms forming the basal plane of the SP are coplanar to within 0.05 Å with the Si atom displaced from this plane in the direction of the apical C atom. The Si–C distances in compounds (LVIII) and (LIX), amounting to 1.854(4) and 1.883(3) Å, are close to the values typical for tetrahedral silicon derivatives.[84]

For a more rigorous quantitative description of the structural distortions in related compounds, the dependence of the *trans*-basal angles θ_{15} and θ_{24} in the SP (which become the axial and equatorial angles respectively in the TBP) on the angle δ_{24} between the normals to the (124) and (245) faces of the TBP with a common equatorial edge (24) was examined.[85] The above dihedral angle, which can be regarded as a coordinate of the Berry pseudorotation, is 53.1° in the ideal TBP and becomes zero when the (24) edge in the SP vanishes.

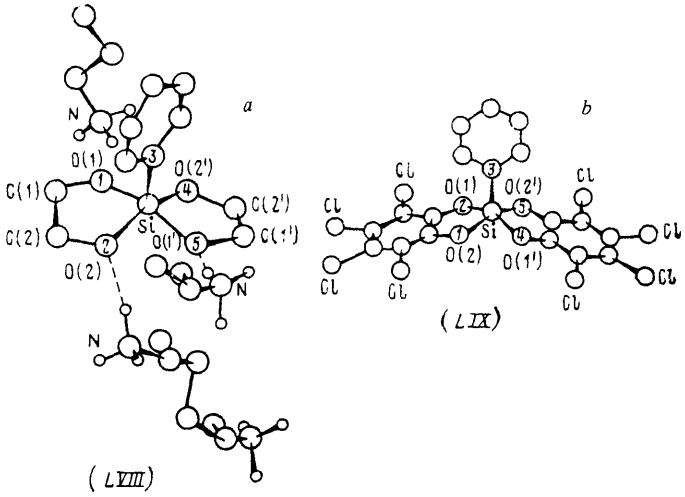
The results of the application of the method of the sums of the dihedral angles[92] to the estimation of the geometrical distortion of the molecules of pentacoordinate silicates have been published.[91] This method makes it possible to estimate (in percentages) the degree of transition of the real structure from the TBP to the SP. For example, the degrees of the TBP → SP transition are 72.1 and 89.8% respectively for compounds (LVIII) and (LIX).

10. Organyl tetrafluorosilicates

The Si atoms in both compounds of this class whose structures have been investigated, 1,10-phenanthrolinium benzoyloxymethyltetrafluorosilicate (LX) [93] and tetrapropyl-ammonium phenyltetrafluorosilicate (LXI),[94] form similar trigonal-pyramidal systems with the organic ligands in the equatorial positions:



(LX) (LXI)



(LVIII) (LIX)

Figure 11. The structure of the anions (LVIII) (*a*) and (LIX) (*b*).[91]

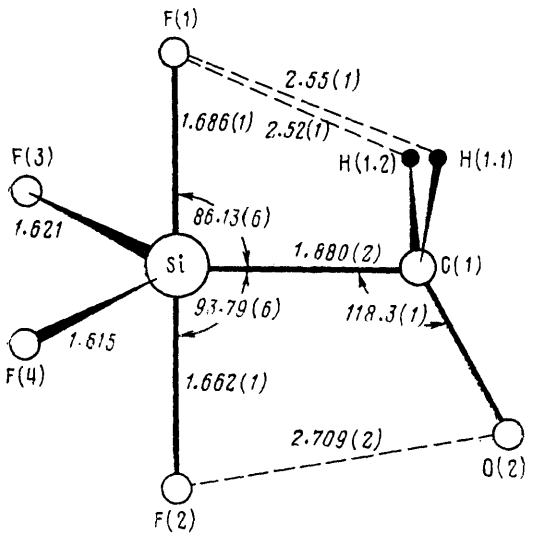
The Si–F axial bonds [1.686 and 1.662(1) Å] in compound (LX) are longer by 0.05–0.06 Å than the equatorial bonds [1.615 and 1.621(1) Å]. Approximately the same picture is observed also in the anion of compound (LXI), where the difference is 0.067 Å. The axial Si–F distances in the anions of compounds (LX) and (LXI) are also greater than in the derivatives of hexacoordinate silicon (see below). For example, the Si–F_a bond length in dipyridinesilicon tetrafluoride is 1.656(3) Å, while the Si–F_e bond length is 1.630(2) Å.[95]

The Si–F = 1.602(2) Å axial bond in compound (XLIV) is also longer than the equatorial bonds [1.582 and 1.585(2) Å], but the difference is smaller than in the anions of compound (LX) and (LXI). Overall, the Si–F distances in compound (LXIV) are appreciably shorter than in the anions of compounds (LX) and (LXI), although they do in fact exceed the Si–F distances in derivatives of tetrahedral silicon [for example, 1.56 Å in SiF_4 or 1.55(1) Å in $F_3SiOSiF_3$ [93]].

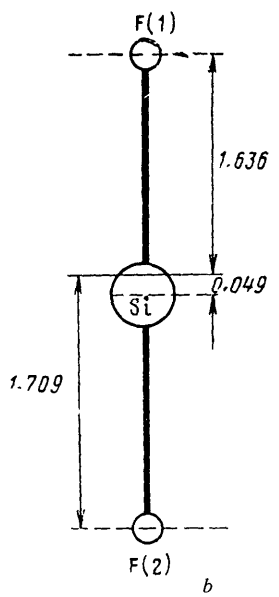
The F(1)–Si–F(2) group in the anion of compound (LX) is actually linear [the F(1)SiF(2) angle is 179.74(5)°]. On the other hand, owing to the presence of non-valence contacts of the type $F_a \ldots$ H-*o*(Ph) as in the anion of compound (LXI) (2.48 and 2.55 Å, while the sum of the van der Waals radii of F and H is 2.67 Å [40]), the F_aSiF angle in this species is 174.6(2)°, as in the molecule of the compound $PhPF_4$ isoelectronic with compound (LXI) (174.0°).[96]

The non-valence contacts F(1)...H in the anion of compound (LX) (Fig. 12*a*) lead to the appearance of the eclipsed orientation of the Si–F(2) and C(1)–O(2) bonds [the torsional angle

F(2)SiC(1)O(2) is 3.29(9)°]. However, such coordination of the anion of compound (LX) promotes in its turn the appearance of a short F(2)...O(2) contact [2.709(2) Å], while the sum of the van der Waals radii of O and F is 2.99 Å,[40] which induces an increase in the F(2)SiC(1) and SiC(1)O(2) valence angles. The latter can be interpreted as a shift of the Si atom from the equatorial plane (Fig. 12*b*). On the other hand, the shift of the Si atom in the direction of the F(2) atom intensifies the non-valence interactions with participation of the F(1) atom, which increases the Si–F(1) distance.



a



b

Figure 12. The coordination environment of the Si atom in the anion (LX) (*a*) and the shifts of the F(1), Si, and F(2) atoms from the equatorial plane passing through the F(3), F(4), and C(1) atoms (continuous horizontal line) (*b*).[93]

11. Complexes of the three-centre Mn–H–Si bond

The oxidative addition of the silanes $HSiR_3$ to the 16-electron coordinatively unsaturated manganese complex $C_5R_5(CO)(L)Mn$ [R = H, or Me; L = CO, PR_3, $P(OR)_3$, or CNR] leads to the formation of the compounds $C_5R_5(CO)(L)Mn(H)SiR_3$ with the two-electron three-centre bond Mn–H–Si. They can be regarded as "frozen" intermediates in this reaction.[97]

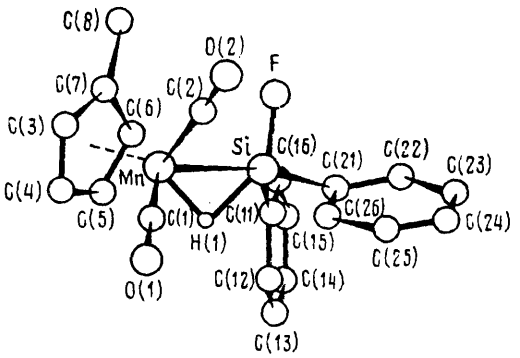


Figure 13. The structure of the molecule of compound (LXII).[99]

In complexes of this type, the "agostic" H atom[98] occupies a bridging position between the Mn and Si atoms. In the structure of the compound $C_5H_4Me(CO)_2Mn(H)SiFPh_2$ (LXII), the Mn–H(1) and Si–H(1) distances are 1.569(4) and 1.802(5) Å respectively according to neutron diffraction data (Fig. 13).[99] The observed Si–H(1) distance is appreciably smaller than the sum of the van der Waals radii of the Si and H atoms (about 3.20 Å [40,85]) and exceeds by only ~0.40 Å the length of the covalent Si–H bond, which is 1.40 ± 0.02 Å according to electron diffraction and microwave spectroscopic data for tetrahedral silane derivatives. The Mn–H(1) distance in compound (LXII) was actually found to be somewhat smaller than the Mn–H = 1.601(16) Å distance in $(CO)_5Mn–H$, where H is the terminal ligand.[100] The Mn–Si = 2.352(4) Å distance in compound (LXII) corresponds to approximately the middle of the range of variation of the Mn–Si distances [2.254(1)–2.461(7) Å] in complexes of the type $MeC_5H_4(CO)_2Mn(H)SiR_3$ with the three-centre Mn–H–Si system.[99]

Owing to the Mn–H–Si interaction indicated above, the Si atom in the complex (LXII) requires quinary coordination. The coordination polyhedron of the Si atom can be described as a strongly distorted trigonal bipyramid with the H(1) and F atoms in the axial positions [the H(1)SiF valence angle is 148.8(2)°] and the Mn, C(11), and C(21) atoms (see Fig. 13) in the equatorial positions [MnSiC(11) = 115.8(1)°, MnSiC(21) = 117.3(1)°, and C(11)SiC(21) = 109.0(1)°]. The absence of an appreciable lengthening of the axial Si–F bond in compound (LXII) [1.634(3) Å compared with 1.624(2) Å in $C_5H_5(CO)_2FeSiFPh_2$ [99]] does not conflict with such a description in view of the large difference between the electronegativities of the apical H and F atoms.

Comparison of the adduct (LXII) with the related complexes $C_5Me_5(CO)_2Mn(H).SiR_3$ shows that, if the substituents R shorten the Mn—Si distance, then the Mn—H distance also diminishes, while the Si—H distance increases slightly. The oxidative addition of the silane $HSiR_3$ to the $C_5Me_5(CO)_2Mn$ fragment proceeds tentatively in accordance with the scheme

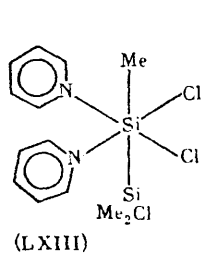
$$L_nMn + \overset{H}{\underset{SiR_3}{\diagdown\!\diagup}} \rightleftarrows L_nMn\cdots H\cdots SiR_3 \rightleftarrows L_nMn\cdots H\cdots SiR_3 \rightleftarrows L_nMn\overset{H}{\underset{SiR_3}{\diagdown\!\diagup}}.$$

It agrees with the observed changes in the distances between the Mn, H, and Si atoms in the series of complexes of type (LXII).

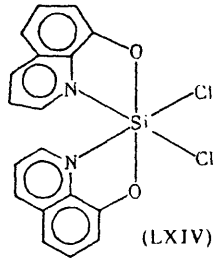
V. Compounds of silicon with coordination numbers of six and above

1. Derivatives of hexacoordinate silicon

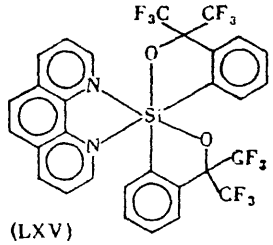
Only three examples of organosilicon compounds with a hexacoordinate silicon atom whose structures have been confirmed are known [compounds (LXIII)—(LXV)].[102-104] Their structure provides important information for the understanding of the structures of the intermediates formed as a result of the wide variety of reactions of organosilicon compounds.



(LXIII)



(LXIV)



(LXV)

According to the hypervalent bonding model, the silicon atom in a hexacoordinate state forms two covalent and two three-centre four-electron bonds.[3] Its coordination polyhedron is therefore an octahedron with four equatorial bonds longer than the axial bonds.

Table 6 shows that the equatorial bonds in compounds (LXIII) and (LXIV) are indeed lengthened compared with the corresponding bonds of tetrahedral silicon, relative to the axial bonds. However, in compound (LXV) the situation is more complicated: the increase in the length of the equatorial and axial bonds is almost the same in this instance. This structure can be described as a trigonal bipyramid with the phenanthroline ligand occupying one coordination site. This treatment agrees with the ability of the complex (LXV) (according to ^1H NMR data) to undergo enantiomeric and diastereoisomeric transformations in solution as a result of the dissociation of the Si—N bond with the phenanthroline ligand.[104]

In contrast to compounds of pentacoordinate silicon, whose coordination can be in most cases described approximately as of the [4 + 1] type with only one lengthened axial bond (for example the Si ← N bond in silatranes), an increase in the length of four [compound (LXIII)], three [compound (LXIV)], or two [compound (LXV)] equatorial bonds has been observed in compounds of hexacoordinate silicon.

Table 6. The lengths of the bonds involving the Si atom in its hexacoordinate derivatives (LXIII)—(LXV) [102-104] and the difference between them and the lengths of the bonds involving tetrahedral silicon.

Compound	Axial bond	*l*, Å	Δ, Å	Equatorial bond	*l*, Å	Δ, Å
(LXIII)	Si—Si	2.367	0.03	Si—Cl	2.274	0.24
	Si—C	1.888	0.02		2.392	0.36
				Si—N	2.007	0.28
					2.029	0.30
(LXIV)	Si—O	1.763	0.08	Si—Cl	2.199	0.17
		1.766	0.09	Si—N	2.016	0.29
					2.014	0.28
				Si—C	1.940	0.07
(LXV)	Si—O	1.772 (7)	0.09	Si—O	1.772 (7)	0.09
	Si—C	1.93 (1)	0.06	Si—N	2.051 (9)	0.33
					2.089 (9)	0.36
				Si—C	1.91 (1)	0.04

Note. Typical lengths of the bonds involving tetrahedral silicon: Si—Si = 2.34 Å,[1] Si—Cl = 2.03 Å,[89] Si—N = 1.73 Å,[66] Si—O = 1.68 Å,[81] and Si—C = 1.87 Å.[1] The subdivision into axial and equatorial bonds is based on the literature data.[102-104]

2. The cluster $[Co_9Si(CO)_{21}]^{2-}$

The great possibilities inherent in the silicon atom as regards coordination can be illustrated in relation to the cobalt carbonyl cluster $[Co_9Si(CO)_{21}]^{2-}$ with an encapsulated silicon atom (Fig. 14).[105] Nine cobalt atoms form a one-cap tetragonal antiprism with the Si atom occupying a cavity within the latter. Eight Si—Co distances are in the range usual for Si—Co bond lengths [cf. 2.299(2) Å]. The Si—Co(1) distance to the atom of the cap is much greater [2.527(4) Å] and can correspond only to a weak interaction. The distances between the cobalt atoms, Co(1)—C(2) = 2.613 Å, Co(2)—Co(2′) = 2.940 Å, Co(2)—Co(3) = 2.688 Å, Co(2)—Co(3′) = 2.593 Å, and Co(3)—Co(3′) = 2.808(1) Å, indicate an appreciable expansion of the core made up of the Co atoms when the Si atom is incorporated in it. The cavity within the regular square antiprism made up of Co atoms (the covalent radius of cobalt is 1.35 Å) has a radius of ~0.85 Å, which is much less than the covalent radius of the Si atom (1.12 Å) [sic]. It is not surprising that the attempt to obtain an analogous cluster with encapsulation of the larger Ge atom (r_{Ge} = 1.22 Å) was unsuccessful.[106] On the other hand, the C atom, whose size is smaller (r_C = 0.77 Å) forms a stable encapsulated square-antiprismatic cluster $(Co_8C(CO)_{18}]^{2-}$, in which the Co—Co distances are 2.47—2.59 Å.[107]

3. Sandwich complexes of silicon

Unexpected results have been obtained in an X-ray diffraction study of the recently synthesised decamethylsilicocene $(C_5Me_5)_2Si$ (LXVI).[108] This is the first silanediyl which is stable under the usual conditions and the first π-complex with a central silicon atom. In the crystal of compound (LXVI), there are two crystallographically independent molecules of A and B (A : B = 1 : 2, Fig. 15). One of them is at the centre of symmetry and the other is in a common position (space group $C2/c$, $Z = 12$). In the A molecule, the pentamethylcyclopentadienyl rings are antiparallel, i.e. are in the crossed conformation. On the other hand, in the B molecule the rings form a dihedral angle of 25.3° whilst retaining the crossed conformation. Whereas the Si–C distances in the A ring are equalised [cf. 2.42(1) Å], in the B molecule they are unequal and amount to 2.324(8) Å [Si(2)–C(22) and Si(2)–C(28)], 2.526(7) Å [Si(2)–C(25)], and 2.541(7) Å [Si(2)–C(26)]. The approximate intrinsic symmetry of this molecule is C_{2h}. On the other hand, the distances from the Si atoms to the centres of the C_5Me_5 rings in the A and B molecules are very close (2.11 and 2.12 Å). The character of the disposition of the molecules in the crystal of compound (LXVI) shows that the non-parallel arrangement of the C_5Me_5 rings in the B molecule is caused by intermolecular interactions.[108]

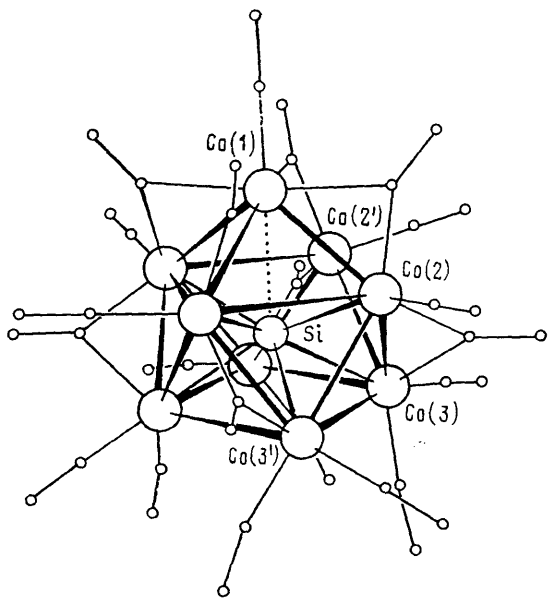


Figure 14. The structure of the anion $[Co_9Si(CO)_{21}]^{2-}$.[105] The Si–Co(1) vector coincides with the fourfold crystallographic axis.

It is of interest that bis[(1,2,4-trimethylsilyl)cyclopentadienyl]-germanium (LXVII) also exists in the crystal as two conformers[109] in which the Cp–Ge–Cp angles of similar size differ little from the linear angle of 180° (by 10.5 and 8.2° respectively). The Ge–Cp distances (Cp corresponds to the centre of the ring) are also almost identical (2.250–2.256 Å) and the Ge–C distances differ very little for all four unsubstituted Cp rings (2.556–2.574 Å).

Using the EENY2 program, the conformational energy of the molecule of compound (LXVII) was calculated by varying the Cp–Ge–Cp angle, the Ge–Cp–C angles of inclination, and the orientations of the rings and $SiMe_3$ groups.[109] It was found that the conformation arising in the crystal does indeed have a low energy, which, however, does not have a distinct minimum. Thus one cannot rule out the possibility of certain changes in the molecular geometry of compound (LXVII) under the influence of the crystal field.

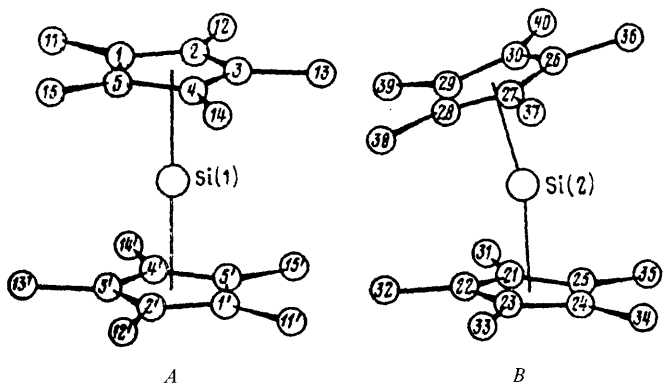


Figure 15. The structure of the crystallographically independent molecules of compound (LXVI) in the crystal:[108] *A*, at the centre of symmetry; *B*, in the common position.

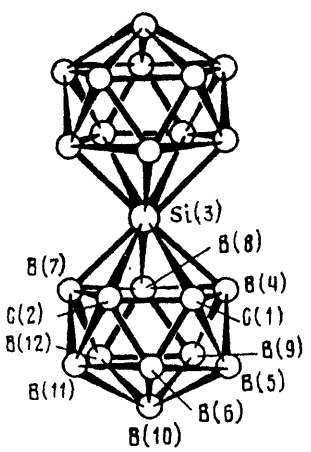


Figure 16. The structure of the centrosymmetrical molecule of compound (LXVIII).[110]

A second confirmation of the possibility of the existence of stable silicon π-complexes has been provided by an X-ray diffraction study of a sandwich derivative of *o*-carbaborane—*commo*-3,3-Si-(1,2-$C_2B_9H_{11}$) (LXVIII) (Fig. 16).[110] The molecule of compound (LXVIII) is centrosymmetrical and the Si(3) atom is

therefore separated by equal distances from the planes of both antiparallel five-membered C_2B_3 rings to which it is coordinated but is displaced relative to their centres towards the B(8) and B(8′) atoms: Si–B(8) = 2.05(1) Å, Si–B(4) and Si–B(7) = 2.14(1) Å, and Si–C(1) and Si–C(2) = 2.22(1) Å. Thus the Si–C distances in compound (LXVIII) are appreciably smaller than in compound (LXVI).

A model has been proposed for the bonding of the Si atom to the dicarbaboryl ligands in compound (LXVIII).[111] At the instant of bonding, these ligands are characterised by the presence of a combination of occupied ligand orbitals (LO): a_g, a_u, e_{1g}, and e_{1u}. The ligand orbitals e_{1u} are suitable as regards symmetry for the π-type bonding interaction with the silicon atomic orbitals (AO) p_x and p_y, while the a_u LO undergoes a σ-type interaction with the p_z AO of the Si atom. If the participation of the silicon *d* AO in bonding is postulated, then the silicon d_{xz} and d_{yz} AO have a symmetry suitable for a π-type overlap with the e_{1g} LO. On the other hand, if the difference between the energies of these AO and LO is large, the two electron pairs of the Si atom remain non-bonding and the ligand electrons remain in the e_{1g} LO. Finally, either the combination of the silicon *s* and d_{z^2} AO or only the *s* AO can interact with the a_g LO, which leads to σ-bonding.

VI. Conclusion

During recent years, extensive information has been obtained about the structure of a wide variety of organosilicon compounds in which a coordination of silicon other than the tetrahedral is realised. Silatranes have been undoubtedly most thoroughly investigated among these compounds. We have obtained recently data on the structure of *N*-(halogenodimethylsilylmethyl)lactams. On the other hand, other classes of compounds of non-tetrahedral silicon have been studied inadequately and are represented by one–two structures.

It is remarkable that the interpretation of the structures of organic silicon compounds with a non-trivial geometry of the Si atom (disilaphosphorane ylides, the complex of silaethylene with THF, and others) is difficult without resorting to the idea of $p_\pi - d_\pi$ bonding with participation of the *d* orbitals of the Si atom. On the other hand, if one uses the results of a precise study of the distribution of electron density, as was done for 1-(trichlorosilyl)-1,2,3,4-tetrahydro-1,10-phenanthroline and 1-fluorosilatrane, then there is no need to consider the *d* orbitals of the pentacoordinate Si atom in order to explain the mechanism of the formation of bonds with its participation.

Analysis of the geometry of compounds with an expanded coordination of the Si atom as intermediates in chemical reactions provides information of greatest chemical interest. The structural correlations of a series of compounds examined have been investigated to different extents. They have been studied in greatest detail for *N*-(halogenodimethylsilylmethyl)lactams (S_N2 reactions) and phenyl spirosilicates (Berry pseudorotation).

Thus structural studies on derivatives of non-tetrahedral silicon not only deepen our ideas about the coordination and valence possibilities of this element but are also of definite general importance for the modelling and mapping of reaction pathways.

References

1. V E Shklover, Yu T Struchkov *J. Organomet. Chem.*, 1987, **322** 269
2. V E Shklover, Yu T Struchkov *Advances in Organosilicon Chemistry* (Edited by M G Voronkov), Mir, Moscow, 1985, 11
3. S N Tandura, M G Voronkov, N V Alekseev *Topics in Current Chemistry*, Springer, Heidelberg, 1986, Vol. 131, p. 101
4. P Hencsei, L Parkanyi *Reviews on Silicon, Germanium, Tin and Lead Compounds* (Edited by M Gielen), Freund Publishing House, Tel-Aviv, 1985, p. 191
5. R West, M J Fink, M J Michalczyk, D J De Yung *Organosilicon Biorganic Chemistry* (Edited by H N Y Sakurai), John Wiley and Sons, 1985, p. 3
6. A G Brook *Organosilicon Biorganic Chemistry* (Edited by H N Y Sakurai), John Wiley and Sons, 1985, p. 15
7. A Wiberg *Organosilicon Biorganic Chemistry* (Edited by H N Y Sakurai), John Wiley and Sons, 1985, p. 25
8. N Wiberg, G Wagner, G Müller *Angew. Chem. Int. Ed. Engl.*, 1985, **24** 229
9. N Wiberg, G Wagner, G Müller, J Riede *J. Organomet. Chem.*, 1984, **271** 381
10. A G Brook, S C Nyburg, F Abdesaken, et al. *J. Am. Chem. Soc.*, 1982, **104** 5667
11. H F Schaefer *Acc. Chem. Res.*, 1982, **15** 283
12. Yu E Ovchinnikov, V E Shklover, Yu T Struchkov, et al. *Zh. Strukt. Khim.*, 1986, **27**(6) 125
13. V E Shklover, Yu T Struchkov *Uspekhi Khim.*, 1980, **49**(3) 518 [English translation in *Russ. Chem. Rev.*, 1980(3)]
14. V E Shklover, Yu T Struchkov, N M Kudyakov, M G Voronkov *J. Organomet. Chem.*, 1986, **303** 83
15. Yu E Ovchinnikov, B E Shklover, Yu T Struchkov, et al. *Z. Anorg. Allg. Chem.*, 1985, **523** 14
16. V E Shklover, Yu T Struchkov, M M Levitskii, A A Zhdanov *Zh. Strukt. Khim.*, 1986, **27**(6), 120
17. M J Fink, M J Michalczyk, K J Haller, et al. *Chem. Commun.*, 1983, 1010
18. R West, M J Fink, J Michl *Science*, 1981, **214** 1343
19. S G Baxter, K Mislow, J F Blount *Tetrahedron*, 1980, **36** 605
20. P B Hitchcock, M F Lappert, S J Miles, A J Thorne *Chem. Commun.*, 1984, 480
21. M J Fink, M J Michalczyk, K J Haller, et al. *Organometallics*, 1984, **3** 793
22. R Daubel, R E Kari, R A Poirier, et al. *J. Mol. Struct.*, 1978, **50** 115
23. R A Poirier, J D Goddard *Chem. Phys. Lett.*, 1981, **80** 37
24. T Fjeldberg, A Haaland, M F Lappert, et al. *Chem. Commun.*, 1982, 1407
25. L Pauling *Proc. Natl. Acad. Aci. USA*, 1983, **80** 3871
26. G Fritz, U Braun, W Schick, et al. *Z. Anorg. Allg. Chem.*, 1981, **472** 45
27. N G Bokii, Yu T Struchkova, A E Kalinin, et al. *Kristallokhimiya. Itogi Nauki i Tekhniki* (Crystal Chemistry. Advances in Science and Engineering), Izd. VINITI, Moscow, 1977, p. 56
28. R Allmann *Monatsh. Chem.*, 1975, **106** 779
29. W Hönle, G Schnering *Z. Anorg. Allg. Chem.*, 1978, **464** 171
30. N H Buttrus, C Eaborn, S H Gupta, et al. *Chem. Commun.*, 1986, 1043
31. R West, D J De Yong, K J Haller *J. Am. Chem. Soc.*, 1985, **107** 4942

32. S Masamume, S Murakami, H Tobita *J. Am. Chem. Soc.*, 1983, **105** 7776
33. M Ishikawa, M Sugisawa, T Higuchi, et al. *Organometallics* 1983, **2** 174
34. S Musamume, T Hanazawa, S Murakami, et al. *J. Am. Chem. Soc.*, 1982, **104** 1150
35. A Schäfer, M Weidenbruch, K Peters, H G V Schnering *Angew Chem. Int. Ed. Engl*, 1984, **23** 302
36. N Wiberg, H Schuster, A Simon, K Peters *Angew Chem. Int. Ed. Engl.*, 1986, **25** 79
37. R Jones, D J Williams, Y Kabe, S Mesamune *Angew. Chem. Int. Ed. Engl.*, 1986, **25** 173
38. M J Fink, K J Haller, R West, J Michl *J. Am. Chem. Soc.*, 1984, **106** 822
39. M J Michalczyk, M J Fink, K J Haller, et al. *Organometallics*, 1986, **5** 531
40. A Bondi *J. Phys. Chem.*, 1964, **68** 441
41. W E Schklover, Y T Strutschkow, L E Guselnikov, et al. *Z. Anorg. Allg. Chem.*, 1983, **501** 153
42. V E Shklover, R Ad'yasuren, G V Kotrelev, et al. *Zh. Strukt. Khim.*, 1980, **21** 94
43. T Halder, W Schwarz, J Weidlein, P Fischer *J. Organomet. Chem.*, 1983, **246** 29
44. Yu V Ovchinnikov, V E Shklover, Yu T Struchkov, et al. *J. Organomet. Chem.*, 1988, **347** 33
45. V E Shklover, Yu T Struckhov, O G Rodin, et al. *J. Organomet. Chem.*, 1984, **266** 117
46. V E Shklover, Yu E Ovchinnikov, Yu T Struchkov, et al. *J. Organomet. Chem.*, 1986, **301** 273
47. Yu E Ovchinnikov, V E Shklover, Yu T Struchkov, et al. *J. Organomet. Chem.*, 1985, **290** 25
48. M J Barrow, E A V Ebsworth *J. Chem. Soc., Dalton Trans.*, 1982, 211
49. R Rudman, W C Hamilton, S Novick, T D Goldfarb *J. Am. Chem. Soc.*, 1967, **89** 5157
50. S Sujishi, S Witz *J. Am. Chem. Soc.*, 1954, **76** 4631
51. A J Blake, E A V Ebsworth, A J Welch *Acta Crystallogr., Sect. C*, 1984, **40** 895
52. H-H Bürgi *Inorg. Chem.*, 1973, **12** 2321
53. H-H Bürgi *Angew. Chem., Int. Ed. Engl.*, 1975, **14** 460
54. D G Anderson, A J Blake, S Cradock, et al. *Angew. Chem., Int. Ed. Engl.*, 1986, **25** 107
55. G Sawtzki, H G Schnering *Chem. Ber.*, 1976, **109** 3728
56. U Kliebisch, D Starke, H G Sheldrick *Angew. Chem., Int. Ed. Engl.*, 1986, **25** 915
57. A A Macharashvili, Yu I Baukov, E P Kramarova, et al. *Zh. Strukt. Khim.*, 1987, **28**(4) 107
58. L Parkanyi, P Hencsei, L Bitatsi *J. Organomet. Chem.*, 1982, **232** 315
59. A A Macharashvili, V E Shklover, V P Struchkov, V P Baryshok *Dokl. Akad. Nauk SSSR*, 1987, **297** 1123
60. A A Macharashvili, V E Shklover, Yu T Struchkov, E Likevics *J. Organomet. Chem.*, 1988, **349** 23
61. L Parkanyi, K Simon, J Nagy, *Acta Crystallogr., Sect. B*, 1974, **30** 2328
62. J W Turley, F F Boer *J. Am. Chem. Soc.*, 1968, **90** 4026
63. L Parkanyi, J Nagy, K Simon *J. Organomet. Chem.*, 1975, **101** 11
64. Yu E Ovchinnikov, T G Kovyazina, V E Shklover, et al. *Dokl. Akad. Nauk SSSR*, 1987, **297** 108
65. L Parkanyi, P Hencsei, L Bitatsi, et al. *Polyhedron*, 1985, **4** 243
66. C Glidewell, D W H Rankin, A G Robiette, G M Sheldrick *J. Mol. Struct.*, 1970, **6** 231
67. K Jurkschat, A Tzschach, J Meunier-Piret, et al. *J. Organomet. Chem.*, 1986, **317** 147
68. L O Atovmyan, J. Bleidelis, A Kemme, R P Shibaeva *J. Organomet. Chem.*, 1970, **11** 318
69. S N Gurkova, S N Tandura, A V Kisin *Zh. Strukt. Khim.*, 1982, **23**(4) 101
70. V E Shklover, Yu T Struchkov, N S Sorokin, M G Voronkov *Dokl. Akad. Nauk SSSR*, 1984, **274** 615
71. M P Demidov, V E Shklover, Yu L Frolov et al. *Zh. Strukt. Khim.*, 1985, **26**(4) 103
72. V E Shklover, M P Demidov, E A Zelbst, et al. *VII International Meeting on Organosilicon Chemistry: Abstracts*, Kyoto, 1984, p. 243
73. A A Kemme, J Bleidelis, V A Pestunovich, et al. *Dokl. Akad. Nauk SSSR*, 1978, **243** 688
74. L Parkanyi, P Hencsei, L Bitatsi, T Müller *J. Organomet. Chem.*, 1984, **269** 1
75. Z Najue, L Yumin *International Symposium on Molecular Structure: Chemical Reactivity and Biological Activity: Abstracts*, China, 1986, p. 272
76. E Kupce, E Liepins, E Lukevics *J. Organomet. Chem.*, 1983, **258** 131
77. E B Chuklanova, A I Gusev *Zh. Strukt. Khim.*, 1987, **28**(6) 147
78. G Klebe, J W Bats, H Fuess *J. Am. Chem. Soc.*, 1984, **106** 5202
79. A Kvick, R Thomas, T F Koetzle *Acta Crystallogr., Sect. B*, 1976, **32** 224
80. E A Zel'bst, V E Shklover, Yu T Struchkov, et al. *Dokl. Akad. Nauk SSSR*, 1981, **259** 1369
81. E A Zel'bst, V E Shklover, Yu T Struchkov, et al. *Zh. Struct. Khim.*, 1981, **22**(3) 82
82. V E Shklover, A A Macharashvili, Yu E Ovchinnikov, Yu T Struchkov *X European Crystallographic Meeting: Abstracts*, Wroclaw, 1986, p. LA-09
83. Yu E Ovchinnikov, V E Shklover, Yu T Struchkov, et al. *Zh. Strukt. Khim.*, 1986, **27**(6) 125
84. A A Macharashvili, Yu I Baukov, E P Kramarova, et al. *Zh. Strukt. Khim.*, 1987, **28**(5) 114
85. A Bondi *J. Phys. Chem.*, 1986, **70** 3006
86. K D Onan, A T McPhail, C H Yoder, R W Hillard *Chem. Commun.*, 1978, 209
87. A A Macharashvily, V E Shklover, Yu T Struchkov, et al. *J. Organomet. Chem.*, 1987, **340** 23
88. F P Boer, F P Van-Remoortere *J. Am. Chem. Soc.*, 1970, **92** 801
89. L V Vilkov, V S Mastryukov, N I Sadova *Opredelenie Geometricheskoi Struktury Svobodnykh Molekul* (Determination of the Geometrical Structure of Free Molecules), Izd. Khimiya, Moscow, 1978, p. 184
90. R S Berry *J. Chem. Phys.*, 1960, **32** 933
91. R R Holmes, R O Dau, J J Harland, et al. *Organometallics*, 1984, **3** 341
92. R R Holmes, J A Deiters *J. Am. Chem. Soc.*, 1977, **99** 3318
93. V E Shklover, Yu T Struchkov, L I Gubanova, M G Voronkov *Zh. Strukt. Khim.*, 1987, **28**(1) 118

94. D Schomburg *J. Organomet. Chem.*, 1981, **221** 137
95. A D Adley, P H Bird, A R Fruser, M Onyszcuk *Inorg. Chem.*, 1972, **11** 1402
96. C Ditterbrandt, H Oberhammer *J. Mol. Struct.*, 1980, **63** 227
97. J L Speier *Adv. Organomet. Chem.*, 1979, **17** 407
98. M Brookhart, M L H Green *J. Organomet. Chem.*, 1983, **250** 395
99. B Wörle *J. Organomet. Chem.*, 1986, **306** 303
100. S J La Placa *Inorg. Chem.*, 1969, **8** 1928
101. U Schubert, G Kraft, E Walter *Z. Anorg. Allg. Chem.*, 1984, **519** 96
102. G Sawitzky, H G Schnering *Chem. Ber.*, 1976, **109** 3728
103. G Klebe, D T Qui *Acta Crystallogr., Sect. C*, 1984, **40** 476
104. W B Farnham, J F Whitney *J. Am. Chem. Soc.*, 1984, **106** 3992
105. K M Mackay, B K Nicholson, W T Robinson, A W Sims, *Chem. Commun.*, 1984, 1276
106. R Groft, D N Duffy, B K Nicholson *J. Chem. Soc., Dalton Trans.*, 1982, 1023
107. V G Albano, P Chini, S Martinengo, M Sansoni *J. Chem. Soc., Dalton Trans.*, 1978, 463
108. P Jutzi, D Kanne, C Krüger *Angew. Chem., Int. Ed. Engl.*, 1986, **25** 184
109. P Jutzi, E Schlüter, M B Hursthouse, et al. *J. Organomet. Chem.*, 1986, **299** 285
110. W S Rees, D M Schubert, C B Knobler, M F Hawthorne *J. Am. Chem. Soc.*, 1986, **108** 5369
111. N S Hosmane, P de Meester, U Siriwardane, et al. *Chem. Commun.*, 1986, 1421

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Factors that determine the reactivity of reactants in normal and catalysed Diels–Alder reactions

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ABSTRACT. The effects of intermolecular stabilisation, the energies of the reacting bonds, and the geometry of the reactants on their reactivity in normal Diels–Alder reactions and those catalysed by Lewis acids have been analysed. The main causes of the small ($1–10^2$ times) or large ($10^4–10^9$ times) increase in the rate of the process in the presence of catalysts and the conditions for synthesising products which often cannot be obtained when the reaction is carried out in the absence of a catalyst are examined.
The bibliography includes 190 references.

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I. Introduction

The increased interest in the Diels–Alder reaction is due both to the considerable synthetic possibilities of using it to obtain various carbocyclic and heterocyclic compounds[1–22] and the high reliability of the quantitative data obtained, which are used as a basis for establishing and verifying many theoretical concepts in organic chemistry.[14–18]

A large amount of information on the kinetics and thermochemistry of the Diels–Alder reaction and the effect of the medium on the enthalpy levels of the reactants, molecular complexes, transition states, and reaction products has been collected. At the present time it is clear that the activity of the addends in the Diels–Alder reaction cannot be accounted for by relying solely on information about the energy of frontier orbitals, namely, using a simple model of molecular orbital perturbation. A large amount of experimental material on the enthalpy of reaction has been collected. With this it is possible to determine the relationship between the activity of the addends and the stability of the adducts and to select the optimum conditions for concurrent displacement of one of the reactants from the reaction adducts. Furthermore, the difference in enthalpies of molecular Diels–Alder reactions primarily reflects the difference in energies of the reacting π-bonds. From this it is possible to understand many "anomalous" kinetic features of the behaviour of a number of reactants. Only when the energy of the donor-acceptor interaction, the energy of the reacting bonds, and the interatomic distance in the diene ($R_{1,4}$) are taken into joint consideration can there be a quantitative representation of the kinetics for conversion of various reactants, the activity of which may differ by a factor of 10^{20}.

With the use of Lewis acids that form highly reactive *n,v*-complexes with one of the reactants, usually the dienophile, it is possible to increase the rate of reaction by a factor of 10^9 and readily obtain products which are often impossible to synthesise by other methods.[23–25]

At the present time a sufficiently large amount of data has been collected to make it possible to correlate the main mechanisms of the course of these reactions, including those carried out in the presence of catalysts.

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In this review the following notation for the physicochemical characteristics and their dimensions has been adopted:

k_2 is the rate constant of a second-order reaction in l mol^{-1} s^{-1};

K_e is the equilibrium constant of reaction or formation of a 1:1 complex in l mol^{-1} s^{-1};

$\Delta G^{\neq}$ is the free energy of activation, $\Delta H^{\neq}$ is the enthalpy of activation, ΔH_{reac} is the enthalpy of reaction, ΔH_{solut} is the enthalpy of solution, ΔH_{solv} is the enthalpy of solvation, ΔH^0_{IC} is the enthalpy of formation of an intermolecular complex, all in kJ mol^{-1};

$\Delta S^{\neq}$ is the entropy of activation of reaction in J mol^{-1} K^{-1};

I_D is the ionisation potential, E_A is the electron affinity, E_{CT} is the energy of the charge-transfer band maximum in the molecular complexes, all in eV;

[*c*] is the concentration of reactants in mol l^{-1}.

II. Position and role of intermolecular complexes in the reaction

Three main types of reaction have been established: 1) "diene donor, dienophile acceptor", 2) "diene acceptor, dienophile donor", and 3) a neutral type corresponding to the case where introduction of donor and acceptor substituents increase the rate of the process.[5–13,26] The most common is the first type of reaction, in which the activity increases as the donor properties of the diene and the acceptor properties of the dienophile increase.[5–18,26] The intermolecular stabilisation energy of the donor-acceptor pairs assists the formation of charge-transfer complexes.[27–29] As the strength of the complexes between the reactants increases, their reactivity also

usually increases.[30-32] According to the theory of frontier orbital interaction,[18,33-36] the stabilisation energy is given by relationship (1), which includes the contributions of charge and orbital interactions to the stabilisation of the system:

$$E_{ST} = -q_D q_A \gamma/\epsilon + 2(c_D c_A \beta)^2/(I_D - E_A) \quad (1)$$

where q_D and q_A are the charges on the reacting atoms of diene (D) and dienophile (A), γ is the Coulomb integral, ε is the dielectric constant of the medium, c_D and c_A are the coefficients of the frontier orbitals on the reacting atoms of diene and dienophile, β is the interaction integral (the values of the interaction and overlap integrals are assumed to be equal), I_D is the ionisation potential of the diene, and E_A is the electron affinity of the dienophile. For neutral molecules the contribution of the charge interaction is usually ignored,[11,37] so the stabilisation energy is determined by the orbital term, the main contribution being made by interaction of the highest occupied molecular orbital (HOMO) of diene and lowest unoccupied molecular orbital (LUMO) of dienophile.[38,39] The variation in reactivity in a series of dienes or dienophiles is quite frequently determined by the variation in ionisation potential of diene or electron affinity of dienophile. This type of dependence in the reaction of cyanoethylenes with cyclopentadiene and 9,10-dimethylanthracene (Fig. 1) has become a select example of the successful application of frontier orbital theory to represent the activity of reactants in the Diels–Alder reaction.[11,37] Similar linear relationships have also been found for many other series of reactants[6,7] (Fig. 2). They are usually parallel lines on the coordinates $\lg k_2$ and $(I_D - E_A)^{-1}$, displaced relative to each other. The question naturally arises as to the reason why there is no single dependence for different classes of reactants. It is clear that for a general representation of the reactivity of addends in the Diels–Alder reaction it is not sufficient to take into account only donor-acceptor interactions. It is therefore advisable to examine the question concerning the position and role of the intermolecular complexes, whose presence in the reaction mixture has been established many times by various methods.[27-29,40-43] This question has been the subject of active discussion for a number of years.[30-32,44,45]

The representation of the stabilisation energy of intermolecular complexes that is given in one monograph[40] is to a considerable degree similar to the representation of the stabilisation energy of the transition state in the Diels–Alder reaction as reported in several studies.[18,33-36] Two reaction schemes involving an intermolecular complex are possible.

1. The intermolecular complex (IC) lies on the reaction pathway:[30-32]

$$A + B \overset{K_e}{\rightleftarrows} IC \overset{k_1}{\rightarrow} \text{Product}. \quad (2)$$

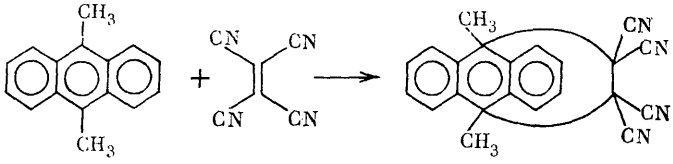
In this case the inherent properties (donor capacity of the diene and acceptor capacity of the dienophile) and the external conditions (solvent and pressure) can equally affect the strength of the complex and the rate of reaction.

2. The intermolecular complex that is formed does not lie on the reaction pathway:

$$IC \overset{K_e}{\rightleftarrows} A + B \overset{k_2}{\rightarrow} \text{Product}. \quad (3)$$

There is thus no similar effect.

It has been found that the donor properties of substituted anthracenes affect in the same way the strength of their molecular complexes with *p*-chloroanils and the rate of reaction with maleic anhydride.[30] Moreover, a similar agreement was noted in a study of the effect of the acceptor properties of a number of *N*-arylmaleimides on the rate of reaction and the stability of their complexes.[31] Thus, by comparing the effect of donor-acceptor properties of the reactants,[30-32] the solvent,[44,46,47] and also the pressure[48,49] on the molecular complex and transition state of the reaction it was possible to conclude that the complexes lay on the reaction pathway.[32] Direct experimental confirmation of this was obtained after determination of the activation parameters of the reaction between the clearly defined donor-acceptor pair—9,10-dimethylanthracene (I_D = 7.04 eV [30]) and tetracyanoethylene (E_A = 2.88 eV [37]):



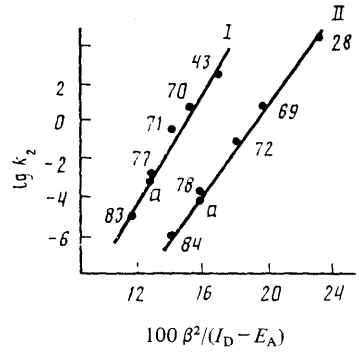


Figure 1. Relationship between the reactivity of cyanoethylenes in the Diels–Alder reaction with cyclopentadiene (*I*) and 9,10-dimethylanthracene (*II*) and the interaction energy of the frontier orbitals of diene and dienophile.[11,37] Point *a* corresponds to the reaction with dinitrilomaleate. Here and in Fig. 2 the value of β is assumed to be equal to 1 eV.

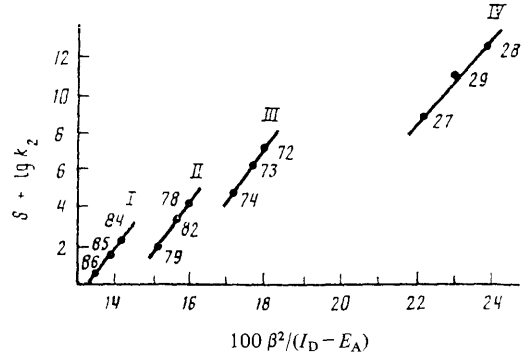


Figure 2. The effect of interaction energies of the frontier orbitals on the reactivity of acrylonitrile (*I*), dinitrilofumarate (*II*), *gem*-dicyanoethylene (*III*), and tetracyanoethylene (*IV*) in reactions with substituted anthracenes.[6,7]

If the reaction occurs in accordance with scheme (2), its rate (v) is given by Eqn. (4)

$$v = k_{exp}[A][B] = k_1[IC] = k_1K_e[A][B]/(1 + K_e[B]), \quad (4)$$

and if it occurs in accordance with scheme (3), v is given by Eqn. (5):

$$v = k_{exp}[A][B] = k_2[A][B]/(1 + K_e[B]), \quad (5)$$

where k_{exp} is the experimentally determined rate constant for reaction, k_1 and k_2 are the rate constants of reaction for formation of product from the molecular complex or from free reactants A and B, K_e is the equilibrium constant of the complex. If $[A] \ll [B]$ and $K_e[B] \ll 1$, the experimentally determined activation parameters include the following parameters for formation of complex:

a) when scheme (2) occurs:

$$\Delta G^{\neq}_{exp} = \Delta G^{\neq}_{real} + \Delta G^{0}_{IC};\ \Delta H^{\neq}_{exp} = \Delta H^{\neq}_{real} + \Delta H^{0}_{IC};\ \Delta S^{\neq}_{exp} = \Delta S^{\neq}_{real} + \Delta S^{0}_{IC}; \quad (6)$$

b) if scheme (3) is true, then:

$$\Delta G^{\neq}_{exp} = \Delta G^{\neq}_{real};\ \Delta H^{\neq}_{exp} = \Delta H^{\neq}_{real};\ \Delta S^{\neq}_{exp} = \Delta S^{\neq}_{real}. \quad (7)$$

Although kinetic schemes (4) and (5) are indistinguishable, their activation parameters differ according to the magnitude of the parameters for complex formation. If the molecular complexes lie on the reaction pathway, for reactants with well-defined donor-acceptor properties a low, zero, or even negative enthalpy of activation can be expected. The results of kinetic measurements (Table 1) are convincing evidence that the geometry of the complex between the reactants corresponds to the structural demands made on the transition state. This assists its formation. The experimentally determined enthalpy of activation contains two components (Fig. 3). If the addends are not capable of intermolecular stabilisation, the energy of activation ($\Delta H_1^{\neq}$) is determined by the distribution of energies of bond cleavage and bond formation. If such a stabilisation takes place (ΔH^{II}_{ST}), formation of the transition state is considerably assisted by using the intermolecular stabilisation energy for expenditure of energy in breaking up the old π-bonds and the apparent energy of activation ($\Delta H^{\neq}_{2,exp}$) is small. When there are considerable intermolecular interactions (ΔH^{III}_{ST}), as a result of such a superposition the energy of activation may be equal to zero and can even acquire a negative value.[50]

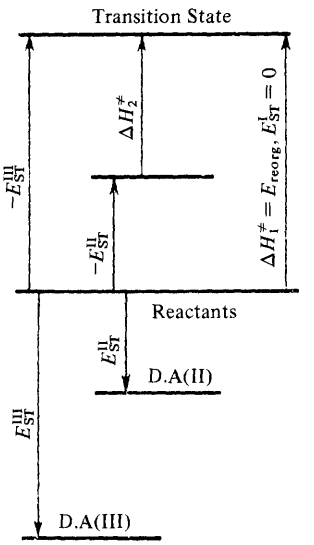


Figure 3. Relationship between the experimental enthalpy of activation ($\Delta H^{\neq}$) and the sum of the contributions from the energy of bond reorganisation (E_{reorg}) and the intermolecular stabilisation energy (E_{ST}).[70]

Since the molecular complex that is formed between the reactants to a considerable extent determines the pathway of the subsequent chemical reaction, the interest shown in studying such complexes

Table 1. Rate constants and activation parameters of the reaction between tetracyanoethylene [TCNE] and 9,10-dimethylanthracene (DMA) in certain solvents when $[TCNE]_0 \gg [DMA]$.[50]

Solvent	$10^4 \times [TCNE]_0$	k_2/T (°C)				$\Delta H^{\neq}$	$-\Delta S^{\neq}$
o-Xylene	10.55	790/13.5	816/14.7	1 050/25	1 605/40.2	18.3	125
Toluene	8.44	2 290/13.5	2 810/25.0	3 790/39.4	3 810/40.2	11.9	138
Benzene	6.56	7 600/13.5	8 480/25.0	10 800/39.4	10 400/40.2	7.2	146
Acetonitrile	8.78	46 500/12.0	43 500/25.1	42 500/40.4	—	—5.0	171
Dichloromethane	6.53	150 000/12.0	136 000/25.3	—	—	—7.5	171
Dichloroethane	4.67	111 000/12.0	110 000/11.8	89 500/40.4	—	—8.1	176
	8.75	102 000/12.9	92 700/24.9	83 000/36.1	—	—8.7	180
	8.90	96 000/12.4	89 000/24.9	83 600/36.1	81 300/43.1	—6.9	171
Chloroform	3.94	290 000/14.0	260 000/24.6	216 000/39.4	—	—11.2	180
	4.20	278 000/12.0	214 000/25.1	185 000/40.4	—	—13.1	186
	4.70	263 000/11.1	226 000/24.8	190 000/42.8	—	—10.2	176
n-Hexane	0.805	14 000/25.0	—	—	—	—	—
Tetrachloromethane	3.34	40 160/25.0	—	—	—	—	—

becomes understandable. There are sufficiently argued proposals for the existence of molecular complexes on the reaction pathway in the acylation of amines,[51,52] electrophilic addition to double bonds,[53,54] and a number of other processes.[27,28,51]

It is important to note that the activity of reactants with different structures cannot be explained solely from the energy of the donor-acceptor interaction, although the difference in reactivity of addends of a single structural type is satisfactorily represented by the change in interaction energy.

III. Kinetic and thermodynamic study of the uncatalysed reaction

Thermochemical enthalpy data assist in establishing the relationship between the activity of the reactants and the stability of the adducts. As will be demonstrated below, when the factors determining reactivity are analysed these data serve as a basis for analysing the change in energy of the reacting bonds in the reactants.

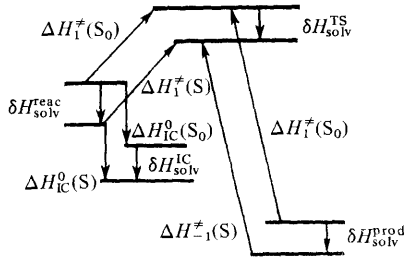


Figure 4. Enthalpies of reactant transfer (δH_{solv}^{reac}), the molecular complex (δH_{solv}^{IC}), the transition state (δH_{solv}^{ST}), and products (δH_{solv}^{prod}) in the Diels–Alder reaction on changing the solvent.[163,164]

1. Effect of solvent

There is a considerable amount of information about the effect of the solvent on the reactivity of the reactants and the stability of the molecular complexes formed by them.[44,46,47,55] However, this does not elucidate the cause of the variation in width of energy gap between the initial and final states of the system. An additional treatment of thermochemical data can be used for such an analysis.[56–58] Examination of the thermodynamic cycle (Fig. 4) shows that the change in enthalpy level of the solvated reactants (δH_{solv}^{reac}) is determined by the difference in enthalpies of solution (ΔH_{solut}^{reac}) in different solvents (S) relative to a given reference solvent (S_0):

$$\delta H_{solv}^{reac} = \Delta H_{solut}^{reac}(S) - \Delta H_{solut}^{reac}(S_0).$$

In order to calculate the change in enthalpy level of the solvated complex (δH_{solv}^{IC}) it is necessary to have data on the enthalpy of formation of the complexes (ΔH_{IC}^0) in different solvents:

$$\delta H_{solv}^{IC} = \Delta H_{IC}^0(S) - \Delta H_{IC}^0(S_0) + \delta H_{solv}^{reac}.$$

Such an analysis was carried out for the first time on complexes formed by the π-donors, mesitylene and benzene, with tetracyanoethylene.[46] The change in transfer enthalpies for mesitylene and benzene was similar to that found for anthracene.[57] A change of medium has a more pronounced effect on tetracyanoethylene than on the π-donors. By using enthalpy of activation data for the reaction of tetracyanoethylene with anthracene in different solvents[55,57] it is possible to calculate the change in enthalpy level of the transition state (ΔH_{solv}^{TS}) relative to cyclohexane chosen as a reference solvent:

$$\delta H_{solv}^{TS} = \delta H_{solv}^{reac} + \Delta H^{\neq}(S) - \Delta H^{\neq}(S_0).$$

The change in enthalpy level of the transition state when the solvent is altered is proportional to the change in enthalpy level of the molecular complex.[46] The type of effect of the medium on the enthalpy levels of solvated reactants and reaction adducts is considerably different from the type of effect of the solvent on the transition state of reaction.[23,46,57] Since a change of solvent leads to a change in enthalpy levels of all states—donor, acceptor, and complex—it becomes obvious that an analysis of the effect of the medium on the enthalpy of formation of the complex based on the change in activity of only one component (usually the acceptor) is not reliable in every case.[59–61]

Table 2. Enthalpy contributions of specific (ΔH_{sol}^{spec}) and nonspecific ($\Delta H_{solv}^{nonspec}$) solvation to the total enthalpy of solvation (ΔH_{solv}) of tetracyanoethylene in given solvents at 22 °C.[23,46]

Solvent No.	Solvent	$[IC]/[TCNE]_0$	K_p	$-\Delta H_{solv}$	$-\Delta H_{solv}^{spec}$	$-\Delta H_{solv}^{nonspec}$	$-\Delta H_{IC}^0$
1	Cyclohexane	0.40	0.072	49.8	1.3	48.5	3.2
2	Tetrachloromethane	0.69	0.217	53.1	4.4	48.7	6.4
3	Chloroform	0.85	0.48	56.9	7.4	49.5	8.7
4	Dichloromethane	0.94	0.98	57.7	10.0	47.7	10.7
5	Benzene	0.96	2.27	66.1	17.3	48.8	18.1

By using information about the equilibrium constants of complexes of tetracyanoethylene with a number of solvents, it is possible to calculate the proportion of specifically solvated acceptor:

$$[IC]/[TCNE]_0 = K_e[S]/(1 + K_e[S]),$$

where [S] is the number of moles of solvent in a litre of solution. By multiplying the proportion of bonded tetracyanoethylene ($[IC]/[TCNE]_0$) by the enthalpy of formation of complex with solvent, it is possible to determine the enthalpy of specific interaction of acceptor with solvent (Table 2). For cyclohexane this interaction proves to be negligible, which is consistent with the results of two studies,[62,63] while on changing to benzene it increases substantially.[46] The contribution of the nonspecific solvation ($\Delta H_{solv} - \Delta H_{solv}^{spec}$) remains constant in this series of solvents.[46] The variation in the enthalpies of solution of tetracyanoethylene (TCNE) in different solvents is virtually the same as the variation in the enthalpies of formation of its complexes with these solvents (Fig. 5).

A similar analysis of the effect of the medium was carried out on n,σ- and π,σ-complexes of iodine with a number of donors using thermochemical solution data[47] and data on the enthalpy of formation of complexes in solution.[59] In these cases also the change

in enthalpy of formation of the complex is determined to a greater degree by the change in solvation of the acceptor—iodine—but the effect of the medium on the enthalpy of formation of the complexes is completely dependent on the change in enthalpy levels of both reactants and the complex. The total enthalpy of solvation of iodine varies mainly as a result of the difference in energy of the specific interaction; consequently, the enthalpy of nonspecific solvation of iodine, as for tetracyanoethylene (see Table 2), does not vary very much in different solvents.[47]

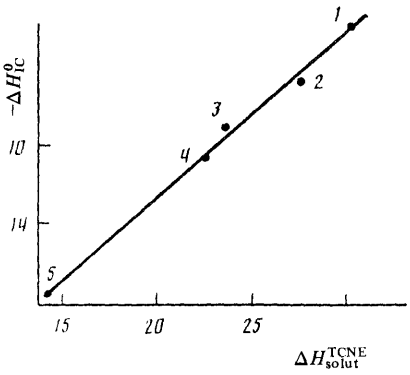


Figure 5. Relationship between the enthalpies of solution of tetracyanoethylene (ΔH^{TCNE}_{solut}) and the enthalpies of complex formation between TCNE and different solvents (ΔH^0_{IC}). The solvents are numbered as in Table 2.

Table 3. Enthalpies of activation for the Diels–Alder reaction between tetracyanoethylene and anthracene ($\Delta H^{\neq}$), enthalpies of solution of tetracyanoethylene (ΔH^{TCNE}_{solut}) and anthracene (ΔH^{An}_{solut}), and the change in enthalpies of solvation of the reactants (δH^{reac}_{solv}) and transition state (δH^{TS}_{solv}) of the reaction at 25 °C.[55,57]

Solvent No.	Solvent	ΔH^{TCNE}_{solut}	ΔH^{An}_{solut}	$\Delta H^{\neq}$	δH^{reac}_{solv}	δH^{TS}_{solv}
1	*o*-Xylene	1.4±0.1	24.0±0.3	51.5	(0)	(0)
2	Toluene	9.4±0.5	24.8±0.8	46.0	9.2	3.6
3	Cyclohexanone	7.6±0.3	20.6±0.6	40.2	2.9	−8.5
4	Benzene	14.9±0.4	24.7±0.4	38.5	14.3	1.2
5	Ethyl acetate	9.2±0.5	25.1±0.2	37.7	8.9	−4.9
6	Chlorobenzene	23.1±0.3	24.6±0.4	31.4	22.3	2.2
7	Methyl acetate	10.5±0.9	25.1±0.2	31.8	10.2	−9.5
8	Acetonitrile	15.2±0.2	28.0±0.3	30.5	17.8	−3.2
9	1,2-Dichloroethane	21.3±0.3	24.9±0.4	26.8	20.9	−3.9
10	Chloroform	24.5±0.3	20.8±0.3	17.6	19.9	−14.0
11	Mesitylene	−2.7±0.4	—	—	—	—

A more extensive analysis of the solvation of the transition state in the Diels–Alder reaction between tetracyanoethylene and anthracene[57] showed that when the solvent was varied there was a change in the enthalpy levels of the reactants and the transition state (Table 3). The considerable increase in the enthalpy of activation on changing to aromatic solvents is due to the sharp decrease in enthalpy level of the reactants with a small change in the level of the transition state. The increased stabilisation of the transition state in chloroform, as noted in a number of studies[44,46,57,58] is due to strengthening of the hydrogen bonds in the activated complex. The kinetics of the reaction between anthracene and tetracyanoethylene in both directions were studied in different solvents.[23] When the large difference in the capacity of tetracyanoethylene and its adduct with anthracene to undergo specific solvation is taken into account, the equal enthalpies of the reactions, calculated from data obtained by direct thermochemical measurement and from the difference in enthalpies of activation for formation and decomposition of the adduct in different solvents, can be taken as proof of the equilibrium solvation of the transition state.[23]

There is a compensating effect between the enthalpies and entropies of activation of this reaction in the given series of solvents (Fig. 6). Consequently, a combined thermochemical and kinetic analysis of the effect of the medium on the enthalpy levels of the reactants and the transition state of the Diels–Alder reaction can explain the change in enthalpy of activation and reactivity as a whole.

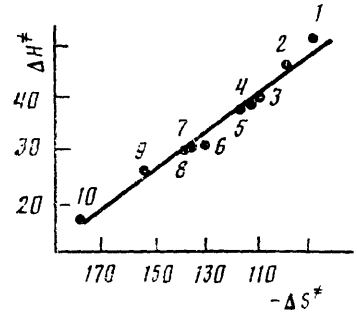


Figure 6. Relationship between the enthalpies and entropies of activation for the reaction of anthracene with tetracyanoethylene in different solvents from published data.[55,57] The solvents are numbered as in Table 3.

Similar studies on solvation effects in the reactions of 9,10-dimethylanthracene with maleic anhydride[64,65] and *trans,trans*-1,4-diphenyl-1,3-butadiene and anthracene with 4-phenyltriazolinedione[58] indicate that in the absence of strong specific interactions between the reactants and the solvent, the effect of the medium on the ground state and transition state is small. Since there is a marked solvent effect on the solvation of the transition state when reactions with effective charge separation are carried out,[66,67] the results of the solvation analysis indicate that the transition state has low polarity.[46,57,58]

2. Main factors determining the reactivity of the reactants

According to the approach of Evans and Polanyi[68] and Semenov,[69] the height of the activation barrier is determined by the distribution of bond cleavage and bond formation energies in the absence of other factors that affect reactivity (Fig. 7). With this approach the enthalpy coordinate of the transition state of reaction is determined

by the relationships:

$$\partial(E_1 + E_2)/\partial R = 0 \quad \text{or} \quad \partial(E_1 + E_3)/\partial R = 0,$$

and the energy of activation is given by the equations:

$$E_{a,4} = (E_1 + E_2)_{R_4} - (E_1 + E_2)_{R_0} \text{ or}$$
$$E_{a,5} = (E_1 + E_3)_{R_5} - (E_1 + E_3)_{R_0},$$

where E_1 is the energy of formation of σ-bonds, and E_2 and E_3 are the energies of cleavage of π-bonds in reactants with a different system of conjugation, R is the reaction coordinate.

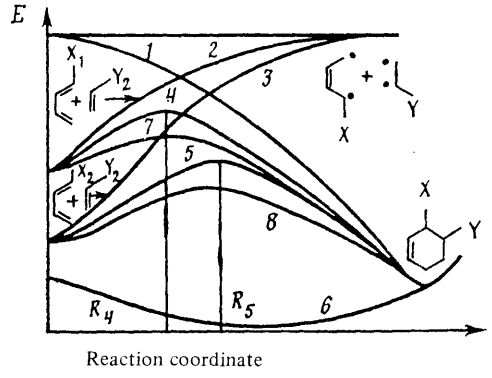
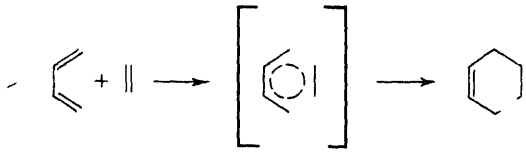


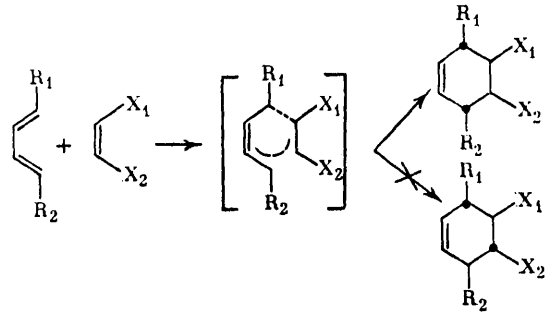
Figure 7. Diagram of energy changes on formation of σ-bonds (*1*) and cleavage of π-bonds in the reactants (*2* for X_1 and Y_1 and *3* for X_2 and Y_2); energies of bond cleavage and bond formation are superimposed (*4* and *5* for a combination of curves *1* + *2* and *1* + *3* respectively), excluding the intermolecular stabilisation energy (*6*) and including it (*7* and *8*).[70]

Since the initial change in energy of cleavage of π-bonds ($\partial E_2/\partial R$ and $\partial E_3/\partial R$) is greater than the change in energy of formation of σ-bonds ($\partial E_1/\partial R$), an activation barrier must occur for exothermic reactions, with a height that increases as the strength of the reacting bonds increases namely with an increase in their conjugation energy [E_3 (Fig. 7, curve *3*)]. If the reactants can undergo intermolecular stabilisation [E_6 (curve *6*)], the compensation of energies of bond cleavage and bond formation must appear at a lower value of the reaction coordinate and hence with lower perturbation energies of the system [E_7 and E_8 (curves *7* and *8*)]. For the Diels–Alder reaction this indicates[70] that both the donor-acceptor stabilisation (E_6) and the energy parameters of the reacting bonds (E_1, E_3, and E_2) affect the height of the activation barrier and the reactivity as a whole. Although the necessity for calculating the energies of cleavage of the reacting bonds in studying the kinetic charactersitics is not in doubt, difficulty arises because there is either no data or insufficient data on these energies and also because there is a wide variety of possible methods of bond cleavage (homolytic, heterolytic with formation of a carbanion, carbocation, etc.).

As regards the Diels–Alder reaction, the wide variety of experimental data on the structural characteristics of the reaction taking place and adherence to the principle of *cis*-addition,[1,26,71] the data on the kinetic isotope effect,[72–76] and on the effect of the solvent[2,77] and pressure,[48,49] and the results of a number of nonempirical calculations[78,79] are consistent with the proposal of a synchronous mechanism for cleavage and formation of bonds in the transition state:



It is suggested that with an increase in asymmetry of the reacting bonds, the asymmetry of the transition state increases,[14,80,81] but for *cis*-addition to be achieved for donor-acceptor systems, the second bond needs to be "fastened" after a shorter time than the period necessary for a change in geometry of the substituents:



For this reason calculation of the energy of the reacting bonds in the molecular Diels–Alder reaction can be carried out more rigorously using the experimental data.

On the basis of the ideas of Evans and Polanyi[68] and Semenov,[69] Hammond[82] predicted an increase in kinetic activity of the reactants as the exothermicity of the process increases. It was suggested[83] that the bislocalisation energy of the electrons on the reacting atoms should be regarded as an index of the reactivity of addends in the Diels–Alder reaction:



For a number of aromatic dienes the calculated 1,4-bislocalisation energies correlate with the reactivity.[83,84] Since the 1,4-bislocalisation energy of π-bonds in a diene by its very nature corresponds to the energy of cleavage of the reacting bonds, it is obvious that in the given series of dienes—polynuclear hyrocarbons—the variation in bond energy is similar to the variation in their activity. The donor properties of dienes also vary in a similar manner to their activity.[83,84] This led to the mistaken assumption that there was a connection between the bislocalisation energy and the donor-acceptor interaction energy.[22,39] For many dienes and the majority of dienophiles such a relationship does not occur. Thus in a number of cyanoethylenes the activity varies inversely to the change in 1,2-bislocalisation energy.[85] In this case the reactivity is related to the acceptor properties of the cyanoethylenes.[85,86] Thus, in far from every case does an increased stability of adducts correspond to more active reactants in the Diels–Alder reaction. The fact that activity series more often reflect the nature of change of donor-acceptor properties of the reactants and also the difficulties in calculating the

bislocalisation energy for substituted dienes and particularly for dienophiles have meant that less attention has been given to the problem of the effect of the conjugation energy on reactivity.

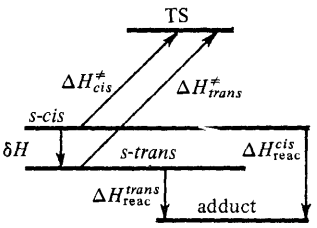


Figure 8. Effect of *trans-cis* conformational change on the enthalpies of activation and reactions of 1,3-butadienes.

Since the cleavage and formation of bonds in the transition state of the Diels–Alder reaction take place according to a concerted mechanism and substituents have a greater effect on the strength of π-bonds than on σ-bonds, the proposal was made[86] that the difference in the enthalpies of reaction reflects the difference in conjugation energies. This proposal is supported by the occurrence of a linear relationship between the change in enthalpy of the reactions of a series of substituted anthracenes with tetracyanoethylene[86] and a series of substituted dienophiles (cyanoethylenes) with 2,5-diphenylisobenzofuran[87] on the one hand and the calculated 1,4- and 1,2-bislocalisation energy on the other hand. These results indicate that the differences in the enthalpies of reaction are due not to steric strain in the adducts formed but to the change in strength of the reacting bonds. The proportional relationship between the enthalpy of reaction and the energy of the reacting π-bonds suggests that there is a small or proportionate change in energy of the σ-bonds formed. To a certain extent data on the change in enthalpy of reaction can provide more information on the reactivity of the reactants in a molecular Diels–Alder reaction than data on the bislocalisation energy. Although the substituents have a greater effect on the strength of the π-bonds than on the strength of the σ-bonds,[88,89] the height of the activation barrier is determined by superimposing the changes in energy of both types of bonds (π and σ) during reaction (see Fig. 7). This effect is reflected in the enthalpy of reaction, whereas the bislocalisation energy in a diene or dienophile only reflects the change in energy of the reacting bonds. Apart from this, the forms of solvation and possible conformational conversions have an effect on the enthalpy of reaction. For example, substituted butadienes mainly have a *trans*-conformation.[84,90] The height of the activation barrier for the reaction of s-*cis*-butadiene is determined by the sum of these factors—the distribution of energies for bond cleavage and bond formation and the donor-acceptor interaction energy (Fig. 8). The experimentally found height of the activation barrier, in addition to the value of $\Delta H^{\neq}_{cis}$ also includes the product of the enthalpy of *trans-cis* conformational change and the proportion of the *trans* form under the experimental conditions (δH). But it is the enthalpies of s-*trans*- and s-*cis*-butadienes and the enthalpies of the reactions involving them which differ by this magnitude of σH. In other words, the enthalpy of the conformational change included in the enthalpy of activation is also included in the enthalpy of reaction.

What results are obtained from a combined calculation of the donor-acceptor interaction energy and the enthalpy of reaction, which reflects mainly the distribution of energies of the reacting bonds, in representing the reactivity of hydrocarbon addends?

By using the enthalpy of reaction as an indicator of reactivity it was possible to account for what appeared at first to be an unusual change in activity of the reactants, occurring sometimes even in the same structural series (Table 4). Thus 9-methoxy- and particularly 9,10-dimethoxy-anthracenes, which exhibit high donating capacity, are appreciably less active when reacting with dienophiles that cannot undergo strong donor-acceptor interaction. The "anomalous" behaviour of these dienes is understandable if the increased conjugation energy (reduced exothermicity of the reaction) is taken into account (Table 4). By calculating at the same time the donor-acceptor interaction energy and the enthalpy of reaction it is possible to determine the overall relationship representing the reactivity of all the reacting pairs of addends. In a number of substituted butadienes the change in donor properties and conjugation energy, which has an opposite effect on the rate of reaction, also results in an "anomalous reactivity" in relation to frontier orbital theory (see Table 4 and Fig. 9).[70] Here also when a combined calculation of both factors is made it is possible to account for the observed activity of the reactants.[70]

Table 4. The reactivity ($8 + \lg k_2$), ionisation potentials (I_D) of dienes, electron affinities (E_A) of dienophiles, characteristics of the donor-acceptor interaction energy [$100\beta^2/(I_D - E_A)$], and enthalpies of Diels–Alder reactions (ΔH_{reac}) at 25 °C.

Reaction No.	Reactants	$100\beta^2/(I_D-E_A)$	$8+\lg k_2$	I_D	E_A	$-\Delta H_{reac}$
	Reactions of dienophiles with 2,5-diphenylisobenzofuran (I_D = 7.62 eV)					
1	Tetracyanoethylene	21.09	16.0		2.88	69
2	Tricyanoethylene	18.12	12.0		2.10	71
3	*gem*-Dicyanoethylene	16.42	11.0		1.53	77
4	Dinitrilofumarate	14.62	7.49		0.78	82
5	Maleodinitrile	14.62	8.12		0.78	84
6	Acrylonitrile	13.16	5.34		0.02	87
7	Maleic anhydride	15.04	8.53		0.97	85
8	*N*-Phenylmaleimide	14.86	8.57		0.89	98
9	*N*-(*p*-Nitrophenyl)maleimide	15.13	9.16		1.01	96
10	*N*-(*m*-Nitrophenyl)maleimide	15.08	9.22		0.99	95
11	*N*-(*p*-Bromophenyl)maleimide	14.99	8.87		0.95	98
12	*N*-(*p*-Methylphenyl)maleimide	14.73	8.56		0.83	98
13	*N*-(*p*-Methoxyphenyl)maleimide	14.68	8.50		0.81	99
14	*N*-(*p*-Dimethylaminophenyl)-maleimide	14.51	8.36		0.73	100
15	4-Phenyltriazolinedione		Very rapid		1.80	104
16	*p*-Benzoquinone	17.01	7.72		1.74	66
17	1,4-Naphthoquinone	16.58	7.03		1.59	58
18	Acrolein	13.39	5.92		0.15	78
19	Acrylic acid	13.28	6.18		0.09	84
20	Methyl acrylate	13.46	5.28		0.19	85
21	Methacrylic acid	—	5.48		—	66
22	Methacrolein	—	5.11		—	62
23	Methyl methacrylate	—	4.32		—	69
24	Methacrylonitrile	—	3.92		—	73
25	Chloromaleic anhydride	15.29	8.58		1.08	82
26	Citraconic anhydride	14.73	5.96		0.83	84
	Reactions of dienes with tetracyanoethylene (E_A = 2.88 eV)					
27	Anthracene	22.47	8.48	7.33		77
28	9,10-Dimethylanthracene	24.04	12.37	7.04		88
29	9-Methylanthracene	23.31	11.35	7.17		85
30	9-Chloroanthracene	22.17	7.74	7.39		66
31	9-Methoxyanthracene	23.31	11.71	7.17		61
32	9,10-Dimethoxyanthracene	23.75	10.94	7.09		53
33	1,3-Butadiene	16.23	5.23	9.03		154
34	2-Methylbutadiene	16.64	6.87	8.89		166
35	2-Methoxybutadiene	17.42	8.47	8.62		159
36	2,3-Dimethylbutadiene	17.45	8.40	8.61		176

Table 4 (contd.).

Reaction No.	Reactants	$100\beta^2/(I_D-E_A)$	$8+\lg k_2$	I_D	E_A	$-\Delta H_{reac}$
	Reactions of dienes with tetracyanoethylene (E_A = 2.88 eV)					
37	*trans*-1-Methylbutadiene	17.45	7.23	8.61		163
38	*trans*-1-Phenylbutadiene	18.94	7.81	8.16		142
39	*trans,trans*-1,4-Diphenylbutadiene	19.19	6.87	8.09		97
40	*trans*-1,2,3-Trimethylbutadiene	—	8.12	—		163
41	*trans,trans*-1-Methyl-4-phenylbutadiene	—	7.66	—		124
42	1,3-Cyclohexadiene	18.62	8.14	8.25		130
43	Cyclopentadiene	17.54	10.63	8.58		113
44	Hexachlorocyclopentadiene	16.53	—	8.93		42*
45	Hexabromocyclopentadiene	—	—	—		29*
46	5,5-Dimethoxytetrabromocyclopentadiene	—	—	—		62*
47	Tetracene	24.21	—	7.01		97
48	5,11-Dichlorotetracene	25.44	—	6.81		78
49	Pentacene	26.59	—	6.64		116
	Reactions of dienes with maleic anhydride (E_A = 0.97 eV)					
50	Anthracene	15.72	2.78	7.33		93*
51	9,10-Dimethylanthracene	16.47	6.09	7.04		104
52	9-Methylanthracene	16.13	4.54	7.17		101
53	9-Chloroanthracene	15.57	2.16	7.39		82*
54	9-Methoxyanthracene	16.13	3.45	7.17		77*
55	9,10-Dimethoxyanthracene	16.33	2.49	7.09		69*
56	1,3-Butadiene	12.41	3.83	9.03		170*
57	2-Methylbutadiene	12.33	4.19	8.89		182*
58	2,3-Dimethylbutadiene	13.07	4.53	8.62		194*
59	*trans*-1-Methylbutadiene	13.09	4.36	8.61		179*
60	*trans*-1-Phenylbutadiene	13.91	4.05	8.16		158*
61	*trans,trans*-1,4-Diphenylbutadiene	14.04	2.47	8.09		113*
62	1,3-Cyclohexadiene	13.74	4.12	8.25		146*
63	Cyclopentadiene	13.14	6.96	8.58		129*
64	Hexachlorocyclopentadiene	12.56	0.06	8.96		58*
65	Hexabromocyclopentadiene	—	0.99	—		45*
66	5,5-Dimethoxytetrabromocyclopentadiene	—	2.38	—		78*
67	Tetracene	16.55	4.88	7.01		103*
68	Pentacene	17.64	6.13	6.64		132*
	Reactions of dienes with tricyanoethylene (E_A = 2.10 eV)					
69	9,10-Dimethylanthracene	20.24	8.77	7.04		90
70	Cyclopentadiene	15.43	8.68	8.58		115
	Reactions of dienes with gem-dicyanoethylene (E_A = 1.53 eV)					
71	Cyclopentadiene	14.18	7.66	8.58		121
72	9,10-Dimethylanthracene	18.15	7.10	7.04		96
73	9-Methylanthracene	17.73	6.18	7.17		93
74	Anthracene	17.24	4.52	7.33		85*
75	9-Methoxyanthracene	17.73	6.16	7.17		69*
76	9,10-Dimethoxyanthracene	17.98	5.64	7.09		61*
	Reactions of dienes with dinitrilofumarate (E_A = 0.78 eV)					
77	Cyclopentadiene	12.82	4.91	8.58		126
78	9,10-Dimethylanthracene	15.97	4.14	7.04		101*
79	Anthracene	15.27	1.62	7.33		90*
80	9-Methoxyanthracene	15.62	2.28	7.17		74*
81	9,10-Dimethoxyanthracene	15.85	1.08	7.09		66*
82	9-Methylanthracene	15.65	3.08	7.17		98*
	Reactions of dienes with acrylonitrile (E_A = 0.02 eV)					
83	Cyclopentadiene	11.68	3.02	8.58		131
84	9,10-Dimethylanthracene	14.24	1.95	7.04		106*
85	9-Methylanthracene	13.99	1.04	7.17		103*
86	Anthracene	13.68	−0.07	7.33		95*
87	9-Methoxyanthracene	13.99	0.70	7.17		79*
	Reactions of dienes with *N*-phenylmaleimide (E_A = 0.89 eV)					
88	9,10-Dimethylanthracene	16.26	6.48	7.04		117
89	9-Methylanthracene	15.92	4.71	7.17		114*
90	Anthracene	15.53	2.86	7.33		106*
91	9-Chloroanthracene	15.38	1.45	7.39		95*
92	9-Methoxyanthracene	15.92	3.45	7.17		90*
93	Tetracene	16.34	5.34	7.01		126
94	5,11-Dichlorotetracene	16.89	4.43	6.81		107
95	Pentacene	17.39	6.98	6.64		145*
96	Cyclopentadiene	13.00	6.34	8.58		142
	Reactions of dienes with *N*-(*p*-nitrophenyl)maleimide (E_A = 1.01 eV)					
97	Cyclopentadiene	13.21	7.31	8.58		140
98	9-Methylanthracene	16.23	5.23	7.17		112
99	Anthracene	15.82	3.93	7.33		104*
100	9-Chloroanthracene	15.67	2.92	7.39		93*
101	9-Methoxyanthracene	16.23	4.43	7.17		88*
102	Tetracene	16.67	5.96	7.01		124
103	Pentacene	17.76	7.75	6.64		143*

Table 4 (contd.).

Reaction No.	Reactants	$100\beta^2/(I_D-E_A)$	$8+\lg k_2$	I_D	E_A	$-\Delta H_{reac}$
	Reactions of dienophiles with cyclopentadiene (I_D = 8.58 eV)					
104	Acrylic acid	11.78	4.77		0.09	128*
105	Acrolein	11.87	3.30		0.15	122*
106	Methyl acrylate	11.91	3.51		0.19	129*
	Reactions of dienes with chloromaleic anhydride (E_A = 1.08 eV)					
107	9,10-Dimethylanthracene	16.78	5.81	7.04		101*
108	9-Methylanthracene	16.42	4.35	7.17		98*
109	Anthracene	16.00	2.49	7.33		90*
110	9-Chloroanthracene	15.85	1.83	7.39		79*
	Reactions of dienes with citraconic anhydride (E_A = 0.83 eV)					
111	9,10-Dimethylanthracene	16.10	3.38	7.04		103*
112	9-Methylanthracene	15.77	1.93	7.17		100*
	Reactions of dienes with 4-phenyltriazolinedione (E_A = 1.80 eV)					
113	1,3-Butadiene	13.83	8.84	9.03		189
114	2,3-Dimethylbutadiene	14.66	10.21	8.62		213
115	2-Methylbutadiene	14.10	9.66	8.89		201
116	*trans*-1-Phenylbutadiene	15.18	9.80	8.16		177
117	*trans,trans*-1,4-Diphenylbutadiene	15.89	8.71	8.09		132
118	Cyclopentadiene	14.75	12.30	8.58		148
119	Hexachlorocyclopentadiene	14.02	4.92	8.96		77
120	Hexabromocyclopentadiene	—	4.74	—		64
121	5,5-Dimethoxytetrabromocyclopentadiene	—	6.34	—		97
	Other systems					
122	1,3-Butadiene + ethylene	9.22	−4.1	9.03	−1.81	166**
123	1,3-Butadiene + acrolein	11.26	0.0	9.03	0.15	163**
124	Cyclopentadiene + ethylene	9.62	−1.4	8.58	−1.81	126**
125	2-Methylbutadiene + acrolein	11.44	0.70	8.89	0.15	175**

Note. The value of β is assumed to be 1 eV.

* Enthalpy of reaction calculated by Konovalov and Kiselev.[70]

** Calculated from published data[88,89] on the enthalpy of formation.

In the majority of cases the parallel displacement of straight lines relative to each other on the coordinates $\lg k_2$ and $(I_D - E_A)^{-1}$ (see Figs. 1 and 2) is consistent with the variation in the experimentally determined enthalpy of reaction. In this connection attempts were made to represent the activity of different reacting pairs on the basis of the two given factors affecting reactivity.[64,70] The range of reactions to be analysed was restricted to compounds with reacting C=C bonds since for heteroatomic reactants considerable differences in the atomic orbital coefficients and a substantial increase in the contribution of charge interaction to the total stabilisation energy are to be expected[80,81,91] [cf. Eqn.(1)]. A study was made of all reactants for which there existed data on reactivity, ionisation potentials of the diene donors, electron affinities of the dienophile acceptors, and the enthalpy of the Diels–Alder reaction. Known kinetic,[5,11,31,55,87,92–97] thermochemical,[70,86,87,98–102] and orbital data[11,30,31,37,41,70,103–106] are presented in Table 4. It transpired that for all the diene-dienophile hydrocarbon systems there was only a slight tendency towards an increase in reactivity with a rise in donor-acceptor interaction energy (the correlation coefficient r equals 0.635).[70] Analysis shows[70] that calculation of only the stabilisation energy cannot represent the reactivity of all the reactants.

Additional treatment of the data on the enthalpy of reaction does not improve the overall correlation.[70] But a plot of the dependence $\lg k_2 = A/(I_D - E_A) + B\Delta H_{reac}$ shows that the points are grouped

in three distinct regions corresponding to the reactions involving 2,5-diphenylisobenzofuran (Fig. 10, line *I*), cyclopentadiene (Fig. 10, line *II*) and substituted anthracenes and butadienes (Fig. 10, line *III*).

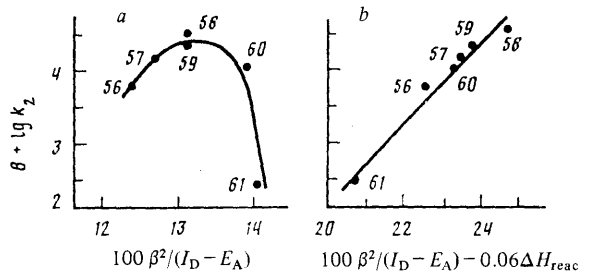


Figure 9. Dependence of the activity of substituted butadienes reacting with maleic anhydride on the intermolecular stabilisation energy excluding (*a*) and with an additional calculation of the change in enthalpy of reaction (*b*). Here and in Figs. 10 and 11 the value of β is assumed to be equal to 1 eV. The reactions are numbered as in Table 4.

It was recently shown[107,108] that the activity of the addends strongly depends on the distance between the reacting diene atoms ($R_{1,4}$). As this distance decreases there is a sharp increase in activity of the dienes. This type of behaviour of dienes in the Diels–Alder reaction can be accounted for[108] by the large variation in overlap of orbitals on the reacting atoms, since there is a proportional dependence $r = 0.999$ [108] between the calculated value of the square of the overlap integral (S^2) and the interatomic distance ($R_{1,4}$) in cyclic 1,2-*bis*-methylenes. In dienophiles the distance $R_{1,2}$ varies insignificantly, although the difference in bond lengths of ethylenic and acetylenic reactants can affect their activity, imparting a higher activity to ethylenic dienophiles when the other conditions are equal.[70]

By arranging the data on the interatomic distance ($R_{1,4}$) in furan (2.19 Å), cyclopentadiene (2.36 Å), anthracene (2.81 Å) and *cis*-1,3-butadiene (2.90 Å) [109] and assuming the corresponding distances in substituted reactants to be unchanged, it was possible to determine the activity of 102 diene-dienophile pairs in relation to the donor-acceptor interaction energy [$\beta^2/(I_D - E_A)$], the enthalpy of reaction (ΔH_{reac}) and the geometrical characteristics of the diene ($R_{1,4}$) [70] (Fig. 11). The significant improvement of the correlation factors ($r = 0.946$, root-mean-square deviation 1.13) achieved by this is shown by the possibility of representing the reactivity of all the pairs of reactants shown in Fig. 11 by a single relationship.

When the proportional relationship identified between the change in the interatomic distance in dienes ($R_{1,4}$) and the square of the overlap integral (S^2) [108] is taken into account, the latter value can be replaced by an experimental factor: $S^2 = A—BR_{1,4}$, where A and B are proportionality coefficients. Then the expression for the stabilisation energy when the resonance integral and overlap integral are equal can be given by the following relationship:

$$E_{ST} = \beta^2/(I_D - E_A) = (A - BR_{1,4})/(I_D - E_A) = A/(I_D - E_A) - BR_{1,4}/(I_D - E_A).$$

The calculated[70] linear regression coefficients lead to the relationship:

$$\lg k_2 = (290 \pm 10)/(I_D - E_A) - (60.8 \pm 2.8)R_{1,4}/(I_D - E_A) - (5.05 \pm 0.39)\Delta H_{reac} - 28.2.$$

The correlation factors in this equation, which has a sounder physical basis, ($r = 0.950$, root-mean-square deviation 1.04) are on the same level as those obtained by Konovalov and Kiselev[70] (see Fig. 11).

It follows from this that calculation of the three main factors that determine reactivity achieves a satisfactory representation of the activity of the compounds, which varies over a wide range (by 10^{20}). Thus, the possibility arises for predicting the reactivity of addends which have not been studied by using the data on donor-acceptor properties of the reactants and the geometric structural features of the diene. In many cases the enthalpy of reaction can be determined from data on the heat effects of other reactions involving the reactants studied.[70] It follows from Table 4 that the low exothermicity of the reaction between hexachlorocyclopentadiene and tetracyanoethylene (–42 kJ mol^{-1}) corresponds to a large displacement of the reaction equilibrium towards the reactants. A similar situation occurs in the reaction of 9,10-dimethoxyanthracene with tetracyanoethylene, the enthalpy of which is equal to –53 kJ mol^{-1}, the equilibrium constant is 6 l mol^{-1}, and the degree of conversion of reactants to adducts under normal conditions does not exceed 2–5%.[86] It is understandable that attempts to obtain an adduct in the reaction between hexachlorocyclopentadiene and tetracyanoethylene at elevated temperatures[110] were not successful.

By using kinetic and thermochemical data it is possible to select reactants for the purpose of liberating concurrently from adducts addends that are difficult to obtain by direct synthesis or from an equilibrium mixture of reactants and also to select addends of equilibrium processes used for the storage of solar energy.[111]

Kinetic and thermochemical studies of the solvation effect in the Diels–Alder reaction[44,57,58] indicate that there is a marked acceleration of the reaction in solvents that form hydrogen bonds with the dienophile. The formation of H-complexes increases the acceptor capacity of the dienophile and consequently its reactivity.[44] Lewis acids form even stronger complexes, which results in a sharp increase in activity of these complexes in the Diels–Alder reaction.

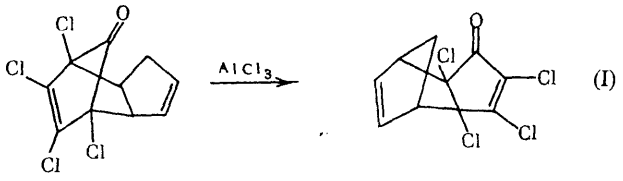
IV. Stoichiometric coordination catalysis

Determination of the factors governing the reactivity of addends does not eliminate the problem concerning the development of methods for involving inactive reactants in the Diels–Alder reaction. The usual methods for accelerating the rate of reaction by increasing the temperature and pressure are not always acceptable because of contamination of the required products with by-products or a displacement of the reaction equilibrium towards the reactants.

1. Catalysts of the Diels–Alder reaction

Data exists on the acceleration of the Diels–Alder reaction by a hydrophobic or cellular effect of the medium.[112–116] However, these only relate to a limited number of compounds, and the rate is not usually increased by more than a factor of 10–10^3.[112–116] A much more marked acceleration effect occurs in the presence of Lewis

acids. The increase in the rate of rearrangement of tetrachlorobicyclopentadien-8-one to tetrachlorobicyclopentadiene-1-one



(I)

in the presence of aluminium chloride[117] served as an impetus for using Lewis acids in the Diels–Alder reaction,[118–129] the ene synthesis,[130–132] [2 + 2]-cycloaddition[130,133] and [2 + 3]-cycloaddition reactions.[134–136] The qualitative prediction of acceleration of the Diels–Alder reaction between anthracene and maleic anhydride in the presence of $AlCl_3$ by a factor of 2×10^5 [118] was recently confirmed by the results of kinetic measurement (acceleration by a factor of 2.60×10^5 found).[137] Such a rapid acceleration of the reaction can be used to obtain adducts at room temperature in a number of minutes. For example, the reaction of anthracene with *p*-benzoquinone to give the bis-adduct in the presence of gallium chloride is complete after 3–5 min.[138] Possibilities arise for the synthesis of carbocyclic and heteroatomic compounds as Diels–Alder adducts which under normal conditions either have a low yield or are not formed at all.[139–141]

Considerable acceleration of the Diels–Alder reaction occurs in the presence of halides of Group II, III, and IV elements of the Periodic Table. The effect of aluminium chloride has been studied

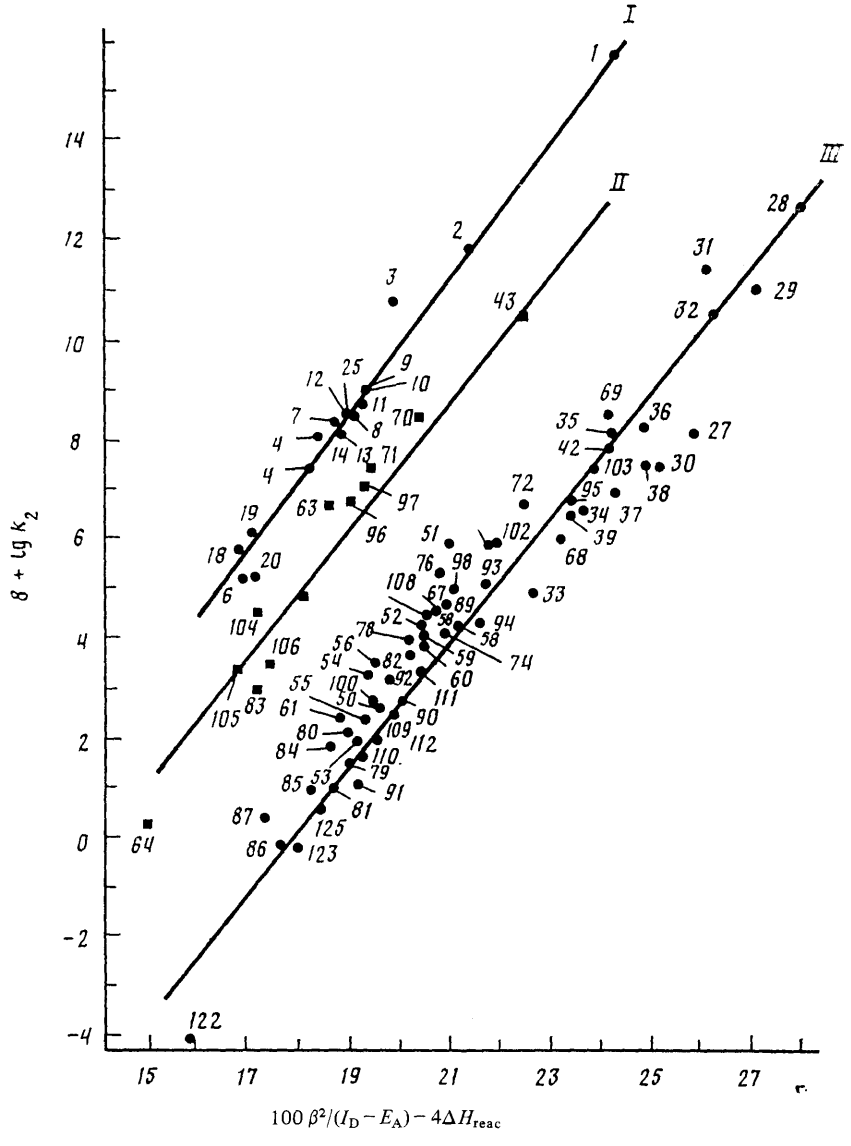
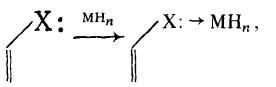


Figure 10. Dependence of the reactivity of reactants in the Diels–Alder reaction on the donor-acceptor interaction energy allowing for the enthalpy of reaction (in eV).

in the greatest detail, but not all reactants are stable in its presence because of the occurrence of polymerisation, isomerisation, or various rearrangements.[118,138,142] The occurrence of these side reactions makes it necessary to find milder Lewis acids and to make a careful selection of solvent and optimum experimental temperature. Traces of moisture in the solvent cause a partial deactivation of the catalyst and the formation of hydrogen halides with side effects that can be avoided in a number of cases by carrying out the reaction in the presence of alkyl halides of metals:[130]

$$RAlCl_2 + HCl \rightleftarrows RH + AlCl_3.$$

Acceleration of the reaction occurs when there are *n*-donor groups in the reactant (usually in the dienophile).[118] It was shown by means of IR, UV, and NMR spectroscopy[43,143–153] that the catalyst interacts with the *n*-donor to form an *n,v*-type molecular complex, which is stabilised by interaction of the unshared electron pair in the functional group of the dienophile with a low vacant orbital of the acceptor:



where X is the dienophile substituent containing a heteroatom with an unshared pair of electrons, M is a Group II, III, or IV element, H is a halogen, alkyl, or aryl.

Organometallic compounds of the type MR_n or MR_mH_{n-m} also form quite strong *n,v*-complexes.

The physicochemical properties of various *n,v*-complexes have been discussed in a review.[43] Analysis of ^{13}C and ^{1}H NMR spectra indicates that there is a considerable reduction in electron density in complexes of unsaturated esters and primarily on the carbonyl and β-carbon atoms of the *n*-donor.[144–146,154,155]

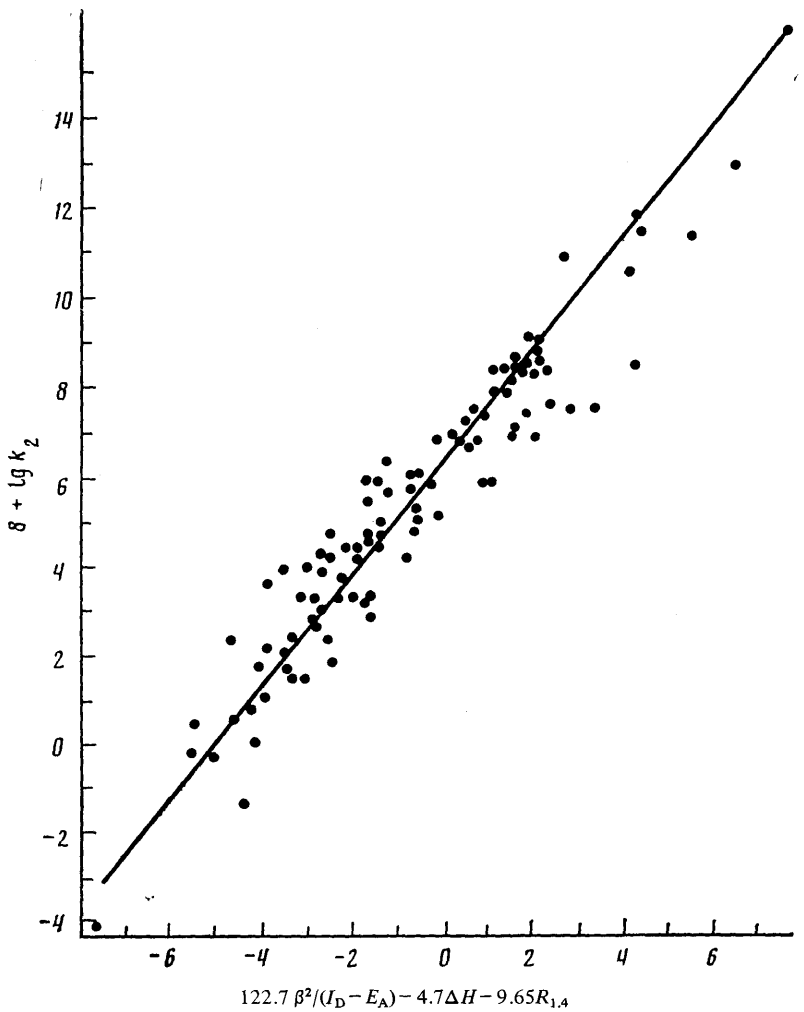
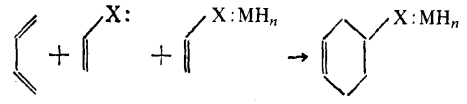


Figure 11. Determination of the reactivity of different compounds in the Diels–Alder reaction by a combined calculation of the donor-acceptor interaction energy, energy of the reacting bonds (from the change in enthalpy of the reactions, in eV) and the distances (in Å) between the reacting atoms in the diene.

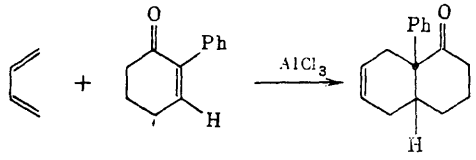
Since *n,v*-complexes of dienophiles with B, Al, and Ga halides are formed almost quantitatively and the acceleration effect on the reaction is quite large (10^4–10^6 times), the rate of reaction between the diene and free dienophile is usually ignored,[23,25] and the diene and *n,v*-complex are regarded as the true reactants.

It was demonstrated by means of thermochemistry[24,138,156] that complexes between the adduct and a Lewis acid does not have inferior stability compared to complexes involving dienophiles:

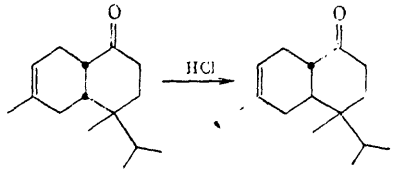


Only when there is a large excess of dienophile relative to the diene and catalyst is there a redistribution of the Lewis acid and its recovery by the dienophile. Only in this case can the reaction strictly be regarded as catalytic, although such a definition has held true for all reactions that occur in the presence of Lewis acids.

A large number of studies have been concerned with the preparation of the necessary adducts in the presence of catalysts and a determination of the structure of the reaction products.[118–130] The main mechanisms of the Diels–Alder reaction—the *cis*-addition principle, steroselectivity, and regioselectivity—are retained in a catalysed reaction. A lack of adherence to the *cis*-addition principle suggests an asynchronous, two-stage formation of bonds in the transition state of the reaction. At the same time, adherence to this principle is not a guarantee of a synchronous mechanism since even in a photochemical [2+2]-cycloaddition the *cis* principle is often fulfilled.[157] Disruption of the orientation of substituents in the adduct of the reaction between 2-phenyl-2-cyclohexen-1-one with butadiene in the presence of aluminium chloride[141] led to the proposal that this reaction had an ionic mechanism:



It was recently shown by ^{13}C NMR that in the presence of trace amounts of hydrogen chloride that develop in the reaction because of the presence of moisture in the solvent, the initially formed adduct with a *syn* configuration of hydrogen atoms rapidly rearranges to a product with an *anti* configuration:[158]



It follows from this that rearrangement occurs after initial formation of an adduct in which the orientation of the substituents is retained.

The conclusion about the asynchronous formation of bonds in the transition state of the reaction between fumaric acid esters and 9,10-dimethylanthracene, catalysed by aluminium chloride, was attributed not to violation of the *cis*-addition principle but to the lack of cooperativity of the asymmetric induction effect.[159] While the existence of the cooperativity of substituents in an uncatalysed reaction can be justified because of the equal effect from the same substituents,[75] in a catalysed reaction the free ester group and the other ester group included in the complex with aluminium chloride can in no way be considered equivalent. The enthalpy of formation of a complex with a 1:1 composition is much higher than half the enthalpy of formation of a complex with a 2:1 composition.[137] Thus the initial condition of cooperativity of the effect is not fulfilled and consequently the proposal about asymmetric formation of bonds in the transition state, despite its attraction, does not have any experimental basis at present.

Since the difference in energies of activation for regioisomers is usually small, formation of an *n,v*-complex between the dienophile and a Lewis acid can lead to both an increase in the difference of the orbital coefficients of the reacting atoms and hence to a predominance of one regioisomer and also to the opposite effect.[160,161] Activation of the dienophile in an *n,v*-complex considerably increases the proportion of *endo* adduct.[121,147]

A study of the kinetics of the Diels–Alder reaction in the presence of catalysts is of particular interest. It should be noted that use of UV spectroscopy, the most common spectrophotometric method for following the course of the reaction, is complicated because during the reaction there is a redistribution of the catalyst between the adduct and the free dienophile, and the *n,v*-complexes between dienophile and Lewis acid are usually brightly coloured.[156,162] Therefore, in the reaction of substituted butadienes with methyl acrylate the relative reactivity was determined from the ratio of adducts of the reaction between two different dienes and the same activated dienophile using GLC.[120–127] However, a more widely used method that has been developed recently is the analysis of kinetic data[156] obtained by following the absorption of *n,v*-complexes and taking into account the redistribution of catalyst.

It is understandable that a marked acceleration of reaction occurs in those solvents which do not form complexes with the catalyst or form complexes that are much less stable than the complexes between catalyst and reactant.[163,164]

In order to determine the true concentration of activated dienophiles it is necessary to know the concentration of catalyst that has lost activity because of the presence of traces of moisture in the solvent. This type of analysis is usually carried out using the data of kinetic or spectrophotometric titration.[156,162,165,166] In Table 5 data on the kientic parameters and the acceleration effect on the Diels–Alder reaction in the presence of a number of Lewis acids have been collected. In all reactions of the type "diene donor, dienophile acceptor" a considerable acceleration effect occurs (10^3–10^9 times) due to a sharp reduction in the enthalpy of activation ($\delta H^{\neq}$ = 30–50 kJ mol^{-1}) with a considerably smaller change in the entropy component of the free energy of activation ($T\delta S^{\neq}$ = 0–10 kJ mol^{-1}).

Although aluminium chloride produces a large acceleration effect on the reaction, a number of dienophiles are oxidised and form tar in its presence. Aluminium bromide accelerates the reaction even more, but kinetic measurements are often complicated by the formation of highly coloured complexes involving hydrogen bromide.[43,156] Boron chloride gives quite strong and active complexes with *n*-donors, and in this case there are only certain disadvantages due to its low boiling point. Boron trifluoride etherate and tin chloride have a weak activating effect because of the low strength of their *n,v*-complexes with dienophiles. Gallium chloride is the most convenient catalyst, and it forms a nondissociated complex which is readily soluble in many inert solvents; its accelerating effect is only slightly less than that of aluminium halides.

Table 5. Enthalpies of formation of *n,v*-complexes (ΔH^0_{IC}), rate constants (k_2), enthalpies ($\Delta H^{\neq}$) and entropies ($\Delta S^{\neq}$) of activation and the apparent acceleration effect in catalysed Diels–Alder reactions (benzene as solvent, 25 °C).

Reaction	Catalyst	Reaction No.	$-\Delta H^0_{IC}$	k_2	$\Delta H^{\neq}$	$-\Delta S^{\neq}$	Acceleration effect	Refs.
9,10-Dimethylanthracene + methyl acrylate	none	1	—	$7.8\cdot10^{-7}$	63	150		[92]
	$AlCl_3$	2	—	0.15	31	155	$1.9\cdot10^5$	[165]
	$GaCl_3$	3	52	$3.5\cdot10^{-2}$	—	—	$4.5\cdot10^4$	[24]
9,10-Dimethylanthracene + methyl methacrylate	none	4		$1.3\cdot10^{-7}$	63	163		[92]
	$AlCl_3$	5	—	$3.8\cdot10^{-2}$	35	155	$2.8\cdot10^5$	[165]
9,10-Dimethylanthracene + dimethyl fumarate	none	6		$6.7\cdot10^{-6}$	52	167		[92]
	$AlCl_3$	7	—	0.43	23	171	$6.4\cdot10^4$	[165]
Anthracene + *N-p*-nitrophenylmaleimide	none	8		$8.5\cdot10^{-5}$	57	129		[97]
	$AlCl_3$	9	—	8.2	33	113	$9.6\cdot10^4$	[138]
	$GaCl_3$	10	48	1.0	—	—	$1.2\cdot10^4$	[138]
Anthracene + *N-p*-bromophenylmaleimide	none	11		$2.5\cdot10^{-5}$	60	129		[97]
	$AlCl_3$	12	—	2.9	34	121	$1.2\cdot10^5$	[165]
	$GaCl_3$	13	53	0.65	34	135	$2.6\cdot10^4$	[138]
Anthracene + *N-p*-methoxyphenylmaleimide	none	14		$8.1\cdot10^{-6}$	68	112		
	$AlCl_3$	15	—	1.2	38	113	$1.5\cdot10^5$	[165]
Anthracene + *N*-phenylmaleimide	none	16		$7.3\cdot10^{-6}$	68	112		[97]
	$AlCl_3$	17	—	1.2	48	105	$1.7\cdot10^5$	[165]
	$AlBr_3$	18	78	5.7	—	—	$7.9\cdot10^5$	[138]
	$GaCl_3$	19	55	0.35	—	—	$4.9\cdot10^4$	[138]
Anthracene + *N-p*-tolylmaleimide	none	20		$6.8\cdot10^{-6}$	68	113		[97]
	$AlCl_3$	**21**	—	1.2	41	105	$1.8\cdot10^5$	[165]
	$GaCl_3$	**22**	57	0.35	—	—	$5.2\cdot10^4$	[138]
9,10-Dimethylanthracene + *N*-phenylmaleimide	none	**23**	23	$3.0\cdot10^{-2}$	—	—		[97]
	$SnCl_4$	**24**	8	$3.6\cdot10^{-2}$	—	—	1.2	[25]
	$Et_2O\cdot BF_3$	**25**	5	3.0	—	—	1.0	[25]
Anthracene + maleic anhydride	none	26		$6.0\cdot10^{-6}$	65	126		[8]
	BCl_3	27	—	$4.1\cdot10^{-2}$	—	—	$6.9\cdot10^3$	[137]
	$GaCl_3$	28	41	0.40	—	—	$6.7\cdot10^4$	[137]
	$AlCl_3$	29	—	1.6	—	—	$2.6\cdot10^5$	[137]
	$AlBr_3$	30	—	7.2	—	—	$1.2\cdot10^6$	[137]
Anthracene + 1,4-naphthoquinone	none	31		$1.8\cdot10^{-7}$	66	140		[138]
	$GaCl_3$	32	54	2.3	34	120	$1.3\cdot10^7$	[138]
	$2GaCl_3$	33	—	600	—	—	$3.4\cdot10^9$	[138]
Anthracene + *p*-benzoquinone	none	34		$2.4\cdot10^{-6}$	64	123		[138]
	$GaCl_3$	35	53	1.9	—	—	$7.8\cdot10^5$	[138]
2,5-Diphenylisobenzofuran + R	none	36		$7.0\cdot10^{-4}$	—	—		[142]
	$GaCl_3$	37	90	0.37	—	—	$5.3\cdot10^2$	[142]
2,5-Diphenylisobenzofuran + *O,O*-diphenyl vinylphosphonate	none	38		$3.7\cdot10^{-5}$	58	121		[142]
	$GaCl_3$	39	76	$3.4\cdot10^{-2}$	42	121	$9.2\cdot10^2$	[142]
9,10-Dimethylanthracene + R	none	40		$8.9\cdot10^{-10}$	90	155		[142]
	$2GaCl_3$	41	148	$1.7\cdot10^{-2}$	40	140	$1.9\cdot10^7$	[142]
Tetraphenylcyclopentadienone + *trans*-stilbene	none	42		$2.8\cdot10^{-8}$	70	144		[166]
	$AlCl_3^*$	43	39*	$5.6\cdot10^{-5}$	39	185	$2.0\cdot10^3$	[166]
Tetraphenylcyclopentadienone + norbornadiene	none	44		$6.0\cdot10^{-7}$	64	137		[166]
	$AlCl_3^*$	45	39*	$5.0\cdot10^{-4}$	34	181	$8.4\cdot10^2$	[166]
Tetraphenylcyclopentadienone + *N*-phenylmaleimide	none	46		$3.9\cdot10^{-5}$	59	120		[167]
	$GaCl_3$	47	55	$1.4\cdot10^{-4}$	—	—	3.6	[167]
	$AlCl_3$	48	—	$1.1\cdot10^{-3}$	45	137	28	[167]
	$2AlCl_3^{**}$	**49**	—	$4.2\cdot10^{-5}$	—	—	1.1	[167]
Tetraphenylcyclopentadienone + *N-p*-tolylmaleimide	none	50		$6.3\cdot10^{-5}$	57	121		[167]
	$GaCl_3$	51	57	$1.5\cdot10^{-4}$	—	—	2.4	[167]
	$AlCl_3$	52	—	$7.1\cdot10^{-4}$	—	—	11	[167]
	$2AlCl_3^{**}$	53	—	$6.5\cdot10^{-5}$	—	—	1.0	[167]
C-Phenyl-*N*-methylnitrone + *N*-phenylmaleimide	none	54		$2.0\cdot10^{-4}$	—	—		[168]
	$GaCl_3$	55	55	~50	—	—	10^5	[168]
9,10-Dimethylanthracene + acrylonitrile	none	56		$2.2\cdot10^{-6}$	63	146		[92]
	$GaCl_3$	57	51	0.13	36	130	$5.9\cdot10^4$	[24]
9-Methylanthracene + acrylonitrile	none	58		$1.1\cdot10^{-7}$	74	122		[24]
	$GaCl_3$	59	51	$1.7\cdot10^{-2}$	42	126	$1.5\cdot10^5$	[24]
Anthracene + acrylonitrile	none	60		$8.6\cdot10^{-9}$	76	138		[24]
	$GaCl_3$	61	51	$5.3\cdot10^{-4}$	47	141	$6.2\cdot10^4$	[24]
9-Chloroanthracene + acrylonitrile	none	62		$1.9\cdot10^{-9}$	79	140		[24]
	$GaCl_3$	63	51	$1.6\cdot10^{-4}$	49	145	$8.4\cdot10^4$	[24]
9-Methylanthracene + methyl acrylate	none	64		$5.8\cdot10^{-8}$	73	191		[24]
	$GaCl_3$	65	52	$1.3\cdot10^{-2}$	—	—	$2.2\cdot10^5$	[24]
9,10-Dimethylanthracene + cyanoacetylene	none	66		$4.0\cdot10^{-6}$	—	—		[24]
	$GaCl_3$	67	—	1.1	—	—	$2.8\cdot10^5$	[24]
9,10-Dimethylanthracene + methyl propiolate	none	68	—	$2.0\cdot10^{-8}$	—	—		[24]
	$GaCl_3$	69		$6.0\cdot10^{-3}$	—	—	$3.0\cdot10^5$	[24]
9,10-Dimethylanthracene + maleic anhydride	none	70		$1.2\cdot10^{-2}$	43	138		[92]
	$GaCl_3$	71	41	277	—	—	$2.3\cdot10^4$	[137]
	$AlCl_3$	72	—	$2.0\cdot10^3$	—	—	$1.7\cdot10^5$	[137]
9-Methylanthracene + maleic anhydride	none	73		$3.4\cdot10^{-4}$	53	134		
	$GaCl_3$	74	41	12.8	27	140	$3.8\cdot10^4$	[8, 137]
	$AlCl_3$	75	—	95.2	—	—	$2.8\cdot10^5$	[137]
9-Chloroanthracene + maleic anhydride	none	76		$1.4\cdot10^{-6}$	67	130		[137]
	$GaCl_3$	77	41	$5.2\cdot10^{-2}$	36	153	$3.7\cdot10^4$	[8, 137]
	$AlCl_3$	78	—	0,38	—	—	$2.8\cdot10^5$	[137]
Anthracene + citraconic anhydride	none	79		$1.5\cdot10^{-8}$	73	135		[137]
	$GaCl_3$	80	49	$1.3\cdot10^{-4}$	—	—	$9.0\cdot10^3$	[137]

Table 5 (contd.)

Reaction	Catalyst	Reaction No.	$-\Delta H^0_{IC}$	k_2	$\Delta H^{\neq}$	$-\Delta S^{\neq}$	Acceleration effect	Refs.
	$AlCl_3$	81	—	$8.5\cdot10^{-3}$	32	164	$5.7\cdot10^5$	[137]
9-Chloroanthracene + citraconic anhydride	none	82		$3.1\cdot10^{-9}$	—	—		[137]
	$GaCl_3$	83	49	$9.5\cdot10^{-6}$	—	—	$3.0\cdot10^3$	[137]
	$AlCl_3$	84	—	$2.9\cdot10^{-3}$	—	—	$9.3\cdot10^5$	[137]
9-Methylanthracene + citraconic anhydride	none	85		$8.5\cdot10^{-7}$	64	135		[137]
	$GaCl_3$	86	49	$2.0\cdot10^{-2}$	41	129	$2.3\cdot10^4$	[137]
	$AlCl_3$	87	—	0,14	28	154	$1.7\cdot10^5$	[137]
9,10-Dimethylanthracene + citraconic anhydride	none	88		$2.4\cdot10^{-5}$	45	169		[137]
	$GaCl_3$	89	49	0.44	31	137	$1.9\cdot10^4$	[137]
	$AlCl_3$	90	—	2.2	29	128	$9.1\cdot10^4$	[137]
Anthracene + chloromaleic anhydride	none	91		$3.1\cdot10^{-6}$	62	128		[137]
	$GaCl_3$	92	40	0.11	—	—	$3.6\cdot10^4$	[137]
	$AlCl_3$	93	—	2.5	—	—	$7.5\cdot10^5$	[137]
9-Chloroanthracene + chloromaleic anhydride	none	94		$6.8\cdot10^{-7}$	—	—		[137]
	$GaCl_3$	95	40	$2.3\cdot10^{-2}$	—	—	$3.4\cdot10^4$	[137]
	$AlCl_3$	96	—	0.14	—	—	$2.1\cdot10^5$	[137]
9-Methylanthracene + chloromaleic anhydride	none	97		$2.3\cdot10^{-4}$	49	139		[137]
	$GaCl_3$	98	40	11.9	28	118	$5.3\cdot10^4$	[137]
	$AlCl_3$	99	—	39.7	—	—	$1.8\cdot10^5$	[137]
9,10-Dimethylanthracene + chloromaleic anhydride	none	100		$6.4\cdot10^{-3}$	46	118		[45, 137]
	$GaCl_3$	101	40	245	—	—	$3.8\cdot10^4$	[137]
	$AlCl_3$	102	—	$1.4\cdot10^3$	—	—	$2.3\cdot10^5$	[137]
Tetracyclone + *N-p*-nitrophenylmaleimide	none	103		$4.0\cdot10^{-5}$	64	100		[167]
	$GaCl_3$	104	48	$2.8\cdot10^{-4}$	—	—	7.1	[167]
	$AlCl_3$	105	—	$1.2\cdot10^{-3}$	57	96	30	[167]
Tetracyclone + *N-p*-bromophenylmaleimide	none	106		$3.6\cdot10^{-5}$	64	100		[167]
	$GaCl_3$	107	53	$2.2\cdot10^{-4}$	—	—	6.2	[167]
	$AlCl_3$	108	—	$1.1\cdot10^{-3}$	53	111	29.4	[167]
Phencyclone + *N-p*-nitrophenylmaleimide	none	109		2,12	31	133		[167]
	$GaCl_3$	110	48	36.3	20	135	17.1	[167]
	$AlCl_3$	111	—	83.3	—	—	39.5	[167]
Phencyclone + *N-p*-bromophenylmaleimide	none	112		1,42	33	137		[167]
	$GaCl_3$	113	53	21.0	20	140	14.8	[167]
	$AlCl_3$	114	—	51.6	—	—	36.3	[167]
Phencyclone + *N*-phenylmaleimide	none	115		0.76	30	146		[167]
	$GaCl_3$	116	55	9.4	28	121	12.4	[167]
	$AlCl_3$	117	—	46.5	14	155	61.2	[167]
Phencyclone + *N-p*-tolylmaleimide	none	118		0.75	34	133		[167]
	$GaCl_3$	119	57	10.4	24	134	13.9	[167]
	$AlCl_3$	120	—	40.1	22	127	53.4	[167]
Phencyclone + methyl acrylate	none	121		$1.2\cdot10^{-3}$	46	133		[167]
	$AlCl_3$	122	—	0.63	32	129	$5.5\cdot10^2$	[167]
Phencyclone + methyl methacrylate	none	123		$7.5\cdot10^{-4}$	46	139		[25, 167]
	$AlCl_3$	124	—	0.22	30	144	$2.9\cdot10^2$	[25, 167]
Phencyclone + dimethyl fumarate	none	125		$4.7\cdot10^{-5}$	54	136		[25, 167]
	$AlCl_3$	126	—	$2.3\cdot10^{-2}$	41	126	$4.9\cdot10^2$	[25, 167]
trans,trans-1,4-Diphenylbutadiene + *N-p*-tolylmaleimide	none	127	—	$9.3\cdot10^{-7}$	54	168		[25]
	$AlCl_3$	128	—	$5.9\cdot10^{-3}$	38	148	$6.3\cdot10^2$	[25]
trans,trans-1,4-Diphenylbutadiene + *N*-phenylmaleimide	none	129		$1.4\cdot10^{-6}$	50	177		[25]
	$AlCl_3$	130	—	$5.6\cdot10^{-3}$	39	143	$3.9\cdot10^2$	[25]
trans,trans-1,4-Diphenylbutadiene + *N-p*-bromophenylmaleimide	none	131		$2.1\cdot10^{-6}$	48	180		[25]
	$AlCl_3$	132	—	$7.1\cdot10^{-3}$	—	—	$3.4\cdot10^2$	[25]
2,3-Dimethylbutadiene + methyl acrylate	none	133		$3.4\cdot10^{-8}$	—	—		[127]
	$AlCl_3$	134	—	$4.2\cdot10^{-2}$	—	—	$1.2\cdot10^6$	[127]
2-Methylbutadiene + methyl acrylate	none	135		$1.9\cdot10^{-8}$	—	—		[120]
	$AlCl_3$	136	—	$1.4\cdot10^{-2}$	—	—	$7.4\cdot10^5$	[120]
trans-1-Methylbutadiene + methyl acrylate	none	137		$1.2\cdot10^{-8}$	—	—		[122]
	$AlCl_3$	138	—	$7.4\cdot10^{-2}$	—	—	$6.3\cdot10^5$	[122]
2-Phenylbutadiene + methyl acrylate	none	139		$2.3\cdot10^{-7}$	—	—		[127]
	$AlCl_3$	140	—	0.11	—	—	$4.7\cdot10^5$	[127]
1,3-Butadiene + methyl acrylate	none	141		$1.0\cdot10^{-8}$	75	151		[123]
	$AlCl_3$	142	—	$1.2\cdot10^{-3}$	44	157	$1.2\cdot10^5$	[123]
2-Chlorobutadiene + methyl acrylate	none	143		$1.3\cdot10^{-8}$	—	—		[127]
	$AlCl_3$	144	—	$6.3\cdot10^{-4}$	—	—	$5.0\cdot10^4$	[127]
2-Trifluoromethylbutadiene + methyl acrylate	none	145		$1.8\cdot10^{-7}$	—	—		[127]
	$AlCl_3$	146	—	$3.7\cdot10^{-4}$	—	—	$2.1\cdot10^3$	[127]
2-Cyanobutadiene + methyl acrylate	none	147		$1.4\cdot10^{-7}$	63	169		[126, 127]
	$AlCl_3$	148	—	$1.2\cdot10^{-4}$	47	169	$8.4\cdot10^2$	[126, 127]
Cyclopentadiene + acrylonitrile	none	149		$3.2\cdot10^{-5}$	—	—		[126, 127]
	$AlCl_3$	150	—	8,99	—	—	$2.8\cdot10^5$	[126, 127]

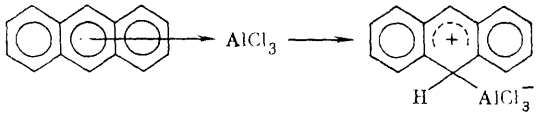
* A 1:1 complex with cyclone.

** A 1:1 complex with imide is formed first, then also a 1:1 complex with cyclone.

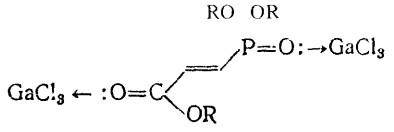
R = *O,O*-diethyl-β-carbomethoxyvinylphosphonate.

In virtually all cases kinetic measurements have been carried out for activated dienophiles in a Lewis acid complex of 1:1 composition. The formation of 2:1 complexes between α,β-dicarbonyl, ester, and

nitrile dienophiles and gallium chloride is usually not quantitative and the free Lewis acid readily gives π- and then σ-complexes with many dienes.[43,153]



In the case of β-carbomethoxyvinylphosphonate a stronger complex involving gallium chloride and the P=O group is mainly formed, and only when the ratio of catalyst to dienophile is higher than 1:1 does the catalyst coordinate also with the β-carbonyl group:[142]



Formation of the first bond P=O·$GaCl_3$ has virtually no effect on the strength of the subsequent complex C=O·$GaCl_3$. Despite the considerably greater strength of the bond between gallium chloride and the phosphoryl group compared to that with the carbonyl group (see Table 5), the acceleration effect on the reaction is greater in the latter case than in the former. By determining the acceleration effect on the reaction from the enthalpy of the *n,v*-complexes formed it was concluded[142] that the action of the catalyst on the system via the phosphorus atom constitutes 30–40% of the effect via the carbonyl carbon atom.

An increased acceleration effect occurs in catalysed reactions involving conjugated acceptor dienophiles such as quinones (see Table 5). It is suggested[169] that on formation of the *n,v*-complex a carbonyl group is excluded from the conjugation system of the quinone.

We shall now examine the factors which determine the acceleration effect in reactions involving a dienophile ligand bonded to a Lewis acid.

2. Solvation effects in a catalysed Diels–Alder reaction

Thermochemical and kinetics methods of approach are the most fruitful in studying the effect of the medium on the enthalpy of solvation of the reactants, *n,v*-complexes, and transition state of a catalysed reaction.[163,164] It follows from the kinetic data that the rate of reaction of tetracyanoethylene, which is an active acceptor dienophile, is substantially reduced in π-donor solvents,[55,57] while the effect of the medium on the rate of reaction of the no less active *n,v*-complexes is small.[163,164] A complete thermochemical analysis of solvation effects in a catalysed reaction requires available data on the change in enthalpy of solvation for each reactant. It follows from Fig. 4 that the change in enthalpy of solvation of an *n,v*-complex is determined by the relationship:

$$\delta H^{IC}_{solv} = \delta H^{A}_{solv} + \delta H^{GaCl_3}_{solv} + \Delta H^{0}_{IC}(S) - \Delta H^{0}_{IC}(S_0).$$

The results of thermochemical measurements made in a series of solvents for the complex of *N*-phenylmaleimide (PMA) with gallium chloride[164] show that the enthalpy of solvation of gallium chloride increases substantially on changing not only to *n*-donor solvents but also to π-donor solvents (Fig. 12). As the enthalpy of solvation of the Lewis acid increases, there is a proportional decrease in the enthalpy of formation of the *n,v*-complex in solution (Fig. 12). The constant enthalpy level of the *n,v*-complex in the series of solvents studied is achieved because the gain in enthalpy of solvation of the reactants in donor solvents is completely balanced by the loss in enthalpy of formation of the complex. This means that on formation of a complex between gallium chloride and imide, which is stronger than a complex with solvent, there is a complete break-up of the weaker complexes. The change in enthalpy of solvation of the reactants (PMA + $GaCl_3$) is mainly determined by the change in enthalpy of solvation of gallium chloride. The constant enthalpy level of the *n,v*-complex of MPA·$GaCl_3$ in the series of solvents indicates that there is approximately the same activation of the dienophile moeity in the complex. This conclusion is consistent with the results of two studies,[43,169] in which cases are noted where the same charge transfer in complexes occurs when there is a different enthalpy of formation of the complexes.

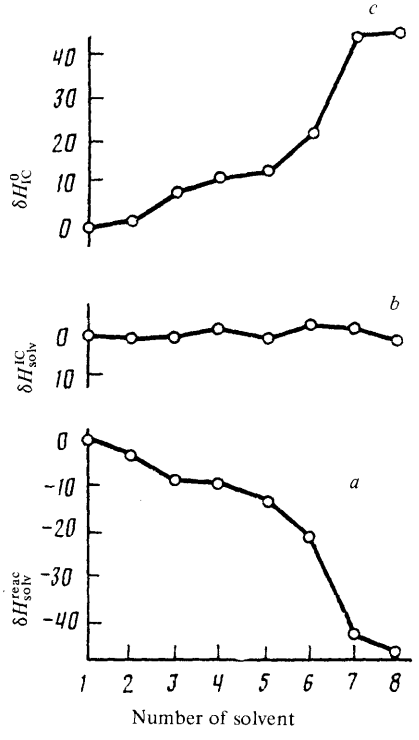


Figure 12. Enthalpies of transfer of the reactants (*a*) and the *n,v*-complex of *N*-phenylmaleimide with gallium chloride (*b*) and also the change in enthalpy of formation of this complex (*c*) in different solvents: *1*, chlorobenzene; *2*, benzene; *3*, toluene; *4*, dichloromethane; *5*, *p*-xylene; *6*, mesitylene; *7*, nitromethane; *8*, nitrobenzene.[163,164]

The insignificant change in enthalpy of solvation of the complex PMA·$GaCl_3$ on changing from nonpolar to polar media is unexpected in view of the high polarity of this complex.[43] A more detailed investigation involving other complexes[170,171] showed that this kind of solvation effect is the rule rather than the exception. More accurate findings on the change in enthalpy of solvation of boron trifluoride etherate[163] are in agreement with this conclusion. The change in enthalpy of solvation of the transition state of a

catalysed reaction[160,163] to a considerable degree corresponds to the nature of the effect of medium on the enthalpy level of a normal reaction involving tetracyanoethylene. The difference in the rate of reactions involving dienophiles that have comparable activity—tetracyanoethylene and imide complexes with gallium chloride—thus becomes clear. The formation of a strong complex between the dienophile and the Lewis acid results in an increase in the rate of reaction by a factor of 10^4, the enthalpy level of this new reactant being insensitive to a change of medium. The complex between tetracyanoethylene and the solvent is less strong, and the specific solvation of this dienophile makes it less active compared to free tetracyanoethylene. In this case the observed rate of reaction is determined mainly by the concentration of free tetracyanoethylene, which varies considerable over a range of π-donor solvents. It is interesting to note that the enthalpy level of a π,π-complex between tetracyanoethylene and a π-donor does not vary very much over this range of solvents.[46]

3. Factors that determine the activity of reactants in a catalysed Diels–Alder reaction

The factors governing the activity of reactants in an uncatalysed Diels–Alder reaction were examined above. In a catalysed process the conversion of the dienophile to an *n,v*-complex only slightly changes the lengths of the C=C bond and hence the magnitude of the overlap integral of the reacting atoms. Thus, the change from ethylene ($R_{1,2}$ = 1.332 Å [172]) to a strong acceptor such as tetracyanoethylene ($R_{1,2}$ = 1.317 Å [173]) is accompanied by only a slight variation in C=C bond length.

Since it is the dienophile and not the diene that forms an *n,v*-complex with the Lewis acid, the value of the ionisation potential of the diene (I_D) and the interatomic distance ($R_{1,4}$) remain constant and do not control the observed acceleration of reaction.[25]

The next factor to affect the reactivity concerns the energies of the reacting bonds, with differences that are reflected in the enthalpy of reaction. This also bears no relation to the observed vigorous acceleration of reaction since the thermochemically determined enthalpies of the reactions with and without involvement of a catalyst differ by not more than 3–5 kJ mol^{-1}.[162]

According to perturbational molecular orbital theory the increase in reactivity of activated dienophiles is due, by analogy with a normal Diels–Alder reaction, to the decrease in energy gap between the HOMO of diene and the LUMO of dienophile.[174,175] In view of the qualitative nature of the calculations carried out, the data obtained by spectrophotometric analysis of *n,v*-complexes containing activated dienophiles[156,176,177] should be considered more reliable. By using the thermodynamic cycle depicted in Fig. 13, it is possible to calculate the change in energy of the LUMO of dienophile on formation of an *n,v*-complex:

$$\Delta E_{LUMO} = E^{II}_{CT}(HMB.(AMA.GaCl_3)) - E^{I}_{CT}(HMB.AMA),$$

where E^{II}_{CT} is the charge-transfer energy in π,π-complexes of hexamethylbenzene (HMB) with *N*-arylmaleimides which are activated due to the formation of an *n,v*-complex with gallium chloride (AMA·$GaCl_3$); E^{I}_{CT} is the charge-transfer energy with unactivated *N*-arylmaleimides.

The formation of π,π-complexes between a π-donor and a π-acceptor which is activated by a Lewis acid is reported in several studies.[144,178,179] A complex between cyclopentadiene and a methyl acrylate–titanium chloride *n,v*-complex has been identified at low temperatures.[179] A large number of ternary complexes of the type B·A·MX_n, where B are π-donors (alkylbenzenes), A are σ-acceptors (acid chlorides) and MX_n are Lewis acids, have been obtained and characterised by IR and NMR spectroscopy.[179] The equlibrium constants and enthalpies of formation of π,π-complexes of styrene and toluene with methyl methacrylate and its *n,v*-complex with tin chloride have been determined.[144]

Hexamethylbenzene is stable in the presence of Lewis acids and has a high π-donor capacity (I_D = 7.85 eV [105]). As the bond energy in the π,π-complex is low, a small perturbation of the HOMO level in the π-donor and the LUMO level in the π-acceptor is to be expected when a complex is formed.[40]

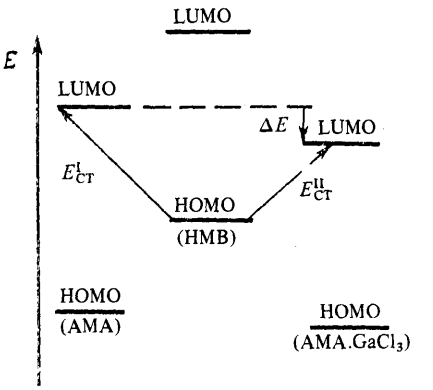


Figure 13. Diagram for determination of the change in energy of the LUMO of *N*-arylmaleimides (AMA) on conversion to an *n,v*-complex with gallium chloride according to the data on the π → π* transfer energy in π,π-complexes with hexamethylbenzene (HMB).[156]

The data from two studies[156,176] (Table 6) indicate an increase in electron affinity of ligands in a complex with gallium chloride (reduction in the LUMO level) by 0.7–1.15 eV. An even larger increase in electron affinity occurs in 1:1 aluminium chloride complexes and 2:1 gallium chloride complexes. The fact that for each group of complexes the difference in energy (ΔE_1 and ΔE_2) is fairly constant is worthy of note. Such a correspondence can occur when the HOMO levels of normal and activated dienophiles vary insignificantly.

The correlation of the acceleration effect on the Diels–Alder reaction with the charge-transfer energy, which is proportional to the electron affinity, is most interesting.[156] The linear nature of such a dependence for the reaction of cyanoethylenes with anthracene has been well established.[11,37] The retention of this type of dependence in the reaction of maleimides activated with Lewis acids (Fig. 14) can serve as experimental evidence that the catalytic effect in a Diels–Alder reaction of the "diene donor, dienophile acceptor" type is due to an increase in orbital interaction because of a significant rise in electron affinity of the dienophile in an *n,v*-complex.[156,165] Moreover, this dependence is regarded as a considerable argument in favour of the invariability of the reaction mechanism.[25] The line for cyanoethylenes is situated below, which is completely consistent with a higher conjugation energy (smaller enthalpy of reaction,

see Table 4) in these compounds compared to maleimides. The values representing the reactivity of all the maleimides activated by gallium or aluminium chlorides lie on a common line which represents the dependence of the reactivity on the three main controlling factors (see Fig. 11).

Table 6. Wavelengths (λ) and energies (E) of band maxima for $\pi \rightarrow \pi^*$ transitions of dienophiles (A), their n,ν-complexes with Lewis acids, and π,π-complexes of hexamethylbenzene (HMB) with unactivated and activated dienophiles.[156,176]

Dienophile	Lewis acid	A·MX$_n$			HMB·(A·MX$_n$)		
		λ, nm	E, eV	ΔE_1, eV	λ, nm	E, eV	ΔE_2, eV
N-*p*-tolyl-maleimide	none	260	4.77		330	3.76	
	$GaCl_3$	342	3.63	1.14	475	2.61	1.15
	$AlCl_3$	—	—	—	488	2.54	1.22
	$2GaCl_3$	405	3.06	1.71	593	2.09	1.67
N-Phenyl-maleimide	none	259	4.79		337	3.68	
	$GaCl_3$	332	3.74	1.05	470	2.64	1.05
	$AlCl_3$	—	—	—	481	2.58	1.10
	$2GaCl_3$	390	3.18	1.61	580	2.14	1.54
N-*p*-Bromophenyl-maleimide	none	265	4.68		345	3.58	
	$GaCl_3$	325	3.82	0.86	470	2.64	0.95
	$AlCl_3$	—	—	—	480	2.59	1.00
	$2GaCl_3$	388	3.20	1.48	590	2.10	1.49
N-*p*-Nitrophenyl-maleimide	none	276	4.49		365	3.40	
	$GaCl_3$	330	3.76	0.73	464	2.67	0.73
Maleic anhydride	none	280	4.43		353	3.51	
	$GaCl_3$	328	3.78	0.65	440	2.82	0.69
	$AlCl_3$	—	—	—	470	2.64	0.87
Citraconic anhydride	none	251	4.94		340	3.65	
	$GaCl_3$	315	3.94	1.00	440	2.82	0.83
	$AlCl_3$	—	—	—	455	2.73	0.92
Chloromaleic anhydride	none	246	5.04		365	3.40	
	$GaCl_3$	303	4.08	0.96	480	2.58	0.82
	$AlCl_3$	—	—	—	505	2.46	0.94
Dichloromaleic anhdyride	none	269	4.61		388	3.20	
	$GaCl_3$	322	3.85	0.76	500	2.48	0.72

unsubstituted, 9-methyl-, and 9,10-dimethyl-anthracenes (3.0, 2200, and 93 000 l mol^{-1} s^{-1} respectively) with only a small change in ionisation potential (ΔI_D = 0.29 eV).[30,50,86] It should be noted that with such changes in electron affinity the reactivity in a series of *N*-arylmaleimides only varies by a factor of 10 (see Table 4).

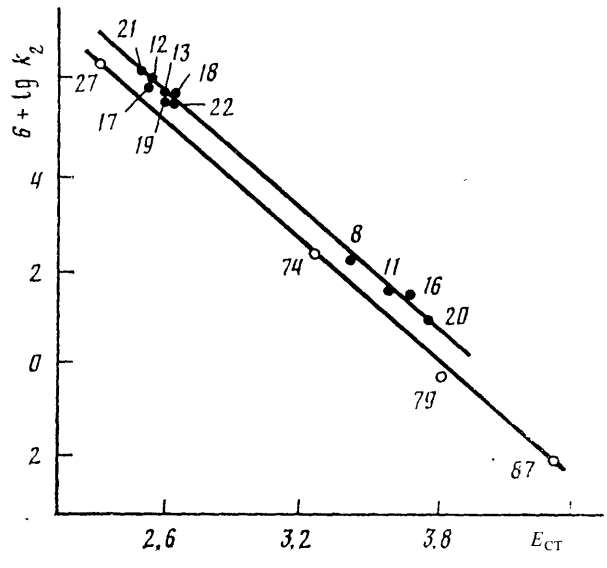


Figure 14. Dependence of the reactivity of anthracene in the Diels–Alder reaction with normal and activated *N*-arylmaleimides on the charge-transfer energy in π,π-complexes with hexamethylbenzene.[25,156] For the numbering of the reactions on the lower line, see Table 4; for those on the upper line, see Table 5.

What is the reason for the differing acceleration of reactions in which the same activated dienophile participates with different dienes?

The Diels–Alder reaction is assumed to be orbital controlled, so that a first-order interaction is usually ignored[11,37] [charge interaction, see, Eqn.(1)]. In a structural series of diene donors and dienophile acceptors the strengthening of donor-acceptor properties of the reactants leads to an increase in nucleophilicity of the reaction centre in the diene and electrophilicity in the dienophile.[180,181] The effective representation of the reactivity of these reactants in terms of frontier orbital interaction energies is possibly due to both types of interaction (charge and orbital) varying in a similar manner.

A combined calculation of the charge and orbital contributions is necessary to elucidate the kinetic mechanisms of reactions involving heteroatomic reactants.[4,80,81,91]

Even in a series of hydrocarbon addends the change in reactivity cannot always be accounted for from a study of the frontier orbital interaction energies. The rate constants of the reaction between 2.5-diphenylisobenzofuran and unsubstituted, methyl-, and dimethylmaleic anhydrides differ considerably (3.36, 9.0 × 10^{-3}, and 1.1 × 10^{-5} l mol^{-1} s^{-1} respectively), whereas the electron affinity remains approximately the same (ΔE_A = 0.30 eV).[137] A substituent effect which is just as marked but works in an opposite direction occurs in the reaction between tetracyanoethylene and

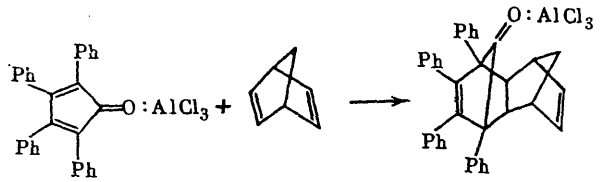
An increase in the charges on the reaction centre in the activated reactants must promote their affect on the reactivity. This effect will be exhibited in those cases where the orbital and charge contributions are not expected to have similar effects.

While in a Diels–Alder reaction of the type "diene donor, dienophile acceptor" the formation of an n,ν-complex with the dienophile leads to a large acceleration due to the increase in electron affinity and electrophilicity of the reacting atoms of dienophile, in reactions of a neutral type and of the type "diene acceptor, dienophile donor" acceleration would be expected when an n,ν-complex was formed with the diene.

Substituted cyclopentadienones—cyclones—can undergo a neutral type of reaction because of the convergence of their HOMO and LUMO levels.[182] An acceleration of the reaction between tetracyclone and alkenes in the presence of aluminium chloride has been recorded.[183] Spectrophotometric measurement showed[166] that tetracyclone forms a strong n,ν-complex with aluminium chloride, which is stable over a period of time and has an intense absorption in the region 800–1000 nm. When stronger Lewis bases are added, the absorption that characterises the free diene is rapidly restored. The enthalpy of formation of the n,ν-complex of tetracyclone with gallium chloride as determined by a thermochemical method

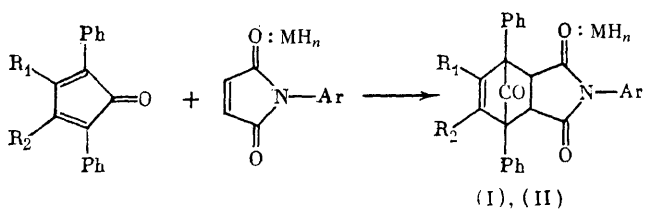
(-39 kJ mol^{-1} [166]) suggests the high strength of the bond in the complex. Phencyclone and indanocyclone decompose even in the presence of gallium chloride.[166]

Dienophiles such as *trans*-stilbene and norbornadiene do not have *n*-donor groups and therefore do not compete with the diene in the formation of a complex:



It is evident from the data given in Table 5 that quite a large acceleration effect occurs in the reaction of alkenes with an activated diene ($\sim 10^3$), but it is noticeably less than the acceleration effect in normal reactions with dienophile activation ($\sim 10^5$).

N-Arylmaleimides form more stable complexes with gallium chloride than does tetracyclone. The results of spectrophotometric titration show that when gallium chloride is added to a solution of tetracyclone and imide, there is no change in the absorption of the diene up to a 1:1 ratio of imide to catalyst. With a further increase in the proportion of Lewis acid an absorption appears in the region 800–1000 nm, which is typical for a complex between the diene and gallium chloride. The Lewis acid bonded to imide in the complex no longer has a destructive effect on cyclones, so it is possible to carry out a kinetic study of the reaction between tetracyclone (I) and phencyclone (II) on the one hand, and a number of dienophiles on the other hand[167] (Table 5):



(I), (II)

I: $R_1 = R_2 =$ Ph; II: $R_1 - R_2 =$ *cis*-*o*,*o*'-biphenylene

The acceleration effect on the reaction of imides in a complex of 1:1 composition with gallium chloride or aluminium chloride is surprisingly small. When aluminium chloride is coordinated with the carbonyl groups of the imide (1:1) and tetracyclone (1:1), the reaction is not accelerated at all (see reactions 49 and 53 in Table 5). Such unusual behaviour of the imides reacting with cyclones cannot be due to the properties of the activated dienophiles. An insignificant acceleration effect also occurs in the reaction of phencyclone with activated esters of unsaturated acids.

V. Conclusion

The considerable progress made in studying the factors that determine the reactivity of compounds in the Diels–Alder reaction has been achieved as a result of involving thermochemical methods. The comprehensive investigation of this reaction using chemical kinetics, spectroscopy, thermochemistry, and structural analysis has led to the identification of three main factors affecting the reactivity: 1) the interaction energy of the frontier orbitals, 2) the energy of the reacting π-bonds, and 3) the interatomic distance in the diene.

The existing data indicate (see Table 4) that the difference in bond energies for dienes (δH_{reac} = 150 kJ mol^{-1}) is greater than for dienophiles (δH_{reac} = 40–50 kJ mol^{-1}). The maximum value of the exothermic reaction between dienophiles and alkylbutadienes corresponds to an increased thermal stability of the addition products. It should be noted that butadiene has the highest interatomic distance $R_{1,4}$ compared to other dienophiles and has a low donor capacity. Since ethylene has the lowest electron affinity, its reaction with butadiene cannot be regarded as a typical example of the Diels–Alder reaction, although it is the simplest for quantum-chemical calculations and therefore a convenient model.

In the series of dienes—isobenzofuran, cyclopentadiene, anthracene, butadiene—the $R_{1,4}$ value increases from 2.19 to 2.90 Å.[109] Taking into account the increasing structural changes which occur when a cyclic adduct is formed with these dienes, a decrease in exothermicity of reaction would be expected if both factors affecting the reactivity ($R_{1,4}$ and E_{C-C}) were interrelated. However, the experimentally found values of the enthalpy of reaction increase in this series of dienes (see Table 4) and hence these factors act independently.

By using reactants that are activated by Lewis acids it is possible to obtain adducts which are difficult to synthesise by other methods.[141,184–187]

The acceleration effect can vary over a very wide range. Thus, in the presence of tin chloride or boron trifluoride etherate the rate of reaction remains virtually unchanged, while in the presence of boron, gallium, or aluminium halides it increases by a factor of 10^4–10^6, and when complexes of composition 2:1 are formed it even increases by a factor of 10^7–10^8 (see Table 5). While, for example, the half-life for formation of an adduct between *O*,*O*-diethyl β-carbomethoxyvinylphosphonate and 9,10-dimethylanthracene at 25 °C and with a concentration of reactants equal to 0.1 mol^{-1} l^{-1} is 350 years, in the presence of two equivalents of gallium chloride only 10 min is needed for this.[142] It is clear that this type of activation, especially in the case of unreactive reagents, is always desirable for the preparation of various cyclic products.

This type of acceleration effect is also possible in other cycloaddition reactions. For example, the rate of addition of a nitrone to an activated dipolarophile approximately increases by a factor of 10^5 (see Table 5).

It follows from an analysis of the spectra of π,π-complexes (see Table 6) that the electron affinity of the dienophile increases in the series of *n*,*v*-complexes with $GaCl_3$, $AlCl_3$, and $2GaCl_3$. In this case the effect of two moles of gallium chloride on the change in electron affinity is considerably less than doubling the effect in a 1:1 complex. These data are consistent with the observed acceleration effect in catalysed reactions (see Table 5).

In reactions of the type "diene donor, dienophile acceptor", activation of the dienophile leads to an increase in stabilisation energy for frontier orbital interaction and a decrease in repulsion energy of the reacting nucleophilic and electrophilic centres in the diene and dienophile. This effect also occurs in a reaction of the type "diene acceptor, deinophile donor" when the diene is activated. In reactions involving dienes that have an acceptor nature (cyclones;[182] 2-cyano- or 2-trifluoromethyl-butadienes[160,161]), the acceleration effect is substantially reduced, possibly because of the increase in repulsion energy between the converging electrophilic atoms in both reactants. The formation of *n*,*v*-complexes by both

partners is clearly unfavourable for reaction (see Table 5). Similar behaviour is noted in the uncatalysed Diels–Alder reaction involving tetracyclone. Here the rate of reaction with tetracyanoethylene is considerably less than with tricyano- and *gem*-dicyano-ethylenes.[182] In a similar manner the rate constant of the reaction between tetracyanoethylene and phencyclone (0.13 l mol^{-1} s^{-1}) is less than the rate constant of the reaction involving *N*-phenylmaleimide (0.76 l mol^{-1} s^{-1}).[182] Since *N*-phenylmaleimide complexed with aluminium chloride has acceptor properties (E_A = 1.99 eV [156]) approaching those of tetracyanoethylene (E_A = 2.88 eV [37]) the small acceleration effect is understandable. The development of various types of acceleration effect has been confirmed experimentally.[117,120–129,142,162,166,167] The kinetic behaviour of normal and activated reactants is consistent with the assumption that there is not always a similar effect from charge and orbital interactions on the stabilisation energy of the transition state of the Diels–Alder reaction.[168,180,181,188–190]

References

1. Yu A Titov *Usp. Khim.*, 1962, **31**(5) 529 [English translation in *Russ. Chem. Rev.*, 1962(5)]
2. Ya K Syrkin, I I Moiseev *Usp. Khim.*, 1958, **27**(11) 1321 [English translation in *Russ. Chem. Rev.*, 1958(11)]
3. M C Kloetzel *Organic Reactions* (Translated into Russian) (Edited by K A Kocheshkov), Vol. 4, Izd. Inostr. Lit., Moscow, 1951, p. 7
4. Yu A Arbuzov *Usp. Khim.*, 1964, **33**(8) 913 [English translation in *Russ. Chem. Rev.*, 1964(8)]
5. A I Konovalov, Doctorate Thesis in Chemical Sciences, Kazan' State University, Kazan', 1973, p. 306
6. A I Konovalov *Stroenie i Reaktsionnaya Sposobnost' Organicheskikh Soedinenii* (Structure and Reactivity of Organic Compounds) (Edited by B A Arbuzov), Izd. Nauka, Moscow, 1978, p. 259
7. A I Konovalov *Usp. Khim.*, 1983, **52**(11) 1852 [English translation in *Russ. Chem. Rev.*, 1983(11)]
8. J Sauer *Angew Chem.*, 1966, **78**(4) 233
9. J Sauer *Angew. Chem.*, 1967, **79**(2) 76
10. J Sauer *Usp. Khim.*, 1969, **38**(4) 624 [English translation in *Russ. Chem. Rev.*, 1969(4)]
11. J Sauer, R R Sustman *Angew. Chem.*, 1980, **92**(10) 773
12. R Huisgen, R Grashey, J Sauer *The Chemistry of Alkenes* (Translated into Russian) (Edited by A A Petrov), Izd. Khimiya, Leningrad, 1969, p. 444
13. A Wasserman *The Diels–Alder Reaction* (Translated into Russian), Izd. Mir, Moscow, 1968, p. 133
14. K N Houk *Pericyclic Reactions*, Acad. Press, New York–London, 1977, Vol. 35-2, p. 181
15. R Woodward, R Hoffmann *Conservation of Orbital Symmetry* (Translated into Russian), Izd. Mir, Moscow, 1971, p. 207
16. T Gilchrist, R Storr *Organic Reactions and Orbital Symmetry* (Translated into Russian), Izd. Mir, Moscow, 1976, p. 352
17. N Epiotis *Theory of Organic Reactions* (Translated into Russian), Izd. Mir, Moscow, 1982, p. 330
18. M V Bazilevskii *Metod Molekulyarnykh Orbit i Reaktsionnaya Sposobnost' Organicheskikh Molekul* (Molecular Orbital Method and Reactivity of Organic Molecules), Izd. Khimiya, Moscow, 1969, p. 303
19. H Kwart, K King *Chem. Rev.*, 1968, **68**(4) 415
20. A S Dneprovskii, T I Temnikova *Teoreticheskie Osnovy Organicheskoi Khimii* Theoretical Principles of Organic Chemistry), Izd. Khimiya, Leningrad, 1979, p. 520
21. W C Herndon *Chem. Rev.*, 1972, **72**(2) 157
22. N Tyutyulkov, P Markov *Monatsh. Chem.*, 1968, **99**(2) 861
23. G V Mavrin, Candidate's Thesis in Chemical Sciences, Kazan' State University, Kazan', 1980, p. 157
24. D G Khuzyasheva, Candidate's Thesis in Chemical Sciences, Kazan' State University, Kazan', 1983, p. 135
25. I M Shakirov, Candidate's Thesis in Chemical Sciences, Kazan' State University, Kazan', 1985, p. 143
26. A S Onishchenko *Dienovyi Sintez* (Diene Synthesis), Izd. Akad. Nauk SSSR, 1963, p. 650
27. L Andrews, R Keefer *Molecular Complexes in Organic Chemistry* (Translated into Russian), Izd. Mir, Moscow, 1967, p. 206
28. R Foster *Organic Charge-Transfer Complexes*, Acad. Press, London–New York, 1969, p. 470
29. B A Arbuzov, A I Konovalov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1965, (7) 1290
30. A I Konovalov, V D Kiselev *Zh. Org. Khim.*, 1966, **2**(1) 142
31. A I Konovalov, V D Kiselev, O A Vigdorovich *Zh. Org. Khim.*, 1967, **3**(2) 2085
32. A I Konovalov, V D Kiselev, M B Metelina *Zh. Org. Khim.*, 1970, **6**(8) 1548
33. M J S Dewar *J. Am. Chem. Soc.*, 1952, **74**(13) 3341
34. K N Houk *Acc. Chem. Res.*, 1975, **8**(11) 361
35. L Salem *J. Am. Chem. Soc.*, 1968, **90**(3) 543
36. R Sustmann *Pure Appl. Chem.*, 1974, **40**(4) 569
37. K N Houk, L L Munchausen *J. Am. Chem. Soc.*, 1976, **98**(4) 937
38. K Fukui *Acc. Chem. Res.*, 1971, **4**(2) 57
39. K Fujimoto, K Fukui *Reactivity and Reaction Pathways* (Translated into Russian) (Edited by G Klopman), Izd. Mir, Moscow, 1977, p. 30
40. R S Mulliken, W B Person *Molecular Complexes*, Interscience Publ., New York, 1969, p. 498
41. G Briegleb *Electronen-Donator-Komplexe*, Springer Verlag, Berlin, 1961, p. 288
42. O Kh. Poleshchuk, Yu K Maksyutin *Usp. Khim.*, 1976, **45**(12) 2097 [English translation in *Russ. Chem. Rev.*, 1976(12)]
43. E N Gur'yanova, I P Gol'dshtein, I P Romm *Donorno-aktseptornaya Svyaz'* (The Donor-Acceptor Bond), Izd. Khimiya, Moscow, 1973, p. 397
44. A I Konovalov, V D Kiselev *Zh. Org. Khim.*, 1974, **10**(1) 6
45. L J Andrews, R M Keefer *J. Am. Chem. Soc.*, 1955, **77**(12) 6284
46. V D Kiselev, G V Mavrin, A I Konovalov *Zh. Org. Khim.*, 1980, **16**(7) 1435
47. V D Kiselev, G V Mavrin, E E Korshin, A I Konovalov *Zh. Obshch. Khim.*, 1980, **50**(5) 1135
48. T Asano, W J le Noble *Chem. Rev.*, 1978, **78**(4) 407
49. W J le Noble *Rev. Phys. Chem. Jpn.*, 1980, **50** 207
50. V D Kiselev, J G Miller *J. Am. Chem. Soc.*, 1975, **97**(14) 4036
51. O B Nagy, I B Nagy, A Bruylants *Bull. Soc. Chim. Belg.*, 1973, **82**(7) 539
52. I E Kardash, A N Pravednikov *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1975, **20**(1) 14
53. Yu N Baryshnikov, G I Vesnovskaya, V N Mushkarinova *Dokl. Akad. Nauk SSSR*, 1972, **205**(6) 1353

54. G B Sergeev *Problemy Khimicheskoi Kinetiki* (Problems in Chemical Kinetics) (Edited by V N Kondrat'ev), Izd. Nauka, Moscow, 1979, p. 312
55. R Brown, R S Cookson *Tetrahedron*, 1965, **21**(8) 1977
56. P Haberfield *J. Am. Chem. Soc.*, 1971, **93**(8) 2091
57. A I Konovalov, V D Kiselev, A N Ustyugov, N G Gess *Zh. Org. Khim.*, 1976, **12**(12) 2541
58. A I Konovalov, I P Breus, I A Sharagin, V D Kiselev *Zh. Org. Khim.*, 1979, **15**(2) 361
59. B B Bhowmik *Spectrochim. Acta, Part A*, 1971, **27**(2) 321
60. R X Ewall, A J Sonessa *J. Am. Chem. Soc.*, 1970, **92**(9) 2845
61. R S Drago, T F Bolles, R J Niedzielski *J. Am. Chem. Soc.*, 1966, **12** 2717
62. B N Solomonov, V B Novikov, V V Gorbachuk, A I Konovalov *Dokl. Akad. Nauk SSSR*, 1982, **265**(6) 1441
63. B N Solomonov, I S Antipin, A I Konovalov, V V Gorbachuk *Dokl. Akad. Nauk SSSR*, 1979, **247**(2) 405
64. A N Ustyugov, Candidate's Thesis in Chemical Sciences, Kazan' State University, Kazan', 1977, p. 144
65. P Haberfield, A K Ray *J. Org. Chem.*, 1972, **37**(20) 3093
66. E M Arnett, W G Bentrude, L L Burke, P M Duggleby *J. Am. Chem. Soc.*, 1965, **87**(7) 1541
67. D G Khuzyasheva, V D Kiselev, A I Konovalov, Manuscript Deposited with ONIITEKhim, Cherkassy, No.3048-79-Dep., p. 37
68. M G Evans, M Polanyi *Trans. Faraday Soc.*, 1936, **32**(9) 1333
69. N N Semenov *O Nekotorykh Problemakh Khimicheskoi Kinetiki i Reaktsionnoi Sposobnosti* (Some Problems Concerning Chemical Kinetics and Reactivity), Izd. Akad. Nauk SSSR, 1958, p. 683
70. A I Konovalov, V D Kiselev *Zh. Org. Khim.*, 1986, **22**(6) 1133
71. B Prantl, E Eibler, J Sauer *Tetrahedron Lett.*, 1982, (11) 1139
72. M J Goldstein, G L Thaer *J Am. Chem. Soc.*, 1965, **87**(9) 1933
73. S Seltzer *J. Am. Chem. Soc.*, 1965, **87**(7) 1534
74. D E Sinkle, J O Rodin *J. Am. Chem. Soc.*, 1964, **86**(15) 3091
75. M J S Dewar, S Olivella, H S Rzepa *J. Am. Chem. Soc.*, 1978, **100**(18) 5650
76. M Taagepera, E R Thornton *J. Am. Chem. Soc.*, 1972, **94**(4) 1168
77. R Huisgen *Pure Appl. Chem.*, 1980, **52**(10) 2283
78. R E Townshend, et al. *J. Am. Chem. Soc.*, 1976, **98**(8) 2190
79. L A Burke, G Leroy *Theor. Chim. Acta.*, 1977, **44**(2) 219
80. L N Koikov, P B Teren'tev, I P Gloriozov, Yu G Bundel' *Zh. Org. Khim.*, 1984, **20**(8) 1629
81. L N Koikov, P B Teren'tev, I P Gloriozov, Yu G Bundel' *Zh. Org. Khim.*, 1984, **20**(5) 919
82. G S Hammond *J. Am. Chem. Soc.*, 1955, **77**(2) 334
83. R D Brown *J. Chem. Soc.*, 1950, (2) 691
84. E Streitwieser *Molecular Orbital Theory for Organic Chemists* (Translated into Russian), Izd. Mir, Moscow, 1965, p.435
85. A I Konovalov *Zh. Org. Khim.*, 1969, **5**(10) 1713
86. V D Kiselev, A I Konovalov, E A Weisman, A N Ustyugov *Zh. Org. Khim.*, 1978, **14**(1) 128
87. V D Kiselev, A N Ustyugov, I P Breus, A I Konovalov *Dokl. Akad. Nauk SSSR*, 1977, **234**(5) 1089
88. D R Stull, E F Westrum Jr., G C Sinke *The Chemical Thermodynamics of Organic Compounds* (Translated into Russian), Izd. Mir, Moscow, 1971, p. 944
89. J D Cox, G Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Acad. Press, London–New York, 1970, 643 pp
90. P W Mui, E Grunwald *J. Phys. Chem.*, 1984, **88**(25) 6340
91. V Z Gabdrakipov *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.*, 1969, (3) 87
92. J Sauer, H Wiest, A Mielert *Chem. Ber.*, 1964, **97**(11) 3183
93. A I Konovalov, V D Kiselev, Ya D Samuilov *Dokl. Akad. Nauk SSSR*, 1968, **179**(4) 866
94. A Mielert, et al. *J. Lieb. Ann. Chem.*, 1980, (6) 954
95. J N Spencer, et al. *J. Phys. Chem.*, 1977, **81**(24) 2237
96. A I Konovalov, B N Solomonov, A N Ustyugov *Dokl. Akad. Nauk SSSR*, 1973, **211**(1) 102
97. A I Konovalov, B N Solomonov, A N Ustyugov *Dokl. Akad. Nauk SSSR*, 1973, **213**(2) 349
98. F E Rogers *J. Phys. Chem.*, 1971, **75**(11) 1734
99. F E Rogers *J. Phys. Chem.*, 1972, **76**(1) 106
100. V D Kiselev, G V Mavrin, A I Konovalov, Manuscript Deposited with ONIITEKhim, Cherkassy, No. 10-khp-80-Dep., p. 6
101. J Jurczak, A L Kawczynski, T Kozluk *J. Org. Chem.*, 1985, **50**(7) 1106
102. V D Kiselev, I P Breus, A I Konovalov, Manuscript Deposited with ONIITEKhim, Cherkassy, No. 2606-77-Dep., p. 15
103. V D Parker, O Hammerich *Acta Chem. Scand., Ser. B*, 1977, **31**(10) 883
104. A I Konovalov, V D Kiselev, Ya D Samuilov *Dokl. Akad. Nauk SSSR*, 1969, **186**(2) 347
105. V N Kondrat'ev (Editor) *Energii Razryva Svyazei. Potentsialy Ionizatsii i Srodstvo k Elektronu: Spravochnik* (Bond Cleavage Energies. Ionisation Potentials and Electron Affinity: Handbook), Izd. Nauka, Moscow, 1974, p. 351
106. G Briegleb *Angew. Chem.*, 1964, **3**(9) 617
107. H D Scharf, H Plum, J Fleischhauer, W Schleker *Chem. Ber.*, 1979, **112**(3) 862
108. R Sustmann, M Bohm, J Sauer *Chem. Ber.*, 1979, **112**(3) 883
109. L E Sutton (Editor) *Tables of Interatomic Distances and Configurations in Molecules and Ions*, Acad. Press, London, 1965, Part 2, p. 208
110. J Sauer, H Wiest *Angew. Chem.*, 1962, **74**(10) 353
111. T G Lenz, L S Hegedus *Proceedings of the International Solar Energy Society. 'Sun II' Silver Jubilee Congress*, Colorado, 1979, Vol. 1, p. 154
112. D C Rideout, R Breslow *J. Am. Chem. Soc.*, 1980, **102**(26) 7817
113. R Breslow, U Maitra, D Rideout *Tetrahedron Lett.*, 1983, (18) 1901
114. P Laszlo, J Lucchetti *Tetrahedron Lett.*, 1984, (20) 2147
115. W L Mock, T A Irra, J P Wepsiec, T L Manimaran *J Org. Chem.*, 1983, **48**(20) 3619
116. P A Grieco, P Garner *Tetrahedron Lett.*, 1983, (18) 1897
117. P Yates, P Eaton *Tetrahedron Lett.*, 1960, (11) 5
118. P Yates, P Eaton *J. Am. Chem. Soc.*, 1960, **82**(16) 4436
119. G I Fray, R Robinson *J. Am. Chem. Soc.*, 1961, **83**(1) 249
120. T Inukai, T Kojima *J. Org. Chem.*, 1966, **31**(4) 1121
121. T Inukai, T Kojima *J. Org. Chem.*, 1966, **31**(6) 2032
122. T Inukai, T Kojima *J. Org. Chem.*, 1967, **32**(4) 869
123. T Inukai, T Kojima *J. Org. Chem.*, 1967, **32**(4) 872
124. A W McCulloch, A G McInnes *Can. J. Chem.*, 1971, **49**(19) 3152
125. A W McCulloch, A G McInnes *Can. J. Chem.*, 1974, **52**(1) 143
126. T Kojima, T Inukai *J. Org. Chem.*, 1970, **35**(5) 1342
127. T Inukai, T Kojima *J. Org. Chem.*, 1971, **36**(7) 924

128. P C Jain, Y N Mukerjee, N Anand *J. Am. Chem. Soc.*, 1974, **96**(9) 2996
129. J Sauer, D Lang, H Wiest *Chem. Ber.*, 1964, **97**(11) 3208
130. B B Snider *Acc. Chem. Res.*, 1980, **13**(3) 426
131. E Klimova, E Treshova, Yu Arbuzov *Dokl. Akad. Nauk SSSR*, 1968, **180**(4) 864
132. M S Malinovskii, V G Dryuk, V I Avramenko *Zh. Org. Khim.*, 1968, **4**(10) 1725
133. B B Snider, G B Phillips *J. Org. Chem.*, 1981, **46**(12) 2563
134. M P Doyle, M Oppenhuizen, R C Elliott, M R Boelkins *Tetrahedron Lett.*, 1978, (26) 2247
135. M P Doyle, M E Buhro, J F Dellaris *Tetrahedron Lett.*, 1979, (46) 4429
136. M P Doyle, et al. *J. Org. Chem.*, 1980, **45**(18) 3657
137. V D Kiselev, I M Shakirov, A I Konovalov *Zh. Org. Khim.*, 1985, **21**(6) 1215
138. V D Kiselev, D G Khuzyasheva, A I Konovalov *Zh. Org. Khim.*, 1983, **19**(6) 1268
139. C F Allen, R W Ryan, J A Van Allan *J. Org. Chem.*, 1962, **27**(3) 778
140. R N Engibaryan, V O Babayan, A A Petrov *Zh. Org. Khim.*, 1966, **2**(8) 1362
141. H W Thompson, D G Mellilo *J. Am. Chem. Soc.*, 1970, **92**(10) 3218
142. V D Kiselev, I M Shakirov, A I Konovalov, D G Khuzyasheva *Zh. Org. Khim.*, 1983, **19**(10) 2064
143. J Brunn, S Peust *Z. Chem.*, 1976, **16**(4) 154
144. V Kuran, S Pasynkiewicz, Z Florjanczyk, E Lucztuk *Macromol. Chem.*, 1976, **177**(9) 2627
145. H Hirai, M Komiyama *J. Polym. Sci.*, 1974, **12**(12) 673
146. H Brunn, R Radeglia, B Lewanscheck, S Peust *Z. Phys. Chem.*, 1977, **258**(4) 4429
147. J Sauer, J Kredel *Tetrahedron Lett.*, 1966, (7) 731
148. I P Romm, E N Gur'yanova, E N Kharlamova, R R Shifrina *Zh. Obshch. Khim.*, 1972, **42**(10) 2246
149. I P Romm, et al. *Dokl. Akad. Nauk SSSR*, 1969, **189**(4) 810
150. I P Romm, E N Gur'yanova *Zh. Obshch. Khim.*, 1968, **38**(9) 1927
151. I P Romm, L I Belen'kii, E N Gur'yanova, Yu K Tovbin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, (11) 2478
152. E N Kharlamova, I P Romm, E N Gur'yanova *Zh. Obshch. Khim.*, 1970, **40**(11) 2352
153. I P Romm, L I Belen'kii, E N Gur'yanova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, (12) 2783
154. L I Belen'kii, I B Karmanova, G P Gromova *Zh. Org. Khim.*, 1973, **9**(7) 1499
155. L I Belen'kii, I B Karmanova, Yu B Vol'kenshtein *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, (8) 1725
156. V D Kiselev, I M Shakirov, A I Konovalov *Zh. Org. Khim.*, 1984, **20**(7) 1454
157. L M Tolbert, M B Ali *J. Am. Chem. Soc.*, 1982, **104**(6) 1742
158. F Frinquelly, F Pizzo, A Tatichi *J. Org. Chem.*, 1985, **50**(6) 890
159. L M Tolbert, M B Ali *J. Am. Chem. Soc.*, 1984, **106**(13) 3806
160. P F Alston, R M Ottenbrite *J. Org. Chem.*, 1975, **40**(8) 1111
161. P F Allston, M Gordon, R M Ottenbrite, T Cohen *J. Org. Khim.*, 1983, **48**(25) 5051
162. V D Kiselev, G V Mavrin, A I Konovalov *Zh. Org. Khim.*, 1982, **18**(12) 2505
163. V D Kiselev, E A Weisman, A I Konovalov *Zh. Org. Khim.*, 1985, **21**(6) 1145
164. V D Kiselev, et al. *Zh. Org. Khim.*, 1983, **19**(8) 1617
165. V D Kiselev, et al., Manuscript Deposited with ONIITEKhim, Cherkassy, 60-khp-80-Dep., p. 18
166. V D Kiselev, I M Shakirov, A I Konovalov *Zh. Org. Khim.*, 1985 **21**(3) 665
167. V D Kiselev, I M Shakirov, A I Konovalov *Zh. Org. Khim.*, 1986, **22**(2) 311
168. V D Kiselev, D G Khuzyasheva, A I Konovalov *Zh. Org. Khim.*, 1983, **19**(4) 884
169. I P Romm, et al. *Zh. Obshch. Khim.*, 1980, **50**(9) 2093
170. S D Ershov, L I shardakova, N A Morozova, Yu V Kondrat'ev, Manuscript Deposited with ONIITEKhim, Cherkassy, No. 915-khp-81-Dep., p. 188
171. S D Ershov, Yu V Kondrat'ev, A V Suvorov *Zh. Obshch. Khim.*, 1983, **53**(3) 494
172. L Pauling, P Pauling *Chemistry* (Translated into Russian), Izd. Mir, Moscow, 1978, p. 683
173. D N Dhar *Chem. Rev.*, 1967, (6) 611
174. N T Anh, J Seyden-Penne *Tetrahedron*, 1973, **29**(20) 3259
175. K N Houk, R W Strozier *J. Am. Chem. Soc.*, 1973, **95**(12) 4094
176. V D Kiselev, I M Shakirov, A I Konovalov *Zh. Org. Khim.*, 1986, **22**(5) 1034
177. V D Kiselev, E A Weisman, A I Konovalov *Zh. Org. Khim.*, 1986, **56**(10), 2378
178. G B Sergeev, V S Komarov, A G Fedorova *Vestnik MGU*, 1982, **23**(2) 114
179. S Brownstein, E Gabe, F Lee, L Tan *J. Chem. Soc., Chem. Commun.*, 1984, (23) 1566
180. G Klopman *J. Am. Chem. Soc.*, 1968, **90**(2) 223
181. R F Hadson *Angew. Chem. Int. Ed. Engl.*, 1973, **12**(1) 36
182. Ya D Samuilov, Doctorate Thesis in Chemical Sciences, Kazan' State University, Kazan', 1984, p. 387
183. C F Allen, R W Ryan J A Allan *J. Org. Chem.*, 1962, **27**(3) 778
184. C K Soo-Hoo, S G Baxter *J Am. Chem. Soc.*, 1983, **105**(25) 7443
185. J Tou, W Reusch *J. Org. Chem.*, 1980, **45**(24) 5012
186. K Hagakawa, Y Kamikawa, K Kanematsu *Tetrahedron Lett.*, 1982, (21) 2171
187. S Danishevsky, J F Kerwin *J. Org. Chem.*, 1982, **47**(16) 3183
188. D J Bellville *J. Am. Chem. Soc.*, 1982, **104**(9) 2665
189. D J Bellville, D D Wirth, N L Bauld *J. Am. Chem., Soc.*, 1981, **103**(3) 718
190. H M Hoffmann, H Vathke-Ernst *Chem. Ber.*, 1981, **114**(6) 2208

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Reactions of *N*-chloramines and *N*-haloamides with unsaturated compounds

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ABSTRACT. The results obtained from studying the reactions of *N*-chloramines, *N*-halocarbamates, and *N*-haloamides of carboxylic, sulphonic, and phosphoric acids with unsaturated compounds have been correlated and classified. It is shown that the direction of addition of *N*-haloamines and *N*-haloamides to alkenes, dienes, alkenynes, and acetylenes, giving saturated adducts, is determined by the conditions of homolytic or heterolytic initiation. The reactions of *N*-chlorodialkylamines with olefins in the presence of sulphur trioxide are discussed. A new method of activating electrophilic reagents by introducing sulphur trioxide on to the N–Cl bond is identified.

An essentially new trend is reported for the reactions of *N,N*-dihaloamides of sulphonic and carboxylic acids and also *N,N*-dihalocarbamates with polyhaloethylenes, giving acylimines of polyhaloaldehydes, which are highly reactive syntones for the synthesis of fine organic chemicals.

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I. Introduction

The chemistry of *N*-haloamines, *N*-halourethanes, and *N*-haloamides of sulphonic and carboxylic acids has undergone considerable development in the last ten years. The interest shown in compounds containing an N–Hal bond is due to their high and varied reactivity, so they have been able to remain for a long time as fertile subjects in theoretical and synthetic organic chemistry. Up to the present time a large amount of experimental material on the study of homolytic and heterolytic addition reactions of *N*-chloramines, *N*-halourethanes, and *N*-halo- and *N,N*-dihaloamides of carboxylic, phosphoric, and sulphonic acids to alkenes, dienes, alkenynes, and acetylenes has been collected.

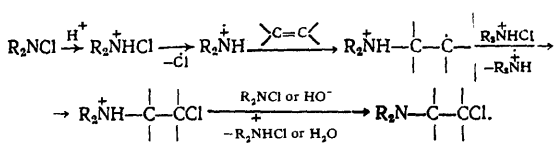
Information on the tendency of compounds with an N–Hal bond to add on to alkenes first appeared in 1930;[1] it was reported that *N*-bromo-*N*-methylbenzenesulphonamide and *N*-monobromoacetamide react with 1-phenylpropylene to give saturated adducts. However, systematic studies of the reactivity of *N*-haloamides in addition reactions to multiple bonds only started 30 years later. The period of rapid development of this branch of chemistry was in the 1960s and 1970s. Progress made up to 1970–1973 in this branch of chemistry was described in reviews.[2–4] Despite the merits of these reviews none of them can be regarded as sufficiently comprehensive. Moreover, in the last 10–12 years the flow of studies devoted to examining the reaction of *N*-haloamides of sulphonic, carboxylic, and carbamic acids with unsaturated compounds has increased steadily. Hence, it is advisable to correlate the literature material on this subject in order to establish the general mechanisms and also the prospects for further development of this branch of chemistry.

We have not examined the problems concerning the methods of forming aminyl and amidyl intermediates since they have been covered in sufficient detail in two reviews[2,5] and three studies.[6–8]

II. Reactions of *N*-chloramines with unsaturated compounds

An extensive series of studies devoted to examining the reactions of *N*-chloramines with unsaturated compounds was carried out in the 1960s by two groups of research workers[3,9–16,17–23] and covered in reviews.[2–4,24] These studies made a decisive contribution to the chemical potentialities of compounds containing an N–Hal bond. In this section the general mechanisms for reactions of this type are summarised.

The reactions of *N*-chloramines with unsaturated compounds mainly take place with homolytic cleavage of the N–Cl bond. Two methods are principally used to initiate them. Thus, the reaction of *N*-chloroalkyl- and *N*-chlorodialkyl-amines with alkenes, dienes, and acetylenes, initiated by UV irradiation or by bivalent iron salts in a mixture of H_2SO_4 and glacial acetic acid, is known to occur.[9–16] The reactions occur rapidly, giving β-chloroalkylamines $(Alk)_2NCH_2CR^1R^2Cl$, β-chloroalkenylamines $(Alk)_2NCH_2CH=CHCH_2Cl$, and α-chloroaldehydes AlkCHClCHO or α-chloroketones AlkCHClCOR. These reactions take place by a free-radical mechanism via the formation of a protonated aminyl radical cation according to the scheme:



The generation of aminyl radicals by redox systems (salts of iron, titanium, and copper) in alcohol solution is also known to occur.[17-24] The addition of these radicals to the multiple carbon–carbon bond of alkenes, dienes, and acetylenes occurs readily:

$$R_2NCl \xrightarrow[-[MCl]^+]{M^+} R_2\dot{N} \xrightarrow{>C=C<} R_2N-\overset{|}{C}-\dot{C}< \xrightarrow[-M^+ \text{ (or } R_2\dot{N})]{[MCl]^+ \text{ (or } R_2NCl)} -R_2NC(Cl)C(Cl)-,\quad M^+ = Cu^+,\ Fe^{2+},\ Ti^{3+}.$$

The most active redox initiators are bivalent iron salts and methanol is the solvent of choice.[3-4] When other solvents—ethanol [23] or an ethanol–acetone mixture[17]—are used, there is no increase in the yield of adducts.

The yield and structure of the adducts depend on the structure of the unsaturated compound and *N*-chloramine and also on the reaction conditions. Thus, the reactions of *N*-chlorodialkyl-, *N*-chlorocycloalkyl-, and *N*-chloro(hexa- or penta-methylene)-amines with aliphatic,[10,13,16] halogenated [$CH_2=C(Hal)R$ (Hal = Cl, Br, F) and $CH_2=C(X)CH_2Cl$ (X = H, Cl)],[13,16] and functionally substituted alkenes [$CH_2=CHCH_2X$ (X = OH, OC_2H_5, OAc, OPh, CN)] [13,15] in 4 M H_2SO_4 in glacial acetic acid or in methanol in the presence of redox systems give β-chloroalkylamines $R(R^1)NCH_2C(Cl)R^2R^3$. *N*-Chloramines add on to 1,2- and 1,3-dienes at the 1,2- and 1,4-position respectively[10,14] to give β-chloro- and γ-chloro-alkenylamines of the type

$$R(R^1)NCH_2CCl=C(R^2)R^3 \text{ and } R(R^1)NCH_2CH=CHCH_2Cl.$$

The reactions of *N*-chloramines with acetylenes occur in an unique manner; α-chloroaldehydes or, in the case of disubstituted acetylenes, α-chloroketones, have been isolated:[10,14]

$$(Alk)_2NCl + RC\equiv CR^1 \xrightarrow{H_2SO_4-AcOH} (Alk)_2NC(R)=C(R^1)Cl \xrightarrow{H_2O} RCOCHClR^1,$$

$$Alk = C_2H_5,\ n\text{-}C_4H_9,\ n\text{-}C_5H_{11}.$$

Finally, reactions involving chloramination of alkenynes such as vinylacetylene, 1-penten-3-yne, and 2-methyl-1-buten-3-yne,[25] are known; these take place in an acid medium to give mainly 1,4-addition products in 60–85% yield.

In the free radical addition of a protonated *N*-chloramine to alkenes that have allyl hydrogen atoms, a competing reaction occurs—electrophilic chlorination leading to chloroalkenes and β-chloroalkyl acetates by stabilisation of carbocation (A):[13]

$$R_2\overset{+}{N}HCl \rightarrow [R_2NH + Cl^+],$$

$$[Cl^+] + >C=C-CH< \rightarrow ClC-\overset{+}{C}-CH< \begin{cases} \longrightarrow ClC-C=C< + H^+ \\ \xrightarrow[-H^+]{AcOH} ClC-C(OAc)-CH< \end{cases}$$

(A)

In a number of cases, namely, in reactions with alkenes that have electron-donating substituents on the double bond (isobutylene, *cis*-2-butene), the yield of products from electrophilic chlorination is considerable (up to 60%). At the same time, electrophilic chlorination occurs to a lesser degree when electron-withdrawing substituents that reduce the stability of the intermediate ion (A) are present in the alkenes, thus assisting the free-radical addition of chloramines to the double bond of unsaturated compounds to give adducts. Thus, in the series $CH_2=CHR$, where R = Cl, F, CH_2Cl, CH_2CF_3, CH_2CN, $CH_2OC_6H_5$, the yield of adducts in the reaction with *N*-chlorodialkylamine increases and it reaches 85%.

It should be noted that chloramination of unsaturated compounds is often accompanied by other side reactions. Thus, *N*-chlorodialkylamines $RCH_2(CH_2)_3N(Cl)R^1$ with long-chain alkyl substituents undergo a Hofmann–Löffler rearrangement to give chlorine-substituted amines, which entails a reduction in yield of 1 : 1 adducts:[3,11,26]

$$RCH_2(CH_2)_3N(Cl)R^1 \xrightarrow[-Cl^\cdot]{H^+} RCH_2(CH_2)_3\overset{\cdot}{\overset{+}{N}}HR^1 \longrightarrow$$

$$\rightarrow R\dot{C}H(CH_2)_3\overset{+}{N}H_2R^1 \xrightarrow{RCH_2(CH_2)_3N(Cl)R^1} RCHCl(CH_2)_3\overset{+}{N}H_2R^1 \rightarrow$$

$$\xrightarrow{OH^-} RCHCl(CH_2)_3NHR^1.$$

Finally, the reaction conditions have a considerable effect on the yield of adducts. Thus, chloramination of aliphatic alkenes takes place with a higher yield of adducts (47–68%) when redox systems are used as initiators and the addition is carried out in methanol[17-24] than when UV irradiation in an acid medium is used for initiation (yield of adducts 16–42%).[10,13-14] At the same time, the use of an acid mixture as solvent and initiation with UV irradiation have proved favourable for the reactions of *N*-chlorodialkylamines with halogenated olefins such as $CH_2=C(Hal)R$ [Hal = Cl, F; R = H, CH_3, $C(CH_3)_3$] and $CH_2=CXCH_2Cl$ (X = H, Cl) (yield of adducts 61–92%) [13,15,16] and also functionally substituted alkenes $CH_2=CHCH_2X$ (X = OC_2H_5, $COCH_3$, CN) (yield of adducts up to 88%).[15] With 1,3-dienes, addition of *N*-chlorodialkylamines takes place both in the presence of redox systems in methanol and with UV irradiation in an acid medium with yields of 44–68%.[10,14]

It should be particularly stressed that the nature of the substituents on the nitrogen atom in *N*-chloramines substantially affects the addition to multiple bonds. In the reactions of substituted *N*-chloroalkylamines of the type $RN(Cl)CH_2Y$ (Y = CH_2OH, CN, $CH(OCH_3)_2$, $CH_2=CH$, $C\equiv CH$, *p*-ClC_6H_4) with 2-chloropropene in a mixture of 4 M H_2SO_4–AcOH at 30 °C in daylight, adducts are not formed,[15] which is probably due to a reduction in the degree of protonation of *N*-chlorodialkylamines by the action of electronegative substituents and also to a decrease in polarity of the N–Cl bond. The only exception to this is *N*-chloromethylbenzylamine (Y = C_6H_5), which gives an adduct in 27% yield.

Introduction of electron-donating substituents into *N*-chloramines, on the other hand, has a favourable effect on their addition to a double bond. An example of this is the reaction of chloramines $CH_3NCl(CH_2)_nN(Cl)CH_3$ with 2-chloropropene, which under similar conditions results in the formation of the bis-adducts $[CH_3CCl_2CH_2N(CH_3)]_2(CH_2)_n$.[15] We should note that their yield depends on the degree of diprotonation of chloraminoalkanes. Thus, as the length of the chain increases to $n = 6$ (a hexamethylenediamine derivative), there is the highest yield of bis-adduct (72%), when $n = 4$ it amounts to 49%, and when $n = 2$ or 3 bis-adducts are not formed. At the same time, steric hindrance, which occurs when a protonated aminyl radical attacks the double bond of the olefin, has a lesser effect, in our opinion. Conformation of this could be the

observation that the reaction of *N*-ethyl-*N*-isopropylchloramine with 2-chloropropene in a mixture of 4 M H_2SO_4–AcOH at 30 °C in daylight does take place (yield of adduct 78%).[15]

Although the method for obtaining *N*,*N*-dichloroamines has been known for a long time,[27] there has been no information in the literature about their addition to a double bond; this is apparently due to the instability and danger of explosion from these compounds. Only after the development of methods for obtaining relatively stable *N*,*N*-dichloroalkylamines that contained functional groups on the α-carbon atom[28–30] was it possible to study their addition to alkenes. Thus, *N*,*N*-dichloro-α-aminonitriles $Alk_2C(CN)NCl_2$ add on to styrene; 1:1 adducts are thereby obtained, but they have low stability and have been isolated as the hydrochloride salts of reduction products:[28]

$$Alk_2C(CN)NCl_2 + C_6H_5CH{=}CH_2 \rightarrow Alk_2C(CN)N(Cl)CH_2CHClC_6H_5 \xrightarrow{HCl} Alk_2C(CN)NHCH_2CHClC_6H_5 \cdot HCl.$$

It transpired in this case that *N*,*N*-dichloramines containing substituents [$OCOCH_3$, $CONH_2$, $P(O)(C_2H_5)_2$] on the α-carbon atom that are less electronegative than a nitrile group do not add on to styrene.[28] *N*,*N*-Dichloro-β-aminopropylnitrile also does not react with styrene (in contrast to *N*,*N*-dichloro-α-aminoalkylnitriles), which suggests that the nitrile group on the β-carbon atom has an insignificant effect on the reactivity of the *N*,*N*-dichloramino group.[28] A similar substituent effect in *N*,*N*-dichloramines occurs in the reaction between *N*,*N*-dichloraminoethyl hypochlorite with hexene, where the *N*,*N*-dichloramino group remains inert and an addition product—$ClCH_2CH(C_4H_9)OCH_2CH_2NCl_2$—is formed with involvement of the O–Cl bond.[28]

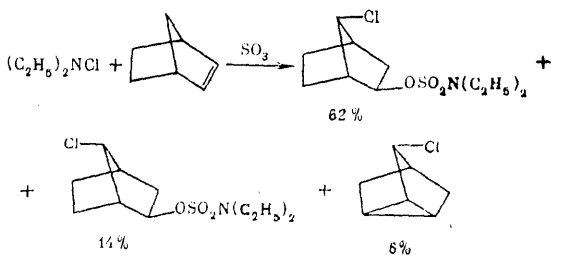
Recently (1984–86), a number of studies have been published,[31–38] in which a new approach to the activation of weak electrophilic reagents in electrophilic addition reactions to olefins is proposed. The authors show that reactions of *N*-chloramines with olefins in the presence of sulphur trioxide initially lead to the formation of highly reactive *O*-chlorosulphamates (R_2NSO_2OCl), which are products derived from introduction of sulphur trioxide into the N–Cl bond of *N*-chloramines, which subsequently add on to the double bond in accordance with Markownikoff's rule to form saturated adducts:

$$R_2NCl + SO_3 \xrightarrow{CH_2Cl_2} R_2NSO_2OCl \xrightarrow{>C=C<} R_2NSO_2OC-CCl$$

The reactions of *O*-chlorosulphamates with ethylene, hexene, styrene, and cyclopentene take place with quite a high yield of adducts (88%).[33,34]

The high regioselectivity of the addition of *N*-chloramines to olefins in the presence of SO_3 was demonstrated in the case of the reaction with 1-hexene [70–88% yield of adducts $C_4H_9CH(CH_2Cl)OSO_2NR_2$, where R_2 = $(C_2H_5)_2$, $(CH_2)_5$, $O(CH_2CH_2)_2$], and there was high stereospecificity—in the reaction with cyclohexene the *trans*-adduct was formed in 85–93% yield.[4] The stereoselectivity and regioselectivity of the addition of *N*-chloramines to olefins are in good agreement with a scheme involving electrophilic addition.

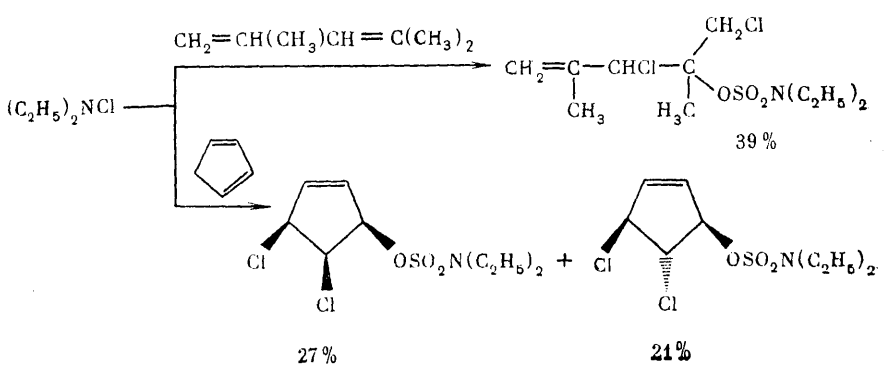
There is an interesting reaction between *O*-chlorosulphamates with norbornene, which results in rearrangement of the adducts, with the adduct in the *syn-exo* configuration for a normal Wagner–Meerwein rearrangement predominating. Formation of the adduct with an *anti-exo* configuration is due to a Wagner–Meerwein rearrangement followed by a 2,6-hydride shift:[33,35]



The skeletal rearrangements that occur in this reaction suggest that *O*-chlorosulphamates have a clearly defined electrophilic nature.

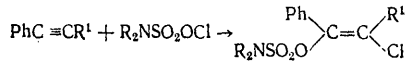
The reactions of *N*-chloramines with dienes (*cis*,*cis*-cyclooctadiene, norbornadiene) in the presence of sulphur trioxide give adducts from 1,2-addition and also isomeric adducts obtained by participation of the second double bond of the diene as well as by-product dichlorides (with a yield of about 34%).[34]

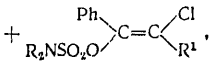
The reactions of *N*-chloramines with cyclopentadiene and 2,4-dimethyl-1,3-pentadiene (with an equimolar ratio of reactants) in the presence of SO_3 take place with the involvement of only one C=C bond of the diene. However, this reaction is complicated by the simultaneous occurrence of electrophilic substitutive chlorination processes:[35]



The reactions of *O*-chlorosulphamates with the dimethyl esters of norbornene and tricyclodecadiene dicarboxylic acids are unusual. Under conditions where the nucleophiles, in particular the ester group and the sulphamate anion, are competing, intramolecular attack by the carbomethoxy group on the double bond of the alkenes is more favourable, giving chlorolactones in 90–95% yield.[34,35]

The possibility of chlorosulphamation of phenyl- and diphenylacetylene has been demonstrated. The reactions take place (at −80 to −60 °C in CH_2Cl_2) in accordance with Markownikoff's law and give the *Z*- (13–36%) and *E*- (5–21%) products:[35,38]





$R_2 = (CH_2)_5$; R = C_2H_5, R^1 = H, Ph.

We should mention in passing the possibility of using *O*-chlorosulphamates as mild chlorinating agents—for ketones or aromatic compounds, for example.[35]

Thus, the reactions of *N*-chloramines with unsaturated compounds are new methods of obtaining β-chloroalkylamines, β-chloroalkenyl- and γ-chloroalkenyl-amines (intermediates in the synthesis of aziridines[3]), and also highly reactive β-chloroaldehydes and β-chloroketones. When these reactions are carried out in the presence of sulphur trioxide there are extensive prospects for the synthesis of β-chloroalkyl- and β-chloroalkenyl-sulphamates, which are biologically active compounds with future potential.

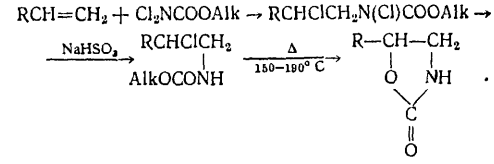
III. The reactions of *N*-haloamides with unsaturated compounds

1. *N*-Halocarbamates

The first successful attempt to obtain *N*-(β-chloro-α-phenylethyl)-*N*-ethoxycarbamate by reactions of *N*, *N*-dichlorourethane with styrene was carried out in 1942.[39] More than 20 years later (in the 1960s) studies by other authors[40–44] on the addition reaction of *N*-halocarbamates to unsaturated compounds started to appear. Three reviews[2–4] cover the reactions of *N*-chloro- and *N*, *N*-dichlorourethanes with styrene, *trans*-stilbene,[43] 2-butene, isobutene,[42] 2-methyl-1-pentene, 1-dodecene, 1-octadecene,[43] cyclic alkenes,[41–43] and alkenes having electron-withdrawing substituents on the double bond (vinyl acetate, methyl vinyl ketone, acrylates).[43,45]

In recent years the number of studies in this area of chemistry has grown considerably, which is due to the perfection of methods for obtaining dihalocarbamates[46] and also because the reactions of *N*, *N*-dihalocarbamates with unsaturated compounds can be used to synthesise highly reactive compounds that are intermediates in the preparation of isocyanates,[47–49] oxazolidinones,[50–51] aziridines,[52] etc.

Investigation of the reactions of *N*, *N*-dichlorourethanes with terminal alkenes was continued in further studies.[47–49] It was established that whatever the method of initiation [UV irradiation (75–80 °C), heating (80–85 °C) in a current of nitrogen or in air] the addition took place with the amidyl fragment being attached to the terminal carbon atom and the formation of saturated adducts—*N*-β-chloroalkyl-*N*-chlorourethanes—with a yield of up to 83%. The N−Cl bond in these products is readily converted to an N−H bond on treatment with sodium bisulphite, and the position of the carbamate group in the adducts obtained has been demonstrated by chemical conversions such as pyrolysis, which gives 5-alkyl-2-oxazolidones:[49]



Products derived from electrophilic chlorination $R^1CHClCH=CH_2$ are formed in side reactions as also are monochlorourethanes, the yield of which increases (from 14 to 42%) in the series of R: $C_4H_9 < C_5H_{11} < C_6H_{13} < C_8H_{17} < C_{10}H_{21} < C_{13}H_{27}$. It should be noted that the occurrence of electrophilic halogenation as a competing reaction is only typical for alkenes that have allylic hydrogen atoms.

The reactions of *N*, *N*-dihalocarbamates with cyclic alkenes in an inert medium with heating (35–40 °C) are interesting; they take place stereospecifically, mainly as a *trans*-addition process, with the formation of adducts and a series of halogenated products, the ratio of which is determined by the nature of the substituents on the nitrogen atom. Thus, methyl *N*, *N*-dibromocarbamate reacts with cyclohexene fairly readily without initiation, giving the *trans*-adduct in high yield (67%).[46] This direction of addition is confirmed by conversion of this adduct to *cis*-perhydrobenzoxazol-2-one, since it is known[53] that only the appropriate compounds having a *trans*-configuration can undergo such a cyclisation .

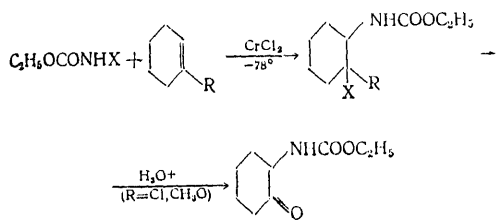
N, *N*-Dichlorocarbamates react with cyclohexene in a more complex manner; in addition to adducts of a similar stereochemistry (44%), a number of chlorinated by-products and monochlorocarbamates are formed.[51]

While heating is required for the reaction of *N*, *N*-dihalocarbamates with aliphatic and cyclic alkenes, the reaction of *N*-monohalocarbamates with cyclic alkenes takes place both with heating (40° to 60 °C) and at low temperatures (0° to −78 °C) in methanol or in a mixture of methanol and chloroform in the presence of Cr(II) halides.[53,54] It was shown[51] that on heating (45 °C) a mixture of *N*-monobromocarbamate and cyclohexene in benzene, the *trans*-adduct was formed in 72% yield. In the presence of Cr(II) at low temperatures (0° to −78 °C), a mixture of *cis*- and *trans*-1,2-adducts was obtained, with their ratio dependent on the reaction conditions (temperature, amount of catalyst, medium) as well as the effect of substituents in the carbamate group and also the nature of the halogen on the nitrogen atom.[53,54] The optimum conditions, ensuring a high yield of adducts, are attained when the reaction is carried out in a mixture of methanol and chloroform cooled to −78 °C in the presence of an equimolar quantity (relative to monochlorocarbamate) of chromium(II) chloride.[53,54] Under these conditions addition of monochlorocarbamate ROCONHCl to cyclohexene takes place with the *cis*-adduct mainly formed in the mixture (by a factor of 4–6). The total yield of isomeric adducts

increases from 65 to 87% in the series of R: $C_2H_5 \leqslant CH_2C_6H_5 < CH_2Cl \leqslant CH_2CCl_3$. A similar dependence of the yield of 1 : 1 adduct (from 61 to 85%) occurs in the analogous series for the reaction with *N*-monobromocarbamates, but the ratio of *cis*- to *trans*-adducts is about 1 : 1. At higher temperatures (0 to −40 °C), carbamates (up to 64%) and halogenated cyclohexene products are mainly formed.[53] When chromium bromide is used as the catalyst, there is a reduction in the yield of adducts and at the same time the yield of carbamates increases up to 53% and that of 1,2-dibromoalkanes rises to 20%.

Similar behaviour occurs in the reaction of *N*-monohalourethanes $C_2H_5OCONHX$ with norbornene (in a mixture of methanol and chloroform at −78 °C in the presence of $CrCl_2$); when X = Cl, the *cis*-adduct is mainly formed, and when X = Br, the *cis*- and *trans*-adducts are formed in equimolar quantites.[53]

The regiospecific and stereospecific nature of the addition of amidyl residues to alkene systems was confirmed when the reactions of *N*-monohalourethanes with 1-chloro-, 1-methyl-, 1-methoxy-, 1-acetyl-, and 1-*N*-(piperidino)-cyclohexene in the presence of Cr(II) in a methanol–chloroform solution at −78 °C were studied. In this case ethyl *N*-(1-halo-1-R-cyclohexyl)carbamates were formed:[5,53,55,56]



X = Cl, Br; R = Cl, CH_3, CH_3O, CH_3CO, $(CH_2)_6N$.

Hydrolysis of the adducts obtained to the corresponding ketones also suggests that these reactions are regiospecific. The addition of benzyl *N*-monochlorocarbamates to trimethylsilyloxynorbornene [56] takes place in a similar manner.

An analysis of the literature data showed that not all *N*-halocarbamates are active in reactions with aliphatic and cyclic alkenes. Thus, *N*-alkyl-substituted *N*-halocarbamates $HalN(R)COOCH_3$ (R = CH_3, $C_6H_5CH_2$) do not add to the double bond of alkenes that contain allylic hydrogen atoms but only form allylic halogenation products in high yield (70–80%).[57-58] Because of this, *N*-alkyl-substituted *N*-bromocarbamates could be recommended as allylic brominating agents.[57] The inertness of *N*-alkyl-*N*-halocarbamates in 1,2-addition reactions to alkenes is apparently due to both steric hindrance and a reduction in electrophilicity of the amidyl radical by the introduction of electron-donating substituents on to the nitrogen atom. On the other hand, for *N*-chlorocarbamates $C_2H_5OCON(R)Cl$ with electronegative substituents on the nitrogen atom (R = CH_3OCO, CH_3CO), an increase in electrophilicity of the amidyl radical is typical. For this reason the reactions of *N*-acyl- and *N*-ethoxycarbonyl-*N*-chloro-urethanes with cyclohexene and 1-octene take place quite readily with UV irradiation (15–20 °C, 3–5 h), and the chlorine atom adds on to the more substituted carbon atom of the C=C bond of 1-octene (yield of adducts 53–67%). Chlorinated alkenes and *N*-substituted urethanes are formed as by-products (39–42%).[58]

The reactions of *N*,*N*-dichlorourethanes with styrene and its derivatives occur readily, with an induction period, most frequently being accompanied by heat liberation, and take place with practically no side reactions to give adducts with an N–Cl bond that readily undergoes reduction with sodium thiosulphate to compounds with an N–H bond. Thus, in the reactions of *N*,*N*-dichloro-substituted methyl, ethyl, and butyl carbamates with styrene, α-chloro-, and α-bromo-styrene, adducts are formed in high yield (59–99%):[51,52,59]

$$AlkOCONCl_2 + C_6H_5CR{=}CH_2 \rightarrow C_6H_5C(R)ClCH_2NClCOOAlk.$$

It is interesting that the nature of the α-substituents has a very marked effect in the reduction of the alkenes. Thus, when ethyl *N*-chloro-*N*-(2-chloro-2-bromo-2-phenylethyl)carbamate, which is obtained by reaction of *N*,*N*-dichlorourethane with α-bromostyrene, is reduced with sodium thiosulphate, hydrogen bromide is eliminated and ethyl *N*-(2-chlorostyryl)carbamate is formed,[59] which is due, in our opinion, to the low strength of the C–Br bond (C–Br bond energy is 68 kcal mol^{-1}, C–Cl bond energy is 81 kcal mol^{-1} [60]):

$$C_6H_5CBr{=}CH_2 + Cl_2NCOOC_2H_5 \rightarrow C_6H_5CClBrCH_2NClCOOC_2H_5 \xrightarrow[-HBr]{Na_2S_2O_3} C_6H_5CCl{=}CHNHCOOC_2H_5.$$

Having analysed the effect of the conditions for initiation, Bal'on and Moskaleva[51,52,59] established that the use of radical initiators—UV irradiation, peroxides, copper powder—accelerated the reaction between *N*,*N*-dichlorocarbamates and substituted styrenes. Thus, the addition of *N*,*N*-dichlorourethane to α-bromostyrene in the absence of radical initiators is complete after 3–5 h and the yield of adduct only reaches 30%, while in the presence of copper powder an almost quantitative yield of adduct is obtained after 40 min. The initiator participates in the reaction both at the initiation and chain transfer stages.[59]

The radical nature of the reaction of *N*,*N*-dichlorourethanes with alkenes is also confirmed by the reaction between *N*,*N*-dichloro-urethane and *trans*-stilbene, which has an induction period, and occurs without stereoselectivity to give a mixture of *erythro* and *threo* isomeric adducts $C_6H_5CHClCH(C_6H_5)NClCOOAlk$.[61] *N*,*N*-Dibromocarbamates and even *N*-alkyl-*N*-bromocarbamates, which are known[57] to be inert to the double bond of aliphatic alkenes, add on to styrene and α-methylstyrene in a similar manner to the corresponding chloro derivatives. However, the yields of the adducts obtained are considerably lower (49–71%) than for the reaction of these alkenes with dichlorocarbamates. A feature of the reaction of *N*-bromo- and *N*,*N*-dibromocarbamates with styrene and its derivatives is that the adducts cannot always be isolated since even on gentle heating they readily cyclise to phenyloxazolidinones with elimination of alkyl bromide.[46,57,62]

In contrast to *N*,*N*-dichlorourethane, *N*-bromo-*N*-alkylcarbamates react with *trans*-β-methylstyene stereoselectively, and in these reactions the stereoselectivity is reduced as the effective size of the substituent on the nitrogen atom decreases. Thus, in the case of *N*-bromo-*N*-benzylcarbamate mainly *trans*-addition products are formed, while *N*-bromo-*N*-methylcarbamate gives an equimolar mixture of *cis*- and *trans*-adducts.[57]

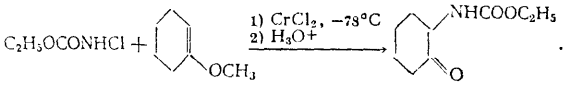
The direction of addition of *N*,*N*-dichlorocarbmates to substituted alkenes containing functional groups—vinyl acetate, methyl vinyl ketone,[45,63] and acrylates[64]—is similar to that for the addition of

amidyl radicals to styrene and its derivatives and is not dependent on the initiation conditions:

$$RCH{=}CH_2 + Cl_2NCOOAlk \rightarrow RCHClCH_2NClCOOAlk \rightarrow \xrightarrow{NaHSO_3} RCHClCH_2NHCOOAlk,$$
$$Alk = CH_3, C_2H_5;\ R = CH_3COO, CN, CONH_2, COOCH_3, COCH_3.$$

An induction period and acceleration by radical initiators are typical for these reactions. Thus, when *N*,*N*-dichlorocarbamates are reacted with acrylonitrile without an initiator the yield of adducts is 25–60% after 4–5 h,[43,51] while in the presence of univalent copper salts the yield is 78–90% after 30–40 min.[64]

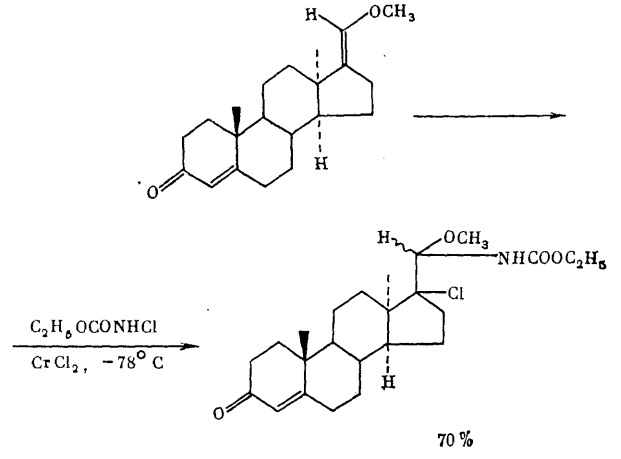
The reactions of *N*-chlorocarbamates with vinyl ethers are interesting; they occur in different directions depending on the initiation conditions. Thus, reaction of ethyl or butyl vinyl ether with *N*,*N*-dichlorocarbamates takes place with the formation of alkyl *N*-chloro-*N*-(2-chloro-1-alkoxyethyl)carbamates if there is no radical initiator present.[65] The direction of addition changes if the same reactions are carried out in the presence of chromium chloride; in this case the amidyl radical becomes attached to the less substituted carbon atom to give adducts $C_2H_5OCHCl-CH_2NHCOOR$, where R = $ClCH_2$, $ClCH_2CH_2$, $C_6H_5CH_2$.[56] The direction of addition of the amidyl radical to the double bond of cyclic vinyl ethers is similar, as is indicated by the structure of the products isolated as a result of hydrolysis or methanolysis of the 1 : 1 adducts:[56]



The products of the 1,2-addition of *N*-monochlorocarbamates to dihydrofuran, triacetyl-*D*-glyoxal, and acetylbenzylidene-*D*-glyoxal have not been isolated, since under the reaction conditions (in the presence of water, methanol) they readily undergo chemical reactions to give acetal derivatives.[56]

The direction of addition of amidyl radicals to the double bond in these reactions, namely, to the 2-position, is determined by electronic effects.

As regards the effect of different factors (electronic and steric) on the direction of addition of the amidyl fragment to the multiple bond of alkenes, the reaction of *N*-monochlorocarbamates with the steroid derivative—17-methoxymethyleneandrost-4-en-3-one—is of interest,[56] attack of the amidyl radical in it being determined to a greater extent by steric rather than electronic effects:



Let us turn to the reaction of *N*,*N*-dichlorourethanes with vinylidene chloride, which enters into the overall scheme of addition of amidyl radicals to unsaturated compounds and takes place independently of the initiation conditions (heating in an atmosphere of argon, in the presence of benzoyl peroxide, or in air) to give alkyl *N*-2,2,2-trichloroethyl-*N*-chlorocarbamates in yields that are almost quantitative:[66]

$$AlkOCONCl_2 + CCl_2{=}CH_2 \rightarrow AlkOCONClCH_2CCl_3.$$

N-Bromo-*N*-alkylcarbamates, in contrast to their dichloro-substituted analogues, undergo reaction with vinylidene chloride with greater difficulty and the yield of adducts amounts to 40–73%,[57] which is due to steric hindrance that occurs during attack by the *N*-alkyl-substituted amidyl radical, which is more bulky than AlkOCONCl.

The reactions of *N*-bromocarbamates with 1,3-alkadienes have been studied in the case of 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 2-methyl-1,3-butadiene, and 1,3-pentadiene.[67] They take place at −5° to −10 °C in chloroform and regardless of the structure of the diene mainly give the thermodynamically more stable *trans*-1,4-adducts in high yield (66–70%).[67] 1,2-Adducts are found only in the reactions with butadiene (20%) and piperylene (8%). Diene dibromides are formed as by-products:[67]

$$CH_2{=}CR^1{-}CR^2{=}CHR^3 \xrightarrow{BrNHCOOCH_3} \begin{cases} \xrightarrow{1,4-} CH_3OCONHCH_2CR^1{=}CR^2CHBrR^3 \\ \xrightarrow{1,2-} CH_2{=}CR^1{-}CBr(R^2)CH_2(R^3)NHCOOCH_3 \\ \longrightarrow C_4H_3R^1R^2R^3Br_2 \end{cases}$$

$R^1{=}R^2{=}R^3{=}H$; $R^1{=}R^2{=}CH_3$, $R^3{=}H$; $R^1{=}CH_3$, $R^2{=}R^3{=}H$; $R^1{=}R^2{=}H$, $R^3{=}CH_3$.

Addition of *N*-bromocarbamate to piperylene gives a mixture of 1,4- and 4,1-adducts in the ratio 1 : 1, which remains unchanged when the initial quantities of the reactants are varied. In the case of isoprene, a compound (about 10%) that corresponds to an adduct of *N*, *N*-dibromocarbamate and isoprene in the ratio 1 : 2—$[BrCH_2CH=C(CH_3)CH_2]_2NCOOCH_3$—is formed together with the main 1,4-isomer (71%).[67]

The regioselectivity and stereoselectivity of the addition of *N*, *N*-dichlorocarbamates to dienes is virtually no different from that in the analogous reactions of *N*-bromocarbamates. Thus, methyl and isopropyl *N*, *N*-dichlorocarbamates with the same 1,3-alkadienes mainly form *trans*-1,4-adducts with a yield of up to 94%.[44] 1,2-Addition products were only isolated in the case of the reaction with butadiene (14% [44] or 37% [53]), 1,3-cyclohexadiene (78%) [53] and piperylene (26%). With piperylene, 4,1-addition products (30%) are also formed.[67]

The reactions of the *N*, *N*-dichlorocarbamate $[NCl_2COOCH_2]_2$ with chloroprene take place with the exclusive formation of 1,4-adducts (96–98%).[44]

The reaction of 1,5-hexadiene with *N*, *N*-dichlorourethane, in which 1,2-addition products of composition 1 : 1 (27.5%) and 1 : 2 (18%) are formed, has been studied.[68] A distinctive feature of the reactions of *N*, *N*-dichlorocarbamates with dienes is the absence of diene dihalides, which are formed in appreciable yield (10–32%) in the reactions of *N*-bromocarbamates.

Alkenynes, which have two reaction centres, have been of definite interest in recent years. The reactions of *N*, *N*-dichloro- and *N*-bromo-carbamates with conjugated alkenynes such as vinylacetylene,[69] 1-hexen-3-yne, 2-methyl-1-buten-3-yne, and 2-penten-4-yne [67] have been studied. The reactions take place at −10 to −5 °C in an inert atmosphere and proceed exothermically by 1,2- and 1,4-addition pathways to give isomers with acetylene and allene structures

$$R^1C{\equiv}C{-}CR^2{=}CHR^3 + CH_3OCONX^1X^2 \xrightarrow{\text{then } NaHSO_3}$$
$$\xrightarrow{1,2} R^1C{\equiv}CC(R^2)CHNHCOOCH_3 \quad (X^1,\ R^3)$$
$$\xrightarrow{1,4} R^1C{=}C{=}C(R^2)CH(R^3)NHCOOCH_3 \quad (X^1)$$

$R^1{=}R^2{=}H$, $R^3{=}H$, CH_3; $R^1{=}C_2H_5$, $R^3{=}R^3{=}H$;
$R^1{=}R^3{=}H$, $R^2{=}CH_3$; $X^1{=}X^2{=}Cl$; $X^1{=}Br$, $X^2{=}H$.

The ratio of isomers depends on the nature of the enyne system and the nature and number of halogen atoms in the *N*-halocarbamate.[69] Thus, *N*, *N*-dichlorocarbamates react with vinylacetylene to give mainly allene derivatives (70%, only 30% acetylene isomer is formed), while in the reaction with *N*-bromocarbamates the ratio of isomers is the reverse, which is due to steric factors.

Introduction of an alkyl substituent into the 1- or 4-positions of a vinylacetylene molecule mainly assists the formation of an acetylene derivative, while its introduction into the 2-position mainly gives an allene isomer. In fact, the acetylene isomer is the predominant product (95–100%) of the reaction between *N*-halocarbamate and 1-hexen-3-yne,[67] while in the reaction with 2-methyl-1-buten-3-yne (isopropenylacetylene) [67] the allene derivative is formed in 85–100% yield.

It has been suggested by Labeish and co-workers[67] that the addition of *N*, *N*-dichloro- and *N*-bromo-carbamates to conjugated alkenynes is a radical process which starts with attack by an amidyl radical on the terminal ethylene atom of the vinylacetylene molecule rather than attack by chlorine on the terminal carbon atom of the triple bond followed by an allene-acetylene rearrangement.

Reactions between *N*-monochlorocarbamates and acetylenic compounds are known. Reaction with 1-octyne gives the adduct $C_6H_{13}CCl=CHNHCOOC_2H_5$ (28%); $C_6H_{13}\underset{\underset{O}{\|}}{C}CH(NHCOOC_2H_5)_2$ is formed as a by-product (13%).[53]

It was recently established that phenylacetylene reacts exothermically under mild conditions with *N*, *N*-dichlorocarbamates, giving alkyl *N*-(2-chlorostyryl)-*N*-chlorocarbamates in 57–59% yield, which rearrange on standing to alkyl *N*-(1,2-dichlorostyryl)-carbamates [70,71]

$$C_6H_5C{\equiv}CH + Cl_2NCOOAlk \rightarrow C_6H_5CCl{=}$$
$$- CHN(Cl)COOAlk \rightarrow C_6H_5CCl{=}CClNHCOOAlk,$$
$$Alk = CH_3,\ C_2H_5.$$

Phenylchloroacetylene (7–9%), *N*-monochlorocarbamate (6–8%), and a compound with a structure that the authors did not establish (24–30%) were isolated as by-products. Unfortunately, Bal'on and Moskaleva[70,71] did not specify any physicochemical constants for this compound in their study. When recent data[72–77] are taken into account, the product of unknown structure is probably a compound with an azomethine bond or a product derived from its subsequent conversion.

Thus, for the reactions of *N*-halo- and *N*, *N*-dihalo-carbamates with unsaturated compounds an induction period is typical; their acceleration in the presence of radical initiators (UV irradiation, peroxides, transition metal salts) and retardation by radical inhibitors as well as the lack of stereospecificity for addition indicate the radical nature of the reaction, which takes place according to the general scheme:

$$AlkOCONX^1X^2 \xrightarrow[-\dot{X}^2]{} AlkOCO\dot{N}X^1 \xrightarrow{>C=C<}$$
$$\rightarrow AlkOCONX^1{-}\overset{|}{\underset{|}{C}}{-}\dot{C}< \xrightarrow[-AlkOCO\dot{N}X^1]{AlkOCONX^1X^2} AlkOCONX^1{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}X^2,$$

$X^1 = H,\ Cl,\ Br,\ Alk;\ X^2 = Cl,\ Br.$

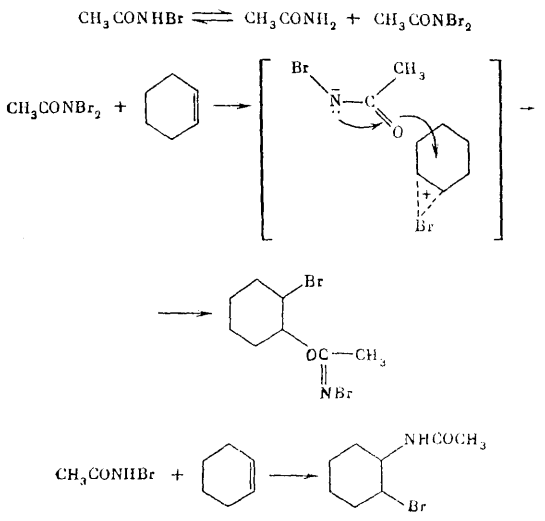
Three studies[53,64,78] describe the mechanism of the reaction between *N*-halocarbamates and olefins in the presence of transition metal salts [CuCl, Cu, Cr(II)] in greater detail.

2. *N*-Halocarboxamides

The addition of *N*-halocarboxamides to unsaturated compounds has been studied in the reactions of quite a large number of *N*-haloamides with cyclohexene and its derivatives,[24,53,55,56,79–83] 1-hexene, 3,3-dimethyl-1-butene,[82] 1-octene, 1-dodecene,[53,81] and also with cyclohexadiene and norbornadiene.[53,55,78]

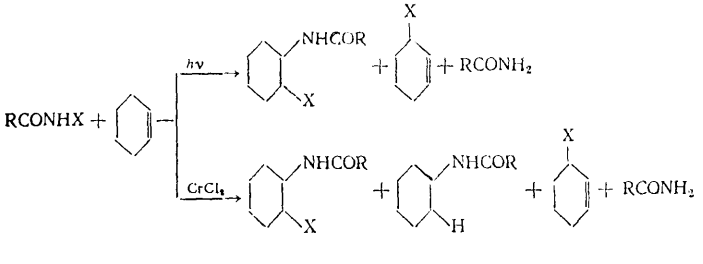
The first known example of a photochemical reaction was the addition of *N*-bromoacetamide to cyclohexene, taking place on refluxing in CCl_4 and giving a low yield of adduct (1%).[79,83] Wolfe and Awang[79,83] maintained that in the main reaction *N*-monobromoacetamide was initially converted to *N*, *N*-dibromo-acetamide, which added on to the double bond of alkene according to

an ionic mechanism, giving *trans*-β-bromoalkyl-*N*-bromoacetimidate in 36% yield:



However, such results were isolated and were not confirmed by subsequent studies.

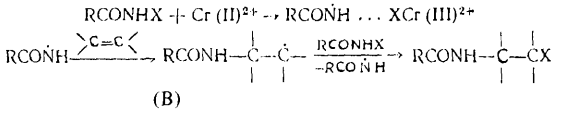
It was possible to carry out the addition of *N*-haloamides to unsaturated compounds both with UV irradiation[55,80,81] and in the presence of $CrCl_2$,[5,53,56,84] substituted adducts being formed in yields of up to 92%. In the case of the reaction of *N*-monohaloamides with cyclohexene a study was made of the dependence of the yield of reaction products on the conditions for carrying out the reaction and on the nature of the halogen atom and substituent R in monohaloamides:



With photochemical initiation the reaction took place in methylene chloride or a chloroform–methanol solution at 20° to −70 °C with a yield of *cis*- and *trans*-adducts of 25 to 99%,[5,55,80,81] in nitromethane the yield was 53%,[55] in benzene it was 42%,[55] while with catalytic initiation the reaction took place in a chloroform–methanol solution at −20 to −78 °C with a yield of isomeric adducts of 34 to 88%.[5,53,56,78]

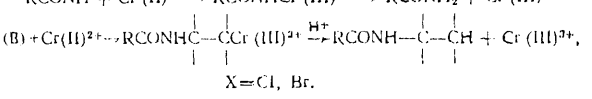
The main competing reaction in the photochemical and catalytic interaction of amidyl radicals with cyclohexene is allylic halogenation, which gives 3-chlorocyclohexene, and *N*-monohaloamide is reduced to amide. One of the main factors that influences the occurrence of electrophilic halogenation is the reaction temperature. At 10–20 °C allylic halogenation is as high as 59%.[81] At lower temperatures (−70° to −78 °C) the formation of adducts is more favourable (64–97%).[55,81]

Driguez and co-workers[53,78] proposed that in allylic halogenation the hydrogen in cyclohexene is removed not by an amidyl radical, as was maintained previously,[85] but by a chlorine free radical. In order to confirm this hypothesis, a study was made of the reactions of *N*-monohaloamides with cyclohexene in the presence of chromium chloride in $CH_3OH-CHCl_3$, in which amidyl radicals were formed but there were no halogen free radicals:[5,24,53,56,78]



(B)

side reaction:



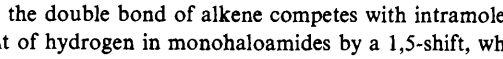
A competing process in these reactions, in addition to halogenation of the olefins, is the formation of 1-*H*-adducts by reduction of the adduct radical (B) with chromium(II) chloride.

The nature of the halogen atom and substituents in *N*-haloamides RCONHX has a considerable effect on the yield of the reaction products. Thus, in photolysis there is an increase in yield of 1,2-adducts in the series of R: $(CH_3)_3C < n\text{-}C_3H_7 < C_2H_5 < CH_3 < CH_2CH_2Cl < CH_2Br < CH_2Cl < CH_2F < CHCl_2 < CCl_3 < CF_3$ ranging from 37 to 99% with the *cis*-adduct predominating (when X = Cl). Although the reaction of *N*-monobromamides occurs more rapidly (4–5.5 h) than with *N*-monochloramides (21–53 h), the yield of 1,2-adducts in the analogous series is considerably lower (from 25 to 84%).[55,80] The increase in the yield of adducts is due to a rise in electrophilicity of the amidyl radical RCONH when electronegative substituents R are introduced.

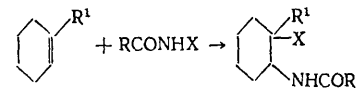
In the presence of chromium chloride when X = Cl, the yield of *cis*- and *trans*-1,2-adducts increases from 34 to 78% in the series of R: $CH_3 \leqslant NH_2 < CCl_3 < CH_2Cl < CF_3$ (there is 1.5–2 times as much *cis*-adduct present compared to *trans*-adduct), while the yield of 1-*H*-adducts, on the other hand, falls (from 36 to 2%).[53]

The effect of the structure of R on the yield of addition products when the reaction is catalysed by $CrCl_2$ is not significant in the case of *N*-monobromamides. Thus, in the reaction of cyclohexene with *N*-bromamides RCONHBr, the yield of 1,2-adducts varies from 66% to 74% with a change of substituents in the series: $CH_3(CH_2)_3 \leqslant CH_3 \leqslant CCl_3 < CH_2Cl$, and the ratio of *cis*- to *trans*-adducts is almost equimolar; the yield of 1-*H*-adducts is insignificant (~2%). In the reaction of bromamides RCONHBr (R = Alk), in contrast to chloramides, there is a side-reaction—electrophilic bromination.[53]

The effect of the length of the alkyl chain in *N*-monohaloamides RCONHX is shown principally with alkyl substituents containing more than four carbon atoms, since in this case addition of amidyl radicals to the double bond of alkene competes with intramolecular detachment of hydrogen in monohaloamides by a 1,5-shift, which gives γ-chloroalkylamides as chlorotropic rearrangement products:[85]

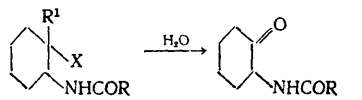


Photochemical and catalytic ($CrCl_2$) addition of amidyl radicals to the double bond occurs regiospecifically, as is suggested by the results of the reactions of 1-chloro-, 1-methyl-, 1-methoxy-, and 1-acetyl-cyclohexene with *N*-monohaloamides, which give a mixture of the *cis*- and *trans*-adducts with yields of 35 to 85%:[5,53,56,80]



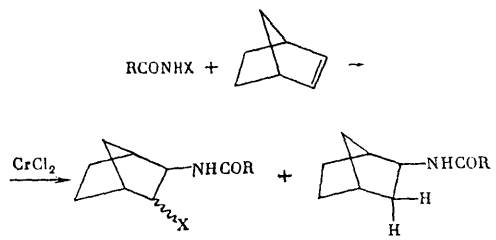
$R=CH_3$, CH_2Cl, CF_3; $R^1=CH_3$, OCH_3, Cl, $COCH_3$.

Confirmation of this orientation of substituents in the adducts is also provided by the conversion of the latter on treatment with water to the corresponding ketones:[55]



$R=CH_2Cl$, CH_3; $R^1=Cl$, OCH_3; X=Cl, Br.

There is high regiospecificity in the reaction of *N*-monohaloamides RCONHX with 1-octene [53,81] and 1,1-diethoxyethylene [55] to form adducts $RCONHCR^1(R^2)CH_2X$ ($R^1 = C_6H_{13}$, $R^2 = H$, $R^1 = R^2 = OC_2H_5$) in 80–92% yield. An adduct with norbornene is also formed in high yield (88–91%), but in a number of cases, namely, in the reaction of the *N*-monochloramide of acetic and monochloroacetic acids with this alkene the yield of 1-*H*-adducts (55 and 93%) is greater than the yield of 1,2-adducts (2 and 33%):[53]



cis, trans

R = CH_3, CH_2Cl; X=Cl, Br.

By studying the reaction of *N*-halocarboxamides with alkenes, the effect of the alkyl substituents on the nitrogen atom has been established. Like *N*-alkyl-*N*-halocarbamates, *N*-alkyl-*N*-halocarboxamides are inert towards reaction with olefins. Thus, attempts to add on the *N*-methyl-*N*-chloramides of acetic and monochloroacetic acids to cyclohexene have proved unsuccessful even with UV irradiation and at a temperature of 20 to −70 °C; in this case only chlorination of cyclohexene and conversion of the *N*-methyl-*N*-chloramides $RCON(CH_3)Cl$ to the corresponding amides occurred (yield 96–98%).[58,81] Exceptions to this were the reactions of *N*-methyl-, *N*-ethyl-, and *N*-chloroacetyl-*N*-chloroacetamides with 1-octene, norbornene, and 1-dodecene, which were initiated by UV irradiation at 20 to −70 °C. Although the main products were the corresponding amides (up to 87%), the 1,2-adducts were however formed in low yield.[55,81] It was only possible to achieve a higher yield of adducts (70–71%) in the reaction of *N*-methyl-*N*-chlorotrifluoroacetylamide with 1-dodecene.[55] It transpired that introduction of electronegative substituents on to the nitrogen atom helped to increase the reactivity of the amidyl radicals. Thus, it was possible to carry out the addition of *N*-acyl-*N*-chloroacetamide to cyclohexene with UV irradiation in CH_2Cl_2 (15–20 °C), although with an insufficiently high yield of adduct (24%).[58]

Cyclic *N*-haloamides are characterised by a fairly high reactivity. In the photochemical initiation of the reaction between *N*-halosuccinimides and ethylene, 3,3-dimethyl-1-butene,[86,87] styrene,[86] 1-octene,[58] and cyclohexene and 1-methylcyclohexene [58] in CH_2Cl_2 or CCl_4 (15–20 °C), adducts are formed with yields ranging from low (16–22%) to high (80%), and the yield for *N*-bromo derivatives is 1.5–2 times lower than with the corresponding chloro derivatives. High yields of adducts (60–85%) were obtained in the photochemical reaction of *N*-bromosuccinimide with 3,3-dimethyl-1-butene and 1-hexene in a mixture of acetonitrile and ethylene oxide at −10 °C.

Finally, there are some individual examples in the study of the reactivity of *N*,*N*-dihalocarboxamides in reactions with unsaturated compounds.

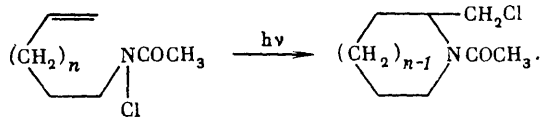
In contrast to monohaloamides, *N*,*N*-dichlorobenzamides are known to react with styrene without secondary processes, forming *N*-(2-chloro-2-phenylethyl)arenamides in high yield (75–92%).[88]

It was possible to react *N*,*N*-dichlorobenzamide with phenylacetylene, resulting in the formation of a mixture of products: *N*-(1,2-dichlorostyryl)benzamide (I) (68.5%) and 1,1-dichloro-1-phenyl-2,2-di(benzoylamino)ethane (II) (12.7%):[89]

$$C_6H_5C{\equiv}CH + Cl_2NCOC_6H_5 \rightarrow$$
$$\rightarrow \underset{\text{(I)}}{C_6H_5CCl{=}CClNHCOC_6H_5} + \underset{\text{(II)}}{C_6H_5CCl_2CH(NHCOC_6H_5)_2}.$$

Unfortunately, the authors did not suggest possible routes for the formation of these compounds.

It is also interesting to note reactions involving intramolecular addition to the double bond in olefinic *N*-haloamides of the type:



These reactions take place with UV irradiation and give various cyclic compounds.[5] A number of studies[90–93] have been devoted to reactions of this type and so they are not examined in detail in the present review. We should also note the tendency of *N*-haloamides RCONHHal with three or more methylene groups to undergo a Hofmann–Löffler rearrangement,[85,94] while *N*-alkyl-*N*-chloramides $RCONR^1Cl$ with alkyl substituents on the nitrogen atom (t-butyl, 1,1-dimethyl-2-phenylethyl, 1,1-dimethylpentyl) tend to undergo intramolecular rearrangements with UV irradiation (20 °C) with migration of the chlorine atom to the alkyl substituent R^1 and formation of *N*-(chloroalkyl)amides, which are readily cyclised on heating to oxazoline and pyrrolidine derivatives.[95,96]

3. *N*-Halosulphonamides

In *N*-halosulphonamides the nitrogen-halogen bond is susceptible to both homolytic and heterolytic cleavage, so that it is possible under different reaction conditions to obtain from *N*,*N*-dihalosulphonamides and alkenes various structural forms of β-haloalkylsulphonamides, which are intermediates in the synthesis of aziridines.[97-99]

The first study in which it was found to be possible to add on *N*-halosulphonamides to the double bond of unsaturated compounds was published in 1930.[1] Several years later, in 1937–38, a series of studies appeared,[100-103] in which in the course of seeking new methods for the chloroalkoxylation of olefins in order to obtain β-chloroethers it was found that when *N*,*N*-dichlorosulphonamides react with alkenes in the presence of phenols,[100] alcohols,[101,102] or carboxylic acids,[103] *N*-(β-chloroalkyl)arenesulphonamides are formed together with β-chloroethers.

At the present time it is established that addition of *N*,*N*-dichloro- and *N*-chloro-*N*-methyl-ethanesulphonamide to terminal alkenes such as 1-hexene, 1-butene, 1-octene, and 1-dodecene takes place with the formation of saturated adducts, the structure of which depends on the initiation conditions.[104,105]

Under conditions where radicals are formed (UV irradiation) the sulphonamide residue adds on to the terminal carbon atom according to the scheme:

$$C_2H_5SO_2NClR \xrightarrow[-Cl^{\cdot}]{} C_2H_5SO_2\dot{N}R \xrightarrow{R^1CH=CH_2}$$

$$\rightarrow C_2H_5SO_2N(R)CH_2\dot{C}HR^1 \xrightarrow[-C_2H_5SO_2\dot{N}R]{C_2H_5SO_2NClR} C_2H_5SO_2N(R)CH_2CH(Cl)R^1,$$

$R=Cl,\ CH_3;\ R^1=C_2H_5,\ C_4H_9,\ CH_3(CH_2)_3,\ CH_3(CH_2)_5,\ CH_3(CH_2)_{10}.$

These reactions are inhibited by oxygen, which also confirms their radical character.

It is interesting to note that with more prolonged UV irradiation the adduct of *N*,*N*-dichloroethanesulphonamide with 1-hexene undergoes a free-radical rearrangement with 1,5-migration of hydrogen to give *N*-(2,4-dichlorohexyl)ethanesulphonamide.[104,105]

Under ionic conditions for initiating the reactions of *N*,*N*-dichloro-substituted arene- and ethane-sulphonamides with 1-hexene, the direction of addition changes, and the reactions lead to the adducts $RCH(NHSO_2C_2H_5)CH_2Cl$.[104,106] A similar direction of addition occurs in the reactions of *N*,*N*-dibromoarenesulphonamides with acyclic alkenes of known stereochemistry—*cis*- and *trans*-3-hexene, *cis*-2-heptene, *cis*-5-decene, and *cis*- and *trans*-9-octadecene; in this case *N*-bromo-*N*-(2-bromo-1,2-dialkylethyl)arenesulphonamides are formed as adducts in 42–70% yield.[107]

The mechanism of this reaction involves the formation of a bromonium ion:

$$ArSO_2NBr_2 + \rangle C{=}C\langle \rightarrow \rangle \overset{Br^+}{C{-}C}\langle + ArSO_2\bar{N}Br \rightarrow$$

$$\rightarrow ArSO_2NBrC{-}CBr$$

This type of mechanism dictates the high stereoselectivity of the process. In fact, as a result of the addition of *N*,*N*-dibromoarenesulphonamides to a *cis*-alkene, an adduct with a *threo*-configuration is obtained, while for reaction with a *trans*-alkene, the adduct has an *erythro*-configuration.[107] It was shown that the yield of adducts in heterolytic reactions of *N*,*N*-dibromoarenesulphonamides with aliphatic alkenes depends on the structure of alkene. Thus, with long-chain alkenes (*cis*- and *trans*-octadecene) the yield of adducts is considerably lower (38–42%) than with C_6 and C_7 alkenes (75 to 80%).[107] With a tertiary alkene (2,3-dimethyl-1-butene) the yield of adduct is only 16%, with a secondary alkene (isobutene) it is 22%,[108] and with 2-butene it increases to 61%,[109] which is due to the effect of steric factors on attack by the amidyl anion on the bromonium ion.

The effect of the substituents on the nitrogen atom in sulphonamides on the yield of adducts during heterolytic reaction should also be noted. The reactions of *N*,*N*-dibromo- and *N*-bromo-*N*-alkyl-substituted arenesulphonamides with alkenes (2-butene and isobutene) take place with a higher yield of adducts.[109,110] In the reactions of the *N*-chloro derivatives, chlorination of the alkenes is preferred, and adducts are only isolated in low yield (10%).[111]

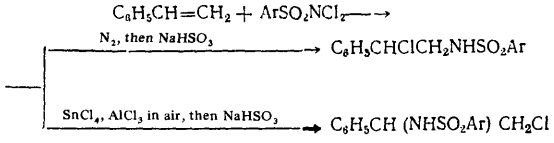
A number of studies by Japanese research workers are devoted to the reactions of *N*,*N*-dihaloarenesulphonamides with cyclohexene [112-116] and cyclopentene.[117] These reactions, as for the addition of *N*,*N*-dihalocarbamates to cyclic alkenes, are stereoselective and take place mainly as a *trans*-addition with the formation of 1 : 1 adducts (yield 50–96%). *cis*-Adducts are also formed, but in low yield. Moreover, reactions with cyclic alkenes are accompanied by side-reactions—halogenation of the double bond of alkene, allylic halogenation, oxidation of cyclohexene to 1-cyclohexen-3-one, and also dehydrogenation of the cycloalkene to a 1,3-cycloalkadiene (with a substantial yield—49%).[112-117]

It is interesting that *N*-bromo-*N*-alkylsulphonamides, by analogy with *N*-bromo-*N*-alkylcarbamates, do not add on to the double bond of cyclohexene but behave as brominating agents.[114] The inertness of *N*-bromo-*N*-alkyl-substituted amides in addition reactions to the double bond of alkenes is probably due to a decrease in electrophilicity of *N*-alkyl-substituted amidyl radicals.

The possibility of heterolytic bromosulphonamidation of cyclic alkenes has been shown for the reactions of *N*-bromosulphonamides with bicyclic alkenes such as bicyclo[2.2.1]heptene, bicyclo[2.2.2]-octene, and *endo*-bicyclo[2.2.1]-5-hepten-2,3-dicarboxyanhydride. The reactions are exothermic and stereoselective and involve the formation of a bromonium ion or a bridgehead carbocation.[118] The yields of 1 : 1 adducts in these reactions, however, are low, the main products being brominated bicycloalkenes.

In contrast to the reactions of aliphatic alkenes, reactions of styrene and its derivatives with *N*,*N*-dichloroalkane-, *N*,*N*-dichloroarene-, and *N*,*N*-dichloro-*N*^{1}-dimethyl-sulphonamides take place with virtually no side reactions and they give the saturated adducts $4\text{-X-}C_6H_4CCl(R^1)CH(R^2)NClSO_2R$ [R = Ar, Alk, $R^1 = R^2 = H$, X = H; R = $(CH_3)_2N$, R^1 = H, C_6H_5, R^2 = H, X = H, *p*-CH_3O] in high yield.[99,106,111,119] The reactions occur readily under mild conditions in chloroform or methyl chloride on cooling[111,119] or in benzene at 20–22 °C in an atmosphere of nitrogen,[106] most frequently exothermically. It was shown that these reactions are considerably accelerated by UV irradiation, with the yields of adducts being almost quantitative. Subsituents at the α- and β-positions of styrene do not have any substantial effect on the yield of adducts. The reactions with both styrene (yield 85–96%) [106] and α-phenylstyrene (85%) or 1-*p*-methoxyphenyl-propene [119] occur with equal ease. Meanwhile, the direction of addition of *N*,*N*-chloroarenesulphonamides to styrene changes

if the reaction is carried out in air in the presence of Lewis acids:[106,111,120,121]



It is interesting that not only the initiation conditions but also the nature of the halogen atom in the sulphonamide affect the direction of addition of *N,N*-dihalosulphonamides to styrene and its analogues. Thus, in contrast to *N,N*-dichlorosulphonamides, *N,N*-dibromosulphonamides add on to styrene,[107,110,116] α-methylstyrene,[98] and propenylbenzenes 3-R-4-$R^1C_6H_3CH=CHCH_3$ (R = H, OMe; R^1 = H, OMe, OBz; RR^1 = OCH_2O [122-123]) with attachment of the amidyl fragment to the more substituted carbon atom of the double bond in these alkenes. *N*-Bromo-*N*-alkyl-substituted sulphonamides add on to styrene in the same direction.

Chlorosulphonamidation of alkanes which contain electron-withdrawing groups on the double bond has been studied in the case of reactions with allyl chloride,[99,120,124] 1,1,1-trichloropropene,[125] and acrylates;[98,108,124,126] they take place with the formation of adducts $ArSO_2NClCH_2CHClR$ (R = CH_2Cl, CCl_3, CN, $CONH_2$, $COOCH_3$).

It has been established that the use of radical initiators considerably accelerates these reactions. Thus, the reaction of allyl chloride with *N,N*-dichloro-*p*-chlorobenzenesulphonamide takes place on heating in CCl_4 (75–80 °C) for 5 h, while in the presence of $(C_6H_{11}OCO_2)_2$ or $(C_6H_5OCO)_2$ only 1.5 h is needed and the yield of the adduct p-$ClC_6H_4SO_2NHCH_2CHClCH_2Cl$ increases from 75% to 93%.[120,124] Another example is the addition of *N,N*-dichloroarenesulphonamides to acrylonitrile, which is complete after 30 h without a catalyst to give a 51% yield of the adduct $C_6H_5SO_2NHCH_2CHClCN$,[98] while with initiation by $(C_6H_{11}OCO)_2$ only 1.5 h is needed and the yield is 84%.[124]

An initiation system such as a mixture of a univalent copper salt and tetraethylammonium bromide has proved effective.[126] When using it, the time of reaction of *N,N*-dichloroarenesulphonamides with acrylates $XCH=CH_2$ could be reduced to 40 min and the yield of adducts $ArSO_2NHCH_2CHClX$ could be increased to 95% (X = CN), 86% (X = $COOCH_3$), or 88% (X = $CONH_2$). The low redox potential of the system $Cu^0 \rightleftarrows Cu^+ \rightleftarrows Cu^{2+}$ favours these reactions involving copper or its univalent salt both at the initiation stage and in chain propagation, thereby increasing the yield of adducts.

N,N-Dibromoarenesulphonamides add on to acrylates in a similar manner to give 1:1 or 1:2 adducts, depending on the ratio of reactants.[108]

An alkene with a trichloromethyl group on the double bond (1,1,1-trichloropropene) during homolytic initiation forms adducts $ArSO_2NHCH_2CHClCCl_3$ in 60–63% yield.[125] Under initiation conditions for formation of ions (in the presence of $SnCl_4$, in air), adducts of the same structure are formed (yield 18–70%), which is in line with the usual principles for electrophilic addition to unsaturated compounds that contain electron-withdrawing substituents on the double bond.[125]

Finally, the reactions of *N,N*-dichloroarenesulphonamides with polyhaloethylenes (vinylidene chloride[120] and 1,1,3-chloropropene[97]) deserve special consideration. A characteristic feature of these reactions is that the direction of addition does not depend on the initiation conditions as was the case for other alkenes.[104,106] The reaction takes place with the same ease both in an inert medium in the presence of peroxides and in air in the presence of $AlCl_3$, with adducts formed in high yield (up to 97%):

$$ArSO_2NCl_2 + CCl_2=CHR \rightarrow ArSO_2NClCHRCCl_3,$$
$$R=H,\ CH_2Cl;\ Ar=C_6H_5,\ p\text{-}ClC_6H_4.$$

In continuing our investigation of the free-radical reactions of halogenated derivatives of ethylene, we have studied for the first time the reactions of 2,2-dichlorovinyl acylates, 2,2-dichlorovinylketones, *N*-(2,2-dichlorovinyl)carboxamides, and 2,2-dichlorovinyl ethers with *N,N*-dichlorosulphonamides.[127-132] Free-radical additions to the double bond were not known for these compounds. Moreover, the reactions of *N,N*-dichloroarenesulphonamides with functional derivatives of 2,2-dichloroethylene attracted our interest as a method for obtaining the previously unknown trichloroethyl derivatives of arenesulphonamides of the type $ArSO_2NHCH(R)CCl_3$, which are biologically active compounds with future potential:

$$ArSO_2NCl_2 + CCl_2=CHR \rightarrow ArSO_2NClCH(R)CCl_3 \rightarrow ArSO_2NHCH(R)CCl_3,$$
$$Ar = C_6H_5,\ p\text{-}CH_3C_6H_4,\ p\text{-}ClC_6H_4;\ R = OCOCH_3,\ NHCOAr^1,\ COR^1,\ OAlk.$$

The reaction of *N,N*-dichloroarenesulphonamides with 2,2-dichlorovinyl acetate is the first example of a free-radical addition to the double bond of this compound. The reaction occurs readily when there is a twofold excess of dichlorovinyl acetate, which also serves as the solvent, and leads to adducts in 90–97% yield.[127,128]

A high regiospecificity for addition was recorded in the reaction of 2,2-dichlorovinylamides with *N,N*-dichloroarenesulphonamides; the adducts were isolated with yields up to 95%.[128,129] It was of particular significance that this reaction showed for the first time the possibility of the enamide tautomeric form of 2,2-dichlorovinylamides participating in free-radical addition reactions to the double bond.

The reaction of 2,2-dichlorovinyl ketones and 2,2-dichlorovinyl ethers with *N,N*-dichlorobenzenesulphonamide is complicated by a side-reaction—reduction of the dichlorosulphonamide to a benzenesulphonamide in about 30–40% yield.[130,131] The high activity of the N–Cl bond in the adducts should be noted; it is very readily converted to an N–H bond even in air and *N*-(2,2,2-trichloro-1-R-ethyl)benzenesulphonamides are formed in about 75% yield.[130,131]

The reactions of functional derivatives of vinylidene chloride with *N,N*-dichloroarenesulphonamides have an induction period, and they are inhibited in the presence of hydroquinone, which is confirmation of their free-radical nature:

$$ArSO_2NCl_2 \xrightarrow[-Cl]{} ArSO_2\dot{N}Cl \xrightarrow{CCl_2=CHR} \rightarrow \dot{C}Cl_2CH(R)NClSO_2Ar \xrightarrow{ArSO_2NCl_2} \rightarrow$$
$$(C)$$
$$\rightarrow CCl_3CH(R)NClSO_2Ar \rightarrow CCl_3CH(R)NHSO_2Ar,$$
$$R=OCOCH_3,\ NHCOAr,\ COR^1,\ OAlk.$$

A characteristic feature of these reactions is that the addition is highly regiospecific. This is due to polar effects of the substituents in the amidyl radical $ArSO_2\dot{N}Cl$ and the vinylidene chloride

derivative and to steric hindrance which would occur if the amidyl radical attacked the β-carbon atom in molecules of the substituted vinylidene chloride derivatives $CCl_2=CHR$ to form the radical $ArSO_2NClCCl_2\dot{C}HR$ (D). The driving force of the reaction would appear to be the formation of the more stable radical (C).

A study has been made of the addition of *N,N*-dichloroarenesulphonamides to dienes that takes place exothermically under mild conditions (−10 °C) at the 1,4-position with a high yield of adducts (77–88%):[111]

$$CH_2=C(R)CH=CH_2 + R^1SO_2NCl_2 \xrightarrow{NaHSO_3} R^1SO_2NHCH_2C(R)=CHCH_2Cl,$$
$$R=H,\ Cl;\ R^1=C_6H_5,\ p\text{-}ClC_6H_4,\ CH_3,\ (CH_3)_2N.$$

Yamasaki and co-workers[68] have shown that the reactions of *N,N*-dihalosulphonamides with 1,5-hexadiene, 1,4-pentadiene, 1,4-diphenyl-1,3-butadiene, and 1,4-cyclohexadiene are not regiospecific and 1 : 1 and 1 : 2 adducts of 1,2- and 1,4-addition are formed. The yields of these compounds, however, are low—only 2–21.3%.

The reactivity of *N,N*-dihaloarenesulphonamides in reactions with alkenynes, resulting in the formation of allene and acetylene isomers, was studied in the case of reactions with vinylacetylene, isopropenylacetylene, and vinylethylacetylene:[133]

$$R^1C\equiv C-CR^2=CH_2 + n\text{-}ClC_6H_4SO_2NCl_2 \xrightarrow{\text{then } NaHSO_3}$$
$$\xrightarrow{1,2-} R^1C\equiv C-C(R^2)ClCH_2NHSO_2C_6H_4Cl\text{-}p$$
$$\xrightarrow{1,4-} R^1CCl=C=CR^2CH_2NHSO_2C_6H_4Cl\text{-}p$$
$$R^1=R^2=H;\ R^1=C_2H_5,\ R^2=H;\ R^1=H,\ R^2=CH_3.$$

It has been established that the direction of addition of *N,N*-dichloro-*p*-chlorobenzenesulphonamide to conjugated vinylacetylenes is similar to that which occurs in the reactions of *N,N*-dihalocarbamates with alkenynes [67] and is determined by the structure of the alkenyne, in other words, when an alkyl substituent is introduced into the 2-position of a vinylacetylene molecule (isopropenylacetylene) the 1,4-adduct is mainly formed (allene isomer), while introduction into the 4-position gives an acetylene isomer. A distinctive feature of the reaction of *N,N*-dichloro-*p*-chlorobenzenesulphonamide with 5,5-dimethyl-1-hexen-3-yne is the absence of a 1,4-adduct—only the acetylene derivative $CH_3C(CH_3)_2C\equiv CCHClCH_2NClSO_2C_6H_4Cl\text{-}p$ is isolated—while in the reaction with an unsubstituted alkenyne (vinylacetylene) the allene isomer predominates (ratio of 1,4- to 1,2-adducts is 2 : 1).[133] In the case of *N,N*-dibromo-*p*-chlorobenzenesulphonamide only the reaction with hexen-3-yne was studied and, in contrast to the analogous reaction of *N,N*-dichloroarenesulphonamides and *N,N*-dihalocarbamates, the main product in this reaction is the dibromide of the 1,2-adduct; the 1,2-adduct is also formed, but in low yield:[133]

$$C_2H_5C\equiv C-CH=CH_2 + p\text{-}ClC_6H_4SO_2NBr_2 \xrightarrow{\text{then } NaHSO_3}$$
$$\longrightarrow C_2H_5CBr=CBr-CHBrCH_2NHSO_2C_6H_4Cl\text{-}p$$
$$\longrightarrow C_2H_5C\equiv C-CHBrCH_2NHSO_2C_6H_4Cl\text{-}p$$

N,N-Dichloroarenesulphonamides also add on to organosilicon derivatives of vinylacetylene such as 1-trimethylsilyl-3-buten-1-yne, 1-trimethylsilyl-3-penten-1-yne, 1-trimethylsilyl-3-methyl-3-buten-1-yne [134–138] both at the 1,2- and 1,4-positions to give allene and acetylene isomers, the ratio of which is determined by the structure of the alkenyne. Thus, in the reaction with 1-trimethylsilyl-3-buten-1-yne the 1,2-adduct is mainly formed, while with an alkenyne containing alkyl substituents on the double bond (1-trimethylsilyl-3-penten-1-yne) the 1,4 adduct is mainly formed:

$$(CH_3)_3SiC\equiv CCR^1=CHR^2 + ArSO_2NCl_2 \rightarrow$$
$$\xrightarrow{1,2-} (CH_3)_3SiC\equiv CCClR^1CHR^2NClSO_2Ar$$
$$\xrightarrow{1,4-} (CH_3)_3SiCCl=C=CR^1CHR^2NClSO_2Ar$$
$$R^1=R^2=H;\ R^1=H,\ R^2=CH_3;\ R^1=CH_3,\ R^2=H.$$

1,2-Adducts and 1,4-adducts tend to undergo allene-acetylene isomerisation. Their reduction with $NaHSO_3$ is also accompanied by allene-acetylene isomerisation. The triple bond of organosilicon vinylacetylene remains inert towards the addition of *N,N*-dichlorosulphonamides.

A characteristic feature of the reactions of *N,N*-dihalosulphonamides with carbon and organosilicon alkenynes is the induction period, which is an indication of the free-radical nature of the course of these reactions. In all cases attack by the amidyl radical is directed at a carbon atom on the double bond with formation of the most stable adduct radicals.[133,134]

In a single study,[139] where the reaction of *N,N*-dichloro-*p*-chlorobenzenesulphonamide with phenylacetylene was investigated, the formation of an azomethine in 66.7% yield was recorded; in this case a saturated adduct was isolated in low yield (5%):

$$C_6H_5C\equiv CH + Cl_2NSO_2C_6H_4Cl\text{-}p \rightarrow C_6H_5CCl=CHNClSO_2C_6H_4Cl\text{-}p \rightarrow$$
(E)
$$\xrightarrow{NaHSO_3} C_6H_5CCl=CHNHSO_2C_6H_4Cl\text{-}p$$
$$\longrightarrow C_6H_5CCl_2CH=NSO_2C_6H_4Cl\text{-}p$$

The authors attribute the formation of an azomethine to an intramolecular 1,3-migration of chlorine in the initial adduct (E).

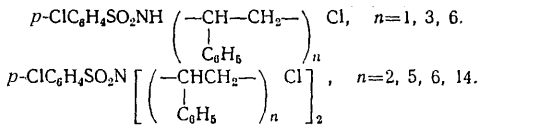
(a) Dichloroarenesulphonamides in telomerisation reactions

Finally, it was established that *N,N*-dichloroarenesulphonamides are initiators for the telomerisation of alkenes. Thus, Freidlina and co-workers[124] carried out the radical telomerisation of allyl chloride and acrylonitrile with *N,N*-dichloroarenesulphonamide to form the telomers $p\text{-}ClC_6H_4SO_2N(X)(-CH_2-\underset{\displaystyle R}{\underset{|}{CH}}-)_nCl$ (X = H, Cl; R = CN, CH_2Cl; *n* = 1, 2).

The radical nature of these reactions is borne out by their significant acceleration on exposure to UV radiation and in the presence of peroxides. It was shown that with an increase in the ratio of acrylonitrile to *N,N*-dichloro-*p*-chlorobenzenesulphonamide the yield of lower telomers decreases and the yield of higher telomers (*n* > 3) increases.[140]

The ionic telomerisation of styrene with *N,N*-dichloro-*p*-chlorobenzenesulphonamide occurs in the presence of $SnCl_4$ in methylene

chloride in air,[141] telomers with the following composition being formed:



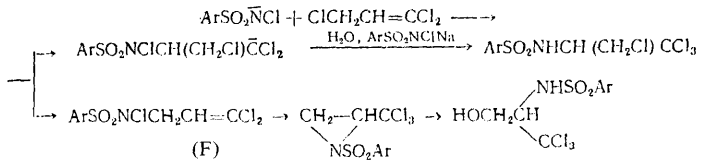
p-$ClC_6H_4SO_2NH$ $\left(-CH(C_6H_5)-CH_2-\right)_n$ Cl, n=1, 3, 6.

p-$ClC_6H_4SO_2N\left[\left(-CHCH_2(C_6H_5)-\right)_n Cl\right]_2$, n=2, 5, 6, 14.

(b) Nucleophilic addition of *N*-chloro-*N*-sodium arenesulphonamides to alkenes

There are several known examples of the nucleophilic addition of *N*-chloro-*N*-sodium arenesulphonamides to alkenes such as 1,1,3-trichloropropene,[142] 3,3,3-trichloropropene,[143], allyl chloride,[144] and acrylonitrile.[144]

Thus, the reaction with 1,1,3-trichloropropene in an aqueous medium mainly gave 1,3,3,3-tetrachloro-2-(arenesulphonamido)-propane (28–49%); this indicates the greater readiness of *N*-chloro-*N*-sodium arenesulphonamides to add on to the dichlorovinyl group of 1,1,3-trichloropropene than to replace the allylic chlorine in this compound:



$ArSO_2\bar{N}Cl + ClCH_2CH{=}CCl_2 \longrightarrow$

$\rightarrow ArSO_2NClCH(CH_2Cl)\bar{C}Cl_2 \xrightarrow{H_2O,\ ArSO_2NClNa} ArSO_2NHCH(CH_2Cl)CCl_3$

$\rightarrow ArSO_2NClCH_2CH{=}CCl_2 \rightarrow CH_2(NSO_2Ar)CHCl_2 \rightarrow HOCH_2CH(NHSO_2Ar)CCl_3$

(F)

Ar=C_6H_5, p-ClC_6H_4.

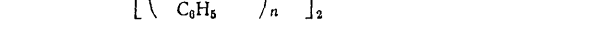
The dichlorovinyl derivative (F) was not isolated pure, since its intramolecular cyclisation to an aziridine took place. Hydrolysis of the latter gave 1-hydroxo-2-(arenesulphonamido)-3,3,3-trichloropropane in low yield (3–5%).

In the reaction of *N*-chloro-*N*-sodium arenesulphonamides with 3,3,3-trichloropropene the product of addition to the double bond $ArSO_2NHCH_2CHClCCl_3$ is only formed in 2–8% yield. The main product of this reaction is 1-hydroxy-2-(arenesulphonamido)-3,3,3-trichloropropane (37–51%), which, as Rybakova and co-workers[143,144] suggest, is formed by migration of the reaction centre when the amidyl anion attacks the terminal carbon atom of the alkene to form the unstable compound (F) and its subsequent conversion during reaction in a similar manner to the scheme suggested above.

In contrast to the reactions mentioned above, chlorosulphonamidation of allyl chloride mainly occurs via substitution of the allylic chlorine to form *N*-chloro-*N*-allyl-*p*-chlorobenzenesulphonamide (about 50%). The competing nucleophilic addition to the double bond does not occur to any significant extent.[144]

The reaction of *N*-chloro-*N*-sodium-*p*-chlorobenzenesulphonamide with a two- or three-fold excess of acrylonitrile in an aqueous medium takes place as a cyanoethylation reaction and *N*,*N*-di(2-cyanoethyl)-*p*-chlorobenzenesulphonamide is formed with a yield of about 61%.[144]

The reaction studied in the greatest detail has been that between the sodium salt of *N*-chloro-*p*-toluenesulphonamide and alkenes (cyclohexene, methylcyclohexene, cyclooctene, norbornene, 1-dodecene, 5-dodecene, 2-methyl-2-hexene, styrene and its derivatives, acrylates, cyclohexadiene, etc.),[145–148] which occurs in an alcoholic medium (60 °C) in the presence of OsO_4 and results in the formation of hydroxyalkyl derivatives of sulphonamides with fairly high yields:



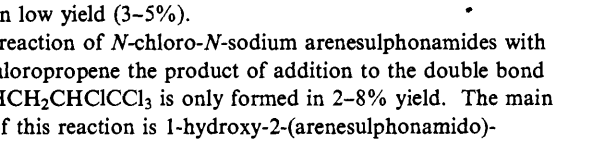
p-$CH_3C_6H_4SO_2NClNa \cdot 3H_2O + RCH{=}CHR^1 \xrightarrow[t\text{-}C_4H_9OH,\ 60\,^\circ C]{1\%\ OsO_4} p$-$CH_3C_6H_4SO_2NHCH(R)—CH(OH)R^1 + NaCl.$

Unfortunately, the number of studies on the reaction of *N*-halo-*N*-sodium arenesulphonamides are not sufficient to make any conclusions about the general mechanisms for these reactions.

Thus, analysis of the literature data on the reactions of *N*-halo- and *N*,*N*-dihalosulphonamides with unsaturated compounds has shown that these reactions take place, depending on the initiation conditions, by homolytic and heterolytic cleavage of the N—Hal bond to form *N*-haloalkyl-substituted sulphonamides, which are important intermediates for the synthesis of aziridines.[97–99,149] *N*-Halosulphonamides add on to functional derivatives of vinylidene chloride $CCl_2{=}CHR$ (R = H, $COOCH_3$, NHCOAr, COAlk, COAr, OR^1), dienes, and vinylacetylenes only according to a radical mechanism, as is suggested by the acceleration of these reactions in the presence of radical initiators and their inhibition in the presence of hydroquinone or atmospheric oxygen.

4. *N*,*N*-Dihalophosphoramidates

The addition of *N*,*N*-dihalophosphoramidates to alkenes has been studied in the case of reactions with ethylene,[150] hexene,[150] 2-ethyl-1-hexene,[150,151] 2-ethyl-1-butene, isobutene, 1-octene,[150,152,153] and styrene.[154–158] In the majority of cases the reactions have an induction period when exposed to UV radiation and on heating in benzene or carbon tetrachloride, and they are regiospecific, with the adducts formed in high yield (70–97%):



$(RO)_2P(O)NX_2 + CH_2{=}CHR^1 \rightarrow (RO)_2P(O)NXCH_2CHR^1X \xrightarrow{NaHSO_3}$

$\rightarrow (RO)_2P(O)NHCH_2CHR^1X \xrightarrow[0\text{–}10\,^\circ C]{HHal} NH_2CH_2CHR^1X,$

X=Cl, Ar; R=C_2H_5, C_3H_7, iso-C_3H_7, C_4H_9, C_6H_5, R^1=C_6H_5;

R=C_2H_5, R^1=H, C_3H_7, C_4H_9, C_5H_{11}, n-C_6H_{13}, t-C_4H_9.

Confirmation of the orientation of the substituents in the adducts, namely, attachment of the amidyl fragment to the less substituted carbon atom of the alkene double bond is the conversion of dialkyl *N*-[2-halo-2-alkyl(phenyl)ethyl]phosphoramidate to the hydrochloride or hydrobromide salts of 2-halo-2-alkyl(phenyl)ethylamine by treatment with hydrogen chloride or bromide.

Addition of *N*,*N*-dibromophosphoramidates to long-chain terminal alkenes $RCH{=}CH_2$ (R = t-C_3H_7, t-C_4H_9, C_4H_9, C_6H_{13}), in contrast to the reactions of the chloro analogues, is complicated by side-reactions involving bromination of alkenes, which reduces the yield of the adducts.[159]

Formation of adducts $PhCCl(R)CH(R^1)NHP(O)(OC_2H_5)_2$ occurs in the reaction of diethyl *N*,*N*-dichlorophosphoramidate with phenylethylenes $Ph(R)C{=}CHR^1$, where R and R^1 = CH_3, Ph.[160]

In order to carry out the reactions of diethyl dihalophosphoramidates with alkyl esters of α,β-unsaturated carboxylic acids,[150,157,158] more prolonged UV irradiation (3–4 h) is required. The addition is

regiospecific, and adducts are formed in high yield:

$$R^1CH{=}C(R^2)COOR^3 + (C_2H_5O)_2P(O)NX_2 \xrightarrow{h\nu} \rightarrow (C_2H_5O)_2P(O)NXCH(R^1)CX(R^2)COOR^3 \xrightarrow{NaHSO_3,\ 0-5^\circ C} (C_2H_5O)_2P(O)NHCH(R^1)CX(R^2)COOR^3,$$

$X{=}Cl,\ Br;\ R^1{=}R^2{=}H,\ R^3{=}C_2H_5;\ R^1{=}H,\ R^2{=}R^3{=}CH_3;$
$R^1{=}R^3{=}CH_3,\ R^2{=}H.$

In contrast to the chloro analogues, diethyl *N,N*-dibromophosphoramidate [157] adds on to these olefins more readily (at 20–45 °C) and with a quantitative yield of adducts.

The occurrence of an induction period, acceleration of the reactions by UV irradiation, and also the regiospecificity in addition of *N,N*-dihalophosphoramidates to terminal $RCH{=}CH_2$ and α,β-substituted alkenes $R^1CH{=}C(R^2)COOR^3$ are indications of the radical nature of the addition taking place according to the scheme:

$$(RO)_2P(O)NX_2 \xrightarrow[-\dot{X}]{h\nu,\Delta} (RO)_2P(O)\dot{N}X \xrightarrow{-\dot{C}{=}\dot{C}-Y} \rightarrow (RO)_2P(O)N(X)\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{\dot{C}}}-Y \xrightarrow[(RO)_2P(O)\dot{N}X]{(RO)_2P(O)NX_2}$$

(G)

$$\longrightarrow (RO)_2P(O)NX\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-Y,$$

$X{=}Cl,\ Br;\ Y{=}Alk,\ COOR,\ CONH_2.$

The regiospecificity of addition is determined by the formation of the adduct radical (G), which is more stable than the adduct radical $>\dot{C}-\underset{|}{C}(Y)NXP(O)(RO)_2$.

N,N-Dihalophosphoramidates are most active in reactions with terminal 1,3-alkadienes. These reactions occur under mild conditions (at 0–15 °C in CH_2Cl_2 for 30 min) and give (*E*)-1,4-adducts in 87–93% yield:[161]

$$(C_2H_5O)_2P(O)NCl_2 + CH_2{=}CR^1{-}CR^2{=}CH_2 \xrightarrow[0-15^\circ C]{CH_2Cl_2} \rightarrow (C_2H_5O)_2P(O)NClCH_2CR^1{=}CR^2CH_2Cl \xrightarrow[0-10^\circ C]{\text{then } 10\%\ Na_2SO_3} \rightarrow (C_2H_5O)_2P(O)NHCH_2CR^1{=}CR^2CH_2Cl,$$

$R^1{=}R^2{=}H;\ R^1{=}CH_3,\ R^2{=}H,\ CH_3.$

The reactions have high regiospecificity. They are inhibited in the presence of hydroquinone. The mechanism proposed by Gajda and Zwierzak[162] involves formation of an allylic type of adduct radical (H):

$$(RO)_2P(O)NCl_2 + >C{=}\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}{=}C< \xrightarrow{-\dot{C}l} (RO)_2P(O)NCl-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-$$

(H)

$$\xrightarrow[-(RO)_2P(O)N\dot{C}l]{(RO)_2P(O)NCl_2} (RO)_2P(O)NCl-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}{=}\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}Cl$$

$$(RO)_2P(O)N\dot{C}l + >C{=}\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}{=}C< \longrightarrow (H)$$

Radical (H) is stabilised by removal of a chlorine atom from the *N,N*-dichlorophosphoramidate, and so the thermodynamically more favourable 1,4-addition product is formed, which dictates the high regiospecificity of the reaction.

N,N-Dichlorophosphoramidates add on to 1,3-alkadienes such as *trans*-piperylene, 2,5-dimethyl-2,4-hexadiene, and 4-methyl-1,3-pentadiene only when initiated with UV irradiation.[162] These reactions are not regiospecific—1,2- and 4,1-addition products are formed together with 1,4-adducts.

It is interesting to note that the reaction of 1,4-diphenyl-1,3-butadiene with diethyl *N,N*-dichlorophosphoramidate has high regiospecificity—only the 1,2-addition product is formed:

$$(C_2H_5O)_2P(O)NCl_2 + PhCH{=}CH{-}CH{=}CHPh \xrightarrow{\text{then } 10\%\ Na_2SO_3} \rightarrow (C_2H_5O)_2P(O)NHCH(Ph)CHClCH{=}CHPh.$$

81%

This orientation of substituents in the adduct is consistent with the proposal[162] about stabilisation of the radical

$$(C_2H_5O)_2P(O)NClCH(Ph)\overset{\dot{}}{\underset{\dot{}}{CH}}{-}CH{-}CHPh \qquad (I)$$

by addition of a chlorine atom to the 2-position with formation of the more stable compound.

There is an interesting study[163] in which the spontaneous addition of *N,N*-dichlorophosphoramidates to α-pinene is investigated; the products isolated are not those from addition of amidyl radicals to the double bond but products in the *trans* configuration formed from them by an intramolecular Wagner–Meerwein rearrangement (33%).

One study[164] was recently published, in which the addition of diethyl *N,N*-dibromophosphoramidate to olefins was examined using conditions for a heterolytic reaction—in the presence of boron trifluoride ethereate. It was shown that the reaction is regiospecific and gives saturated adducts:

$$PhCR{=}CHR^1 + Br_2NP(O)(C_2H_5O)_2 \xrightarrow[-20^\circ C]{BF_3\cdot(C_2H_5)_2O} \rightarrow PhC(R)CH(Br)R^1 \xrightarrow{NaHSO_3} PhC(R)CH(Br)R^1,$$

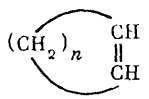
$\quad\quad\quad

The addition of *N,N*-dibromophosphoramidates to 1,2-dialkyl-substituted ethylenes is not regiospecific:

$$R^1CH{=}CHR^2 + Br_2NP(O)(OC_2H_5)_2 \xrightarrow[2)\ NaHSO_3]{1)\ BF_3\cdot(C_2H_5)_2O} \rightarrow \underset{(C_2H_5O)_2P(O)NH\ \ Br}{R^1CH{-}CHR^2} + \underset{Br\ \ NHP(O)(OC_2H_5)_2}{R^1CH{-}CHR^2}$$

(I) (II)

With terminal alkenes ($R^1 = C_4H_9$, $R^2 = H$ and $R^1 = C_3H_7$, $R^2 = H$), mainly products (I) are formed, while the 2-pentene and 2-hexene products (I) and (II) are formed in equimolar quantities. The reactions with 3-hexene and 2-butene are highly stereoselective (only products with the *erythro*-configuration are formed, in 84–92% yield).[164] The addition of diethyl *N,N*-dibromophosphoramidates to cyclic



alkenes is highly stereospecific, only the *trans*-isomers are formed (79–80%). A similar reaction with indene has high regiospecificity and stereospecificity and gives *trans*-2-bromo-3-(diethoxyphosphoramido)indane (yield 96%).[164]

It is interesting that, in contrast to *N*-alkyl-*N*-halocarbamates, N–R-substituted *N*-halophosphoramidates $(C_2H_5O)_2P(O)N(R)Br$ undergo a reaction with styrene on heating to form saturated adducts in appreciable yield: 40% (R = C_2H_5); 76% (R = CH_3).[165] The introduction of stronger electron-donating substituents on to the nitrogen atom (R = OAlk, OCH_2Ph) hinders the addition to styrene, since stabilisation of the amidyl radicals $(C_2H_5O)_2P(O)\dot{N}OR^1$ occurs with elimination of nitrogen and formation of alkyl diethyl phosphates.[166] In this case chlorination of styrene is the preferred process (about 66%). It was also possible to identify products from the non-regiospecific addition of amidyl radicals to styrene, with the adduct $(C_2H_5O)_2P(O)N(OR)CH_2CHClPh$ present in threefold excess. It was not possible to isolate adducts in the reaction between *N*-methyl- or *N*-ethyl-*N*-bromophosphoramidate with 2-methyl-1-butene. However, when the reaction mixtures were treated with hydrogen chloride in tetrahydrofuran, the formation of *N*-alkyl-*N*-(2-bromoalkyl)amine hydrochlorides occurred in 10–28% yield.[165]

The introduction of bulkier alkyl substituents on to the nitrogen atom in the phosphoramidates $(AlkO)_2P(O)N(R)Br$ (R = n-C_4H_9, t-C_4H_9) hinders the addition of amidyl radicals to the double bond of an alkene or prevents it completely.[165]

In the presence of boron trifluoride etherate the addition of similar *N*-alkyl-*N*-halophosphoramidates to styrene or cyclohexene gives saturated adducts or products derived from their subsequent conversion.[165,167,168]

Thus, the direction of addition of dialkyl *N*-halophosphoramidates to the C=C bond is mainly determined by the conditions of homolytic and heterolytic initiation.

IV. Reactions of *N,N*-dihaloamides with polyhaloethylenes—a new method for the synthesis of compounds with an azomethine bond

In the large number of studies discussed in the preceding sections of this review it was shown that the *N,N*-dihaloamides of different acids add on to unsaturated compounds, including halogenated products (vinylidene chloride,[120] 1,1,3-trichloropropene,[97] chloroprene [44]), to form saturated adducts.

It was of interest to study the reaction of polyhaloethylenes with amidyl radicals in order to extend the range of homolytic reactions of haloolefins as well as amidyl radicals centred on nitrogen.

The results obtained from studying the reactions of homolytic thiylation of trichloroethylene and 1,2-dichloroethylene[169–173] and chlorovinylation of triethylsilane with trichloroethylene[174] suggest that the adduct radical $RCHCl\dot{C}Cl_2$ formed is stabilised not by formation of a saturated adduct but by elimination of a halogen atom from the α-position relative to the radical site, and an unsaturated compound $RCH{=}CCl_2$ is isolated. In the reaction of amidyl radicals with trichloroethylene, formation of an unsaturated compound could also be expected.

In fact, when *N,N*-dichloroarenesulphonamides react with trichloroethylene, chloral *N*-arylsulphonylimines are formed in quantitative yield. The saturated adducts $CCl_3CHClNClSO_2Ar$ were not detected in this reaction even though the ratio of reactants, the reaction conditions, and the structure of the aromatic group were varied:[72,74]

$$ArSO_2NCl_2 + CHCl{=}CCl_2 \rightarrow CCl_3CH{=}NSO_2Ar + Cl_2 + CHCl_2CCl_3,$$
$$Ar = C_6H_5,\ p\text{-}ClC_6H_4,\ p\text{-}CH_3C_6H_4.$$

The reactions were carried out in a stream of inert gas (nitrogen or argon) with UV irradiation (30 °C) in the presence of azobisisobutyronitrile or benzoyl peroxide (50–60 °C) and also without an initiator (85 °C). The maximum yield of imines (98–99%) was achieved when a four- to six-fold excess of trichloroethylene was used and the reactants were heated at 85 °C for 12–14 h. The chlorination of trichloroethylene to pentachloroethane by the chlorine generated occurred as a parallel process.

The acceleration of the reaction by radical initiators and its retardation in the presence of radical inhibitors (hydroquinone, atmospheric oxygen, etc.) suggests that the reaction of *N,N*-dichloroarenesulphonamides with trichloroethylene has a radical nature. The following reaction scheme has been proposed:[74]

N-Arylsulphonylimines are obtained via the formation of adduct radical (J). It can be stabilised in several ways: by 1,2- or 1,3-migration of a chlorine atom followed by elimination of a chlorine atom from the α-position of the isomerised radicals or by formation of an enamide derivative (K) followed by its chlorotropic rearrangement (the possibility of stabilising the adduct radicals by elimination of a chlorine atom from the α-position relative to the radical site to give enamides has been reported[169–174]).

The possibility that *N*-arylsulphonylimines are synthesised by dehalogenation of the saturated adducts (L) cannot be ruled out, but this reaction route is not the main one, as is indicated by the ^1H NMR spectroscopic data.[74]

The routes involving 1,2-migration of a chlorine atom in radical adduct (J) and also formation of enamide (K) from it seem less probable because of the greater tendency of the N–Cl bond towards homolytic cleavage (37 kcal mol^{-1}) than the C–Cl bond (81 kcal mol^{-1}).[60] When the reaction mixtures were studied by IR and ^1H NMR spectroscopy there was no indication that compounds with the $CCl_2=CH-NCl$ group were present in them. 1,1,1,2-Tetrachloroethylsulphonamides $ArSO_2NHCHClCCl_3$ were also not detected.

The previously known methods for obtaining chloral sulphonylimines [175–179] are characterised by multiple-stage reactions, the use of catalysts, and the toxicity and instability of the reactants. The new method for obtaining chloral sulphonylimines that has been developed is based on a large-tonnage organochlorine feedstock. As a result of the high yield of the products, the single-stage reaction, and technological effectiveness of the method it can be recommended as a new convenient method for the synthesis of highly reactive azomethines.

In order to extend the limits of the reaction that had been found for the synthesis of compounds with an azomethine bond and also to verify its mechanism, a study was made of the reaction between *N*,*N*-dichlorobenzenesulphonamide and tribromoethylene.[75] The reaction took place in an inert solvent by heating (85–90 °C) the dichloramide with a four- to six-fold excess of tribromoethylene for 9–14 h. The previously unknown dibromochloroacetaldehyde *N*-benzenesulphonylimine was formed (yield 80%) as a mixture of *syn*- and *anti*-isomers.[75] The reaction was accompanied by the evolution of chlorine and bromine and the formation of 1,2-dichloro-1,2,2-tribromoethane. Dibromochloroacetaldehyde *N*-benzenesulphonylimine is formed in a similar manner to that given in Scheme 1.

The structure of this imine can be used to verify the reaction mechanism, namely to exclude the reaction pathway via a 1,2-halotropic rearrangement in the adduct radical $C_6H_5SO_2NClCHBr\dot{C}Br_2$ since this would lead to the formation of the corresponding bromal derivative $C_6H_5SO_2N=CHCBr_3$. Exclusion of the reaction pathway via a 1,2-halotropic rearrangement in the adduct radical (see Scheme 1) is also confirmed by the reaction between *N*,*N*-dibromobenzenesulphonamide and trichloroethylene, which gives dichlorobromoacetaldehyde *N*-benzenesulphonylimine:[180]

$$C_6H_5SO_2NBr_2 + CHCl=CCl_2 \rightarrow C_6H_5SO_2N=CHCCl_2Br.$$

In order to obtain highly reactive sulphonylimines of polyhaloaldehydes, the reaction of *N*,*N*-dichloroarenesulphonamides with 1,2-dichloroethylene [73,181,182] has been studied.

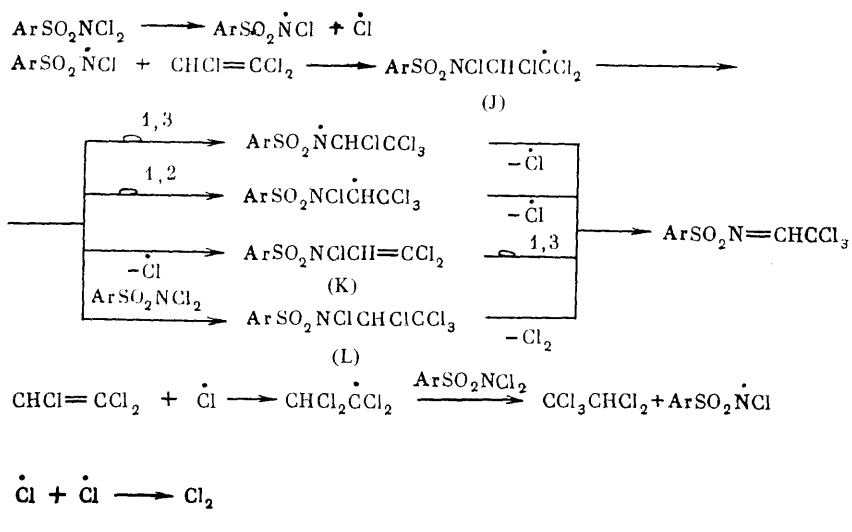
It should be noted that an attempt to react 1,2-dichloroethylene with compounds containing an N–Cl bond was made in an earlier study,[3] where the inertness of this olefin towards amidyl radicals was noted. However, it was later established that the reaction of 1,2-dichloroethylene with *N*,*N*-dichloroarenesulphonamides, occurring on exposure to UV radiation (47–55 °C) for 4 h and a ratio of reactants of 10:1, takes place in a similar manner to the reactions of *N*,*N*-dichloroarenesulphonamides with trichloro- and tribromo-ethylene and gives the corresponding azomethines in 50–60% yield. When the reaction time is increased to 9–26 h and the initiation conditions are also changed, the result is that the reaction is complicated by a number of subsidiary processes, which give 2,2-dichloro-1,1-di(*N*-arenesulphonamido)ethanes, chloral *N*-arylsulphonylimines, sulphonamides, and also products derived from chlorination of 1,2-dichloroethylene:[73]

$ArSO_2NCl_2 + CHCl=CHCl$ →
- $ArSO_2N=CHCHCl_2$
- $(ArSO_2NH)_2CHCHCl_2$
- $ArSO_2N=CHCCl_3$
- $ArSO_2NH_2$
- $CHCl_2CHCl_2 + CHCl=CCl_2 + CCl_2=CCl_2$

Ar = C_6H_5, *p*-ClC_6H_4, *p*-$CH_3C_6H_4$.

The yield of the reaction products depends on the conditions. When mixtures of 1,2-dichloroethylene and *N*,*N*-dichloroarenesulphonamides (in the ratio 1:8–10) are exposed to UV radiation at

Scheme 1



47–55 °C for 8–9 h the main reaction products are dichloroacetaldehyde sulphonylimines and 2,2-dichloro-1,1-di(*N*-arenesulphonamido)-ethanes. On heating without UV irradiation there is a considerable increase in the proportion of 1,2-dichloroethylene chlorination products and chloral sulphonylimines formed as a result of a side reaction between trichloroethylene and *N*,*N*-dichloroarene-sulphonamides.[74]

The reaction of *N*,*N*-dichlorourethane with trichloroethylene occurred under conditions similar to those for the reaction between *N*,*N*-dichloroarenesulphonamides and trichloroethylene[74] and led to the formation of chloral *N*-ethoxycarbonylimine in 75% yield.[76–77] When the reactants were heated for a longer period and water was introduced into the reaction mixture, the main reaction products isolated were 2,2,2-trichloro-1,1-di(*N*-ethoxycarbonylamino)ethane (50%) and 2,2,2-trichloro-1-hydroxy(1-*N*-ethoxycarbonylamino)ethane (20%) as a result of the reaction between chloral *N*-ethoxycarbonyl-imine and urethane which is formed in a side reaction and by reaction with water:[76]

$$C_2H_5OCONCl_2 + CHCl{=}CCl_2 \rightarrow C_2H_5OCON{=}CHCCl_3 \rightarrow$$
$$\rightarrow \begin{cases} \xrightarrow{C_2H_5OCONH_2} (C_2H_5OCONH)_2CHCCl_3 \\ \xrightarrow{H_2O} C_2H_5OCONHCH(OH)CCl_3 \end{cases}$$

The reaction of *N*,*N*-dibromourethane with trichloroethylene takes place in a similar manner, the main product being dichloro-bromoacetaldehyde *N*-ethoxycarbonylimine $C_2H_5OCON{=}CHCCl_2Br$, which is isolated in 67% yield. 2-Bromo-2,2-dichloro-1,1-di(*N*-ethoxy-carbonylamino)ethane—derived from the addition of a urethane molecule to the double bond of the dichlorobromoacetaldehyde imine—is formed as a by-product (10%):[183]

$$C_2H_5OCON{=}CHCBrCl_2 \xrightarrow{C_2H_5OCONH_2} \rightarrow (C_2H_5OCONH)_2CHCBrCl_2$$

The reaction occurs in a similar manner to that given in Scheme 1. Since the dichlorobromacetaldehyde acylimine is formed, the possible route involving a 1,2-chlorotropic rearrangement of the adduct radical (M) followed by elimination of bromine can be excluded, as in this case the reaction product would be chloral acylimine:

$$C_2H_5OCONBrCHCl\dot{C}Cl_2 \xrightarrow{1,2}$$
(M)
$$\rightarrow C_2H_5OCONBr\dot{C}HCCl_3 \xrightarrow[-Br^{\cdot}]{} C_2H_5OCON{=}CHCl_3$$

It was possible to carry out the reaction of *N*,*N*-dichlorobenzamide and *N*,*N*-dichloroacetamide with trichloroethylene under similar conditions, with products from further reaction of azomethines $RCON{=}CHCCl_3$ being formed, namely, *N*-(2,2,2-trichloro-1-hydroxy-ethyl)-substituted benzamide or acetamide and 1,1-di(*N*-benzamido)- or 1,1,-di(*N*-acetamido)-2,2,2-trichloroethanes.[184]

In the presence of atmospheric oxygen these reactions are complicated by the concurrent oxidation of trichloroethylene to dichloroacetyl chloride and the reaction of by-products to give the mixed amide $C_6H_5CONHCOCHCl_2$.

The reaction of diethyl *N*,*N*-dichlorophosphoramidate with trichloroethylene also takes place in accordance with Scheme 1 as proposed and gives 1,1,1-trichloro-2,2-bis(diethylphosphamido)-ethane.[185]

A study of the reactions of *N*,*N*-dihaloamides of sulphonic and carboxylic acids as well as *N*,*N*-dihalourethanes and dialkyl *N*,*N*-dichlorophosphoramidates with trichloro-, tribromo-, and 1,2-dichloro-ethylene showed that the reactions were accelerated by photochemical and thermal initiation as well as in the presence of peroxides and were inhibited in the presence of air or hydroquinone, which was an indication of their free-radical nature. The free-radical nature of the process was confirmed by chemically induced polarisation of ^1H nuclei and EPR spectroscopy.[186]

A study of the photochemically induced reaction of *N*,*N*-dichlorobenzenesulphonamide with trichloroethylene and 1,2-dichloroethylene by EPR in the presence of a 2-methyl-2-nitroso-propane trap (in benzene) demonstrated the formation during reaction of adduct radicals $C_6H_5SO_2NClCHClCXCl$ (J) (see Scheme 1), for which the EPR spectrum showed a characteristic splitting on the nitrogen atom with hyperfine coupling constant = 12.2 G, on the two non-equivalent chlorine nuclei $a_{Cl(1)}$ = 4.1 G, $a_{Cl(2)}$ = 1.0 G (X = Cl) and the chlorine atoms: $a_{^{35}Cl}$ = 6.2 G, $a_{^{37}Cl}$ = 4.7 G (X = H). Thus, the reactions of amidyl radicals $R\dot{N}Hal$ (R = SO_2Ar, COOAlk, COAlk, COAr) with polyhaloethylenes are of a common type and constitute an essentially new method for the synthesis of compounds with an azomethine bond. By selecting suitable partners the synthesis of azomethines $CHal_3CH{=}NR$ can likewise be carried out with different combinations of halogen atoms.

At the same time mention should be made of the high reactivity of synthesised polyhaloaldehyde acylimines in nucleophilic addition reactions of alcohols,[74–76] phenols, carboxylic acids,[127,184] sulphonamides and carboxamides,[129,176,184,187] thiols,[176] oximes, hydrazines,[187,188] bifunctional compounds,[176,187] chloroalkanols, α-halocarboxylic acids,[189] and benzalazine.[190]

Diene condensation reactions of chloral sulphonylimines with butadiene, isoprene, piperylene, and cyclopentadiene [178,191] have been carried out. For the first time the possibility of using chloral sulphonylimines as *C*-amidoalkylation agents of aromatic compounds (anisole, thioanisole, *N*,*N*-dimethylaniline),[192] heterocycles (thiophene, furan and its derivatives),[193] etc. has been demonstrated.

V. Conclusion

Thus, a common property of the reactions of *N*-haloamines, *N*-halocarbamates, and *N*-haloamides of carboxylic, sulphonic, and phosphoric acids with unsaturated compounds is the formation of saturated adducts. An analysis of the literature data showed that the majority of these reactions have a radical nature. The abundance of experimental and theoretical material which has been collected makes it possible to propose a general scheme for these reactions, involving the formation of a radical adduct $RN(X)\underset{|}{\overset{|}{C}}-\dot{C}\diagdown$ [R = Alk, R^1COO, R^1CO, $ArSO_2$, $AlkSO_2$, $(AlkO)_2P(O)$; X = H, Alk, Cl, Br] obtained by attack of an amidyl radical on the less substituted carbon atom at the double bond of alkene derivatives. Thus, the driving force of the process is formation of the most stable radical.

It follows from the material presented in this review that in recent years a new trend has developed in the sphere of radical reactions between *N*-haloamides and olefins—the reaction of acid

N,N-dihaloamides with polyhaloethylenes to form polyhaloaldehyde acylimines, which are highly reactive syntones in organic synthesis.

From among the known ionic reactions of *N*-haloamides and *N*-haloamines with unsaturated compounds, in recent years there has been active study of the reaction of *N*-chloramines with olefins in the presence of SO_3, which can give a new type of highly reactive electrophilic reagent at the first stage—*O*-chlorosulphamates—which then readily add on to the double bond of different alkenes.

Nevertheless, there are still a number of unresolved problems relating to the study of the mechanism of reactions between acid *N*-haloamides with alkenes under ionic initiation conditions. The reactions of acid *N*-haloamides with acetylene and polyhaloethylenes have not been studied in sufficient detail. There are no quantitative data on these reactions.

The various reactions described in this review illustrate the extensive reaction possibilities which are opened up by the chemistry of aminyl and amidyl intermediates.

Various types of compounds which have extensive application both in fine organic synthesis and in practical work can be obtained from these reactions (Scheme 2).

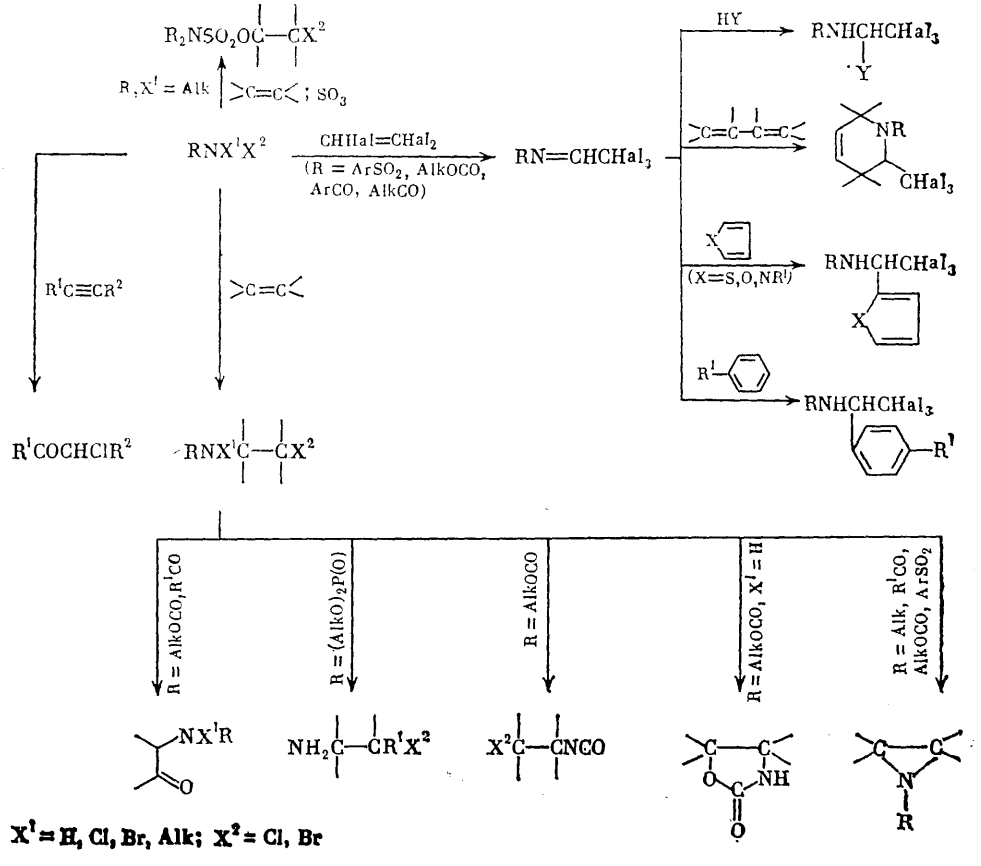
Among these products there are biologically active compounds with neurotropic and antibactericidal activity,[188] and insecticides,[194-198] herbicides,[199,200] and plant growth regulators[201] have been identified.

Aziridine derivatives—compounds with anticancer activity—have attracted considerable attention in recent years.[149] Various derivatives of isocyanates and oxazolidines have been widely used in the production of foamed plastics,[202] lacquers,[203] electrical insulating materials,[203] components of rubber mixtures,[204,205] etc.

The recent results should act as a stimulus for carrying out new studies aimed at investigating the reactions of *N*-haloamines and *N*-haloamides with different unsaturated compounds.

We can draw the attention of research workers to this field of chemistry by indicating the studies in which are reported the methods for synthesising *N*-chloramines,[23,27-30,206-208] *N*-monohalo- and *N,N*-dihalo-carbamates,[43,46,50,209] *N*-alkyl-*N*-halo- and *N,N*-dihalo-carboxamides,[95,210,211] *N,N*-dihaloarenesulphonamides,[112,212] and dialkyl *N,N*-dihalo- and *N*-alkyl-*N*-halophosphoramidates.[152,153,165,166,213-216]

Scheme 2



References

1. Z Földi *Ber. Bunsenges. Phys. Chem.*, 1930, **63** 2257
2. P Kovacic, M K Lowery, K W Field *Chem. Revs.*, 1970, **70** 639
3. R S Neale *Synthesis*, 1971, 1
4. A N Nesmeyanov et al. (Editors) *Metody Elementoorganicheskoi Khimii. Khloralifaticheskie Soedineniya* (Methods in Heteroorganic Chemistry. Chloroaliphatic Compounds), Izd. Nauka, Moscow, 1973, p. 50
5. P Mackiewicz, R Furstoss *Tetrahedron*, 1978, **34** 3241
6. C Brown, A J Lawson *Tetrahedron Lett.*, 1975, 191
7. T Koenig, R A Wielesek *Tetrahedron Lett.*, 1975, 2007
8. J Lessard, D Griller, K U Ingold *J. Am. Chem. Soc.*, 1980, **102** 3262
9. R S Neale, R L Hinman *J. Am. Chem. Soc.*, 1963, **85** 2665
10. R S Neale *J. Am. Chem. Soc.*, 1964, **86** 5340
11. R S Neale, M R Walsh *J. Am. Chem. Soc.*, 1965, **87** 1255
12. R S Neale, M R Walsh, N L Marcus *J. Org. Chem.*, 1965, **30** 3683
13. R S Neale *Tetrahedron Lett.*, 1966, 493
14. R S Neale *J. Org. Chem.*, 1967, **32** 3263
15. R S Neale, N L Marcus *J. Org. Chem.*, 1967, **32** 3273
16. R S Neale, N L Marcus *J. Org. Chem.*, 1968, **33** 3457
17. F Minisci, R Galli *Chim. Ind. (Milan)*, 1963, **45** 1400
18. F Minisci, R Galli *Chim. Ind. (Milan)*, 1964, **46** 546
19. F Minisci, R Galli *Tetrahedron Lett.*, 1964, 167
20. F Minisci, R Galli *Tetrahedron Lett.*, 1964, 3197
21. F Minisci, R Galli *Tetrahedron Lett.*, 1965, 1679
22. F Minisci, R Galli, M Cecere *Tetrahedron Lett.*, 1966, 3163
23. F Minisci, R Galli, G Pollina *Chim. Ind. (Milan)*, 1965, **47** 736
24. M B Gasc, A Lattes, J J Perie *Tetrahedron*, 1983, **39** 703
25. M L Poutsma, P A Ibarbia *J. Org. Chem.*, 1971, **36** 2572
26. M E Wolff *Chem. Revs.*, 1963, **63** 55
27. H Bock, K-L Kompa *Z. Anorg. Allg. Chem.*, 1964, **332** 238
28. A M Pinchuk, Abstract of Doctorate Thesis in Chemical Sciences, Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev, 1975, p. 8
29. L N Markovskii, A M Pinchuk, G K Bespal'ko, V V Borisoglebskaya *Zhur. Org. Khim.*, 1969, **5** 2119
30. A M Pinchuk, L N Markovskii, E S Levchenko, V I Shevchenko *Zhur. Obshch. Khim.*, 1967, **37** 852
31. N S Zefirov, N V Zyk, S I Kolbasenko, A G Kutateladze *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 959
32. S I Kolbasenko, N V Zyk, N S Zefirov *Tezisy Dokladov IV Konferentsii po Organicheskoi Khimii i Tekhnologii* (Abstracts of Reports at the IVth Conference on Organic Chemistry and Technology), Moscow, 1985, p. 198
33. N S Zefirov, N V Zyk, S I Kolbasenko, A G Kutateladze *Sulfur Lett.*, 1984, **2** 95
34. N S Zefirov, N V Zyk, S I Kolbasenko, A G Kutateladze *J. Org. Chem.*, 1985, **50** 4539
35. S I Kolbasenko, Abstract of Candidate's Thesis in Chemical Sciences, Moscow State University, 1985, p. 17
36. N V Zyk, S I Kolbasenko, A G Kutateladze, et al. *Tezisy Dokladov Vsesoyuznoi Konferentsii po Khimii Nepredel'nykh Soedinenii* (Abstracts of Reports at the All-Union Conference on the Chemistry of Unsaturated Compounds), Part 2, Kazan', 1986, p. 53
37. N V Zyk, A S Koz'min, N S Zefirov *Tezisy Dokladov Vsesoyuznoi Konferentsii po Khimii Nepredel'nykh Soedinenii* (Abstracts of Reports at the All-Union Conference on the Chemistry of Unsaturated Compounds), Part 1, Kazan', 1986, p. 19
38. N S Zefirov, N V Zyk, S I Kolbasenko, E M Itkin *Zhur. Org. Khim.*, 1986, **22** 449
39. P Chabrier, L Saulniere, Ann. Chim., 1942, **17** 353
40. K Schrage *Tetrahedron Lett.*, 1966, 5795
41. K Schrage *Tetrahedron*, 1967, **23** 3033
42. K Schrage *Tetrahedron*, 1967, **23** 3039
43. T A Foglia, D Swern *J. Org. Chem.*, 1966, **31** 3625
44. F A Daniher, P E Butler, *J. Org. Chem.*, 1968, **33** 2637
45. T A Foglia, D Swern *J. Org. Chem.*, 1968, **33** 766
46. N I Filenko, V B Mochalin *Zhur. Org. Khim.*, 1979, **15** 475
47. Ya G Bal'on, V E Paranyuk *Zhur. Org. Khim.*, 1973, **9** 2424
48. Ya G Bal'on *Zhur. Org. Khim.*, 1974, **10** 408
49. Ya G Bal'on, R N Moskaleva *Zhur. Org. Khim.*, 1975, **11** 2497
50. V B Molchalin, N I Filenko *Khim. Geterotsikl. Soedin.*, 1979, 1628
51. Ya G Bal'on, R N Moskaleva *Zhur. Org. Khim.*, 1978, **14** 1462
52. Ya G Bal'on, R N Moskaleva *Zhur. Org. Khim.*, 1979, **15** 1207
53. H Driguez, J M Paton, J Lessard *Can. J. Chem.*, 1977, **55** 700
54. J Lessard, J M Paton *Tetrahedron Lett.*, 1970 4883
55. J Lesard, M Mondon, D Touchard *Can. J. Chem.*, 1981, **59** 431
56. H Driguez, I P Vermes, J Lessard *Can. J. Chem.*, 1978, **56** 119
57. T V Khenkina, Abstract of Candidate's Thesis in Chemical Sciences, Lomonosov Moscow Institute of Fine Chemical Technology, Moscow, 1982, p. 5
58. J Lessard, Y Couture, M Mondon, D Touchard *Can. J. Chem.*, 1984, **62** 105
59. Ya G Bal'on *Zhur. Org. Khim.*, 1980, **16** 2606
60. A L Terney, Jr. *Contemporary Organic Chemistry* (Translated into Russian), Vol. 2, Izd. Mir, Moscow, 1981, p. 363
61. Ya G Bal'on, R N Moskaleva *Zhur. Org. Khim.*, 1980, **16** 2599
62. H Terauchi, K Kowata, T Minematsu, S Takemura *Chem. Pharm. Bull. (Japan)*, 1977, **25** 556
63. Ya G Bal'on, V E Paranyuk *Zhur. Org. Khim.*, 1979, **15** 1203
64. Ya G Bal'on, V E Paranyuk *Zhur. Org. Khim.*, 1980, **16** 556
65. Ya G Bal'on, V E Paranyuk *Zhur. Org. Khim.*, 1980, **16** 2246
66. Ya G Bal'on, V E Paranyuk *Zhur. Org. Khim.*, 1976, **12** 522
67. N N Labeish, Yu I Porfir'eva, A A Petrov *Zhur. Org. Khim.*, 1984, **20** 477
68. A Yamasaki, H Terauchi, S Takemura *Chem. Pharm. Bull. (Japan)*, 1976, **24** 2841
69. N N Labeish, Yu. I Porfir'eva, A A Petrov *Zhur. Org. Khim.*, 1984, **20** 477
70. Ya G Bal'on, R N Moskaleva *Zhur. Org. Khim.*, 1977, **13** 664
71. Ya G Bal'on, R N Moskaleva *Zhur. Org. Khim.*, 1978, **14** 147
72. A N Mirskova, G G Levkovskaya, T I Drozdova, M G Voronkov, USSR P. 899 543; *Byull. Izobret.*, 1982, (3)
73. A N Mirskova, G G Levkovskaya, T I Drozdova, et al. *Zhur. Org. Khim.*, 1981, **17** 1101
74. A N Mirskova, G G Levkovskaya, T I Drozdova *Zhur. Org. Khim.*, 1982, **18** 452
75. A N Mirskova, G G Levkovskaya, T I Drozdova, et al. *Zhur. Org. Khim.*, 1982, **18** 1632
76. A N Mirskova, G G Levkovskaya, T I Drozdova, et al. *Zhur. Org. Khim.*, 1983, **19** 1110
77. Ya G Bal'on, V E Paranyuk *Zhur. Org. Khim.*, 1983, **19** 1346

78. H Driguez, J Lessard *Can. J. Chem.*, 1977, **55** 720
79. S Wolfe, D V C Awang *Can. J. Chem.*, 1971, **49** 1384
80. D Touchard, J Lessard *Tetrahedron Lett.*, 1971, 4425
81. D Touchard, J Lessard *Tetrahedron Lett.*, 1973, 3827
82. F L Lu, Y M A Naguib, M Kitadani, Y L Chow *Can. J. Chem.*, 1979, **57** 1967
83. S Wolfe, D V C Awang *J. Am. Chem. Soc.*, 1967, **89** 5287
84. M Mondon, J Lessard *Can. J. Chem.*, 1978, **56** 2590
85. R S Neale, N L Marcus, R G Schepers *J. Am. Chem. Soc.*, 1966, **88** 3051
86. J C Day, M G Katsoros, W D Kocher, et al. *J. Am. Chem. Soc.*, 1978, **100** 1950
87. R W Vip, Y L Chow, C Beddard *J. Chem. Soc., Chem. Commun.*, 1981, 955
88. Ya G Bal'on, N N Kovalenko *Zhur. Org. Khim.*, 1978, **14** 2011
89. Ya G Bal'on, R N Moskaleva *Zhur. Org. Khim.*, 1983, **19** 2456
90. M E Kuehne, D A Horne *J. Org. Chem.*, 1975, **40** 1287
91. Y L Chow, A Perry *Tetrahedron Lett.*, 1972, 531
92. P Mackiewicz, R Furstoss, B Waegell *J. Org. Chem.*, 1978, **43** 3746
93. J Lessard, R Cote *J. Org. Chem.*, 1978, **43** 3750
94. D Berube, J Caza, F M Kimmerle, J Lessard, *Can. J. Chem.*, 1975, **53** 3060
95. R A Johnson, F D Greene *J. Org. Chem.*, 1975, **40** 2186
96. R A Johnson, F D Greene *J. Org. Chem.*, 1975, **40** 2192
97. N A Rybakova, N A Pochkailo, L N Kiseleva *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 2793
98. V I Markov, S I Burmistrov, D A Danilenko, et al. *Zhur. Org. Khim.*, 1971, **7** 602
99. N A Rybakova, L N Sharonova, R Kh Freidlina *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 1357
100. M V Likhosherstov, R A Arkhangel'skaya *Zhur. Obshch. Khim.*, 1937, **7** 1914
101. M V Likhosherstov, G V Shalaeva *Zhur. Obshch. Khim.*, 1938, **8** 370
102. M V Likhosherstov, V E Zhabotinskaya, L D Pavlovskaya *Zhur. Obshch. Khim.*, 1938, **8** 997
103. M V Likhosherstov, A A Petrov *Zhur. Obshch. Khim.*, 1939, **9** 2000
104. T Ohashi, M Sugie, M Okahara, S Komori *Tetrahedron*, 1969, **25** 5349
105. T Ohashi, M Sugie, M Okahara, S Komori *Tetrahedron Lett.*, 1968, 4195
106. N A Rybakova, P V Petrovskii, P O Okulevich, R Kh Freidlina *Izv. Akad Nauk SSSR, Ser Khim.*, 1970, 1577
107. T A Foglia, E T Haeberer, G Maerker *J. Am. Oil Chem. Soc.*, 1970, **47** 27
108. H Terauchi, A Yamasaki, S Takemura *Chem. Pharm. Bull. (Japan)*, 1975, **23** 3162
109. F A Daniher, T Melchior, P E Butler *Chem. Commun.*, 1968, 931
110. M S Kharasch, H M Pristley *J. Am. Chem. Soc.*, 1939, **61** 3425
111. F A Daniher, P E Butler *J. Org. Chem.*, 1968, **33** 4336
112. Y Ueno, S Takemura, Y Ando, H Terauchi *Chem. Pharm. Bull. (Japan)*, 1965, **13** 1369
113. Y Ueno, S Takemura, Y Ando, H. Terauchi *Chem. Pharm. Bull. (Japan)*, 1967, **15** 1193
114. Y Ueno, S Takemura, Y Ando, H. Terauchi *Chem. Pharm. Bull. (Japan)*, 1967, **15** 1198
115. H Terauchi, S Takemura, Y Ueno *Chem. Pharm. Bull. (Japan)*, 1975, **23** 640
116. H Terauchi, S Takemura *Chem. Pharm. Bull. (Japan)*, 1975, **23** 2410
117. S Takemura, H Terauchi, Y Ando, Y Ueno *Chem. Pharm. Bull. (Japan)*, 1967, **15** 1328
118. A C Oehlschlager, C D Kennedy, L H Zalkow *J. Org. Chem.*, 1966, **31** 1682
119. D Greatbanks, T P Seden, R W Turner *Tetrahedron Lett.*, 1968, 4863
120. N A Rybakova, V I Dostovalova, A A Slepushkina, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 359
121. T P Seden, R W Turner, *J. Chem. Soc. C*, 1968, 876
122. T Abachi, K Otsuki *Chem. Pharm. Bull. (Japan)*, 1976, **24** 2803
123. K Otsuki, T Irino *Chem. Pharm. Bull. (Japan)*, 1975, **23** 482
124. R Kh Friedlina, N A Rybakova, G K Semin, E A Kravchenko *Dokl. Akad. Nauk SSSR*, 1967, **176** 352
125. N A Rybakova, L N Kiseleva, N A Pochkailo *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 627
126. V I Markov, V A Doroshenko *Zhur. Org. Khim.*, 1972, **8** 1251
127. A N Mirskova, T I Drozdova, G G Levkovskaya, et al. *Zhur. Org. Khim.*, 1982, **18** 1451
128. A N Mirskova, G G Levkovskaya, T I Drozdova, M G Voronkov *Tezisy Dokladov III Vsesoyuznoi Konferentsii 'Sovremennoe Sostoyanie i Perspektivy Razvitiya Teoreticheskikh Osnov Proizvodstva Khlororganicheskikh Produktov'* (Abstracts of Reports at the IIIrd All-Union Conference on 'The Current State and Prospects for Development of Theoretical Principles in the Production of Organochlorine Products'), Azneftekhim, Baku, 1981, p. 242
129. A N Mirskova, T I Drozdova, G G Levkovskaya, et al. *Zhur. Org. Khim.*, 1981, **17** 1108
130. A N Mirskova, G G Levkovskaya, T I Drozdova, et al. *Zhur. Org. Khim.*, 1985, **21** 620
131. T I Drozdova, G G Levkovskaya, A N Mirskova *Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Khimii Khlororganicheskikh Soedinenii* (Abstracts of Reports at the IVth All-Union Conference on the Chemistry of Organochlorine Compounds), Azneftekhim, Baku, 1985, p. 116
132. A N Mirskova, G G Levkovskaya, I T Gogoberidze, I D Kalikhman *Tezisy Dokladov XVI Konferentsii po Khimii i Tekhnologii Organicheskikh Soedinenii Sery i Sernistykh Neftei* (Abstracts of Reports at the XVIth Conference on the Chemistry and Technology of Organic Compounds of Sulphur and Sulphur-containing Oils), Riga, 1984, p. 36
133. N N Labeish, Abstract of Candidate's Thesis in Chemical Sciences, Lensovet Leningrad Technological Institute, Leningrad, 1984, p. 14
134. I S Vorob'eva, Abstract of Candidate's Thesis in Chemical Sciences, Lensovet Leningrad Technological Institute, Leningrad, 1984, p. 11
135. I S Vorob'eva, M D Stadnichuk *Zhur. Obshch. Khim.*, 1983, **53** 2654
136. I S Vorob'eva, M D Stadnichuk *Tezisy Dokladov XVI Konferentsii po Khimii i Tekhnologii Organicheskikh Soedinenii Sery i Sernistykh Neftei* (Abstracts of Reports at the XVIth Conference on the Chemistry and Technology of Organic Compounds of Sulphur and Sulphur-containing Oils), Riga, 1984, p. 153

137. I S Vorob'eva and M D Stadnichuk *Tezisy Dokladov VII Vsesoyunoi Konferentsii po Khimii Atsetilena* (Abstracts of Reports at the VIIth All-Union Conference on the Chemistry of Acetylene), Erevan, 1984, p. 115
138. I S Vorob'eva and M D Stadnichuk *Tezisy Dokladov VI Vsesoyuznoi Konferentsii po Khimii i Primeneniyu Kremnii-organicheskikh Soedinenii* (Abstracts of Reports at the VIth All-Union Conference on the Chemistry and Use of Organosilicon compounds), Riga, 1986, p. 243
139. N N Labeish, Yu I Porfir'eva, A A Petrov *Zhur. Org. Khim.*, 1985, **21** 659
140. N A Rybakova, R Kh Freidlina *Izv. Akad Nauk SSSR, Ser. Khim.*, 1969, 1194
141. N A Rybakova, R Kh Freidlina *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1971, 429
142. N A Rybakova, L N Kiseleva, V I Dostovalova, R Kh Freidlina *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 1107
143. N A Rybakova, L N Kiseleva, V I Dostovalova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 2571
144. N A Rybakova, L N Kiseleva *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 1662
145. D W Patrick, L K Truesdale, S A Biller, K B Sharpless *J. Org. Chem.*, 1978, **43** 2628
146. J-E Bäckvall *J. Org. Chem.*, 1979, **44** 1953
147. K B Sharpless, A O Chong, K Oshima *J. Org. Chem.*, 1976, **41** 177
148. E Herranz, K B Sharpless *J. Org. Chem.*, 1975, **43** 2544
149. V S Petrenko, O G Garnitskaya, V I Markov *Fiziologicheski Aktivnye Veshchestva* (Physiologically Active Compounds), Izd. Naukova Dumka, 1982, No. 14, p. 64
150. A Koziara, A Zwierzak *Tetrahedron*, 1976, **32** 1649
151. A M Pinchuk, L N Markovskii, T V Kovalevskaya *Zhur. Obshch. Khim.*, 1969, **39** 2594
152. A Zwierzak, S Zawadzki *Synthesis*, 1971, 323
153. A Zwierzak, A Koziara *Tetrahedron*, 1970, **26** 3521
154. L N Markovskii, A M Pinchuk, T V Kovalevskaya *Zhur. Obshch. Khim.*, 1970, **40** 1011
155. A M Pinchuk, L N Markovskii, T V Kovalevskaya *Zhur. Obshch. Khim.*, 1969, **39** 2142
156. S Zawadski, A Zwierzak *Tetrahedron*, 1973, **29** 315
157. A Zwierzak, S Zawadski, *Synthesis*, 1972, 416
158. A Zwierzak *Synthesis*, 1975, 507
159. S Zawadzki, A Zwierzak *Tetrahedron*, 1981, **37** 2675
160. A Zwierzak, A Koziara *Tetrahedron*, 1970, **26** 3527
161. A Zwierzak, T Gajda *Tetrahedron Lett.*, 1974, 3383
162. T Gajda, A Zwierzak *Tetrahedron*, 1985, **41** 4953
163. B Olejniczak, K Osowska, A Zwierzak *Tetrahedron*, 1978, **34** 2051
164. K Osowska-Pacewicka, A Zwierzak *Tetrahedron*, 1985, **41** 4717
165. K Osowska, A Zwierzak *Synthesis*, 1979, 577
166. A Zwierzak, I Brylikowska *Synthesis*, 1975, 712
167. A Zwierzak, K Osowska *Angew. Chem.*, 1976, **88** 302
168. A Zwierzak, K Osowska *Angew. Chem., Int. Ed. Engl.*, 1976, **15** 302
169. A V Martynov, A N Mirskova, M G Voronkov, et al. USSR P. 690013; *Byull. Izobret.*, 1979, (37)
170. A N Mirskova, A V Martynov, I D Kalikhman, et al. *Zhur. Org. Khim.*, 1979, **15** 1834
171. A N Mirskova, A V Martynov, M G Voronkov, *Zhur. Org. Khim.*, 1980, **16** 2076
172. A N Mirskova, A V Martynov, M G Voronkov *Zhur. Org. Khim.*, 1982, **18** 1555
173. A V Martynov, A N Mirskova, M G Voronkov *Zhur. Org. Khim.*, 1984, **20** 23
174. R Aloni, L A Rajenbach, A Horowitz *J. Organometal. Chem.*, 1979, **171** 155
175. G Schulz, G Kresze *Angew. Chem., Int. Ed. Engl.*, 1962, **2** 736
176. R Albrecht, G Kresze, R Mlakar *Chem. Ber.*, 1964, **97** 483
177. G Kresze, W Wucherpfenning *Angew. Chem.*, 1967, **79** 109
178. G Kresze, R Albrecht *Chem. Ber.*, 1964, **97** 490
179. B S Drach, A P Martynyuk, G N Miskevich, O P Lobanov *Zhur. Org. Khim.*, 1977, **13** 1404
180. T I Drozdova, A N Mirskova, G G Levkovskaya, et al. *Zhur. Org. Khim.*, 1988, **24**
181. A N Mirskova, G G Levkovskaya, T I Drozdova, M G Voronkov *Tezisy Dokladov III Vsesoyuznoi Konferentsii 'Sovremennoe Sostoyanie i Perspektivy Razvitiya Teoreticheskikh Osnov Proizvodstva Khlororganicheskikh Produktov'* (Abstracts of Reports at the IIrd All-Union Conference on 'The Current State and Prospects for Development of Theoretical Principles in the Production of Organochlorine Products'), Azneftekhim. Baku, 1981, p. 241
182. M G Voronkov, A N Mirskova *Zhur. Vses. Khim. Obshch. im. Mendeleeva*, 1985, **30** 294
183. A N Mirskova, I T Gogoberidze, G G Levkovskaya, M G Voronkov *Zhur. Org. Khim.*, 1984, **20** 2235
184. A N Mirskova, G G Levkovskaya, I T Gogoberidze *Zhur. Org. Khim.*, 1985, **21** 269
185. A N Mirskova, G G Levkovskaya, M G Voronkov *Zhur. Org. Khim.*, 1987, **23** 1119
186. M B Taraban, V I Mar'yasova, T V Leshina, et al. *Zhur. Org. Khim.*, 1986, **22** 925
187. A N Mirskova, T I Drozdova, G G Levkovskaya, et al. *Zhur. Org. Khim.*, 1982, **18**
188. A N Mirskova, T I Drozdova, G G Levkovskaya, et al. *Khim.-Farm. Zhur.*, 1982, (12) 71
189. A N Mirskova, I T Gogoberidze, G G Levkovskaya, et al. *Zhur. Org. Khim.*, 1984, **20** 1502
190. A N Mirskova, G G Levkovskaya, A A Bryuzgin, et al. *Zhur. Org. Khim.*, 1985, **22** 377
191. A N Mirskova, I T Gogoberidze, G G Levkovskaya, et al. *Zhur. Org. Khim.*, 1983, **19** 1744
192. I T Gogoberidze, G G Levkovskaya, A N Mirskova, et al. *Zhur. Org. Khim.*, 1985, **21** 633
193. I T Gogoberidze, G G Levkovskaya, A N Mirskova, M G Voronkov *Zhur. Org. Khim.*, 1984, **20** 1110
194. Yu D Ochirov, V N Zarubina, I F Zhovtyi, et al. *Sovremennye Aspekty Profilaktiki Zoonoznykh Infektsi* (Current Aspects of the Preventive Treatment of Zoonosis Infections) (Edited by E P Golubinskii), Izd. Gosudarstvennogo Nauchno-Issledovatel'skogo Protivochumnogo Institute, Irkutsk, 1984, Part 1, p. 101
195. K V Nikiforov, E A Gurylev, F F Mertsalova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, 603
196. I D Neklesova, K V Nikiforov, M A Kudrina, et al. *Fiziologicheski Aktivnye Veshchestva* (Physiologically Active Compounds), Izd.Naukova Dumka, 1980, No. 12, p. 29
197. T Kay, N Punja *J. Chem. Soc. C*, 1968, 3011
198. N N Mel'nikova, K V Novozhilov, S P Belan, T N Pylova *Spravochnik po Pestitsidam* (Handbook on Pesticides), Izd. Khimiya, Moscow, 1985, pp 51, 156

199. T A Dashevskaya, V M Cherkasov, I F Vladimirtsev, et al. *Fiziologicheski Aktivnye Veshchestva* (Physiologically Active Compounds), Izd. Naukova Dumka, 1973, No. 5, p. 70
200. V M Cherkasov, T A Dashevskaya *Ukr. Khim. Zh. (Russ. Ed.)*, 1966, **32** 486
201. P S Makovetskii, Ya P Shaturskii, B S Drach, et al. *Nauchnye Trudy Ukrainskoi s/kh Akademii*, 1975, (145) 118
202. C H Schramm, US P. 3 313 747; *Chem. Abs.*, 1967, **67** 12 134
203. K Ashida, K C Frisch, P Kardomenos, US P. 4 066 628; *Chem. Abs.*, 1978, **88** 106 204
204. T Koyama, T Narahara, Japanese P. 79 117 598; *Chem. Abs.*, **91** 212 230
205. V A Pankratov, Ts M Frenkel', A M Fainleib *Uspekhi Khim.*, 1983, **52**(6) 1018 [English translation in *Russ. Chem. Rev.*, 1983(6)]
206. L K Jackson, G N Smart, G F Wright *J. Am. Chem. Soc.*, 1947, **69** 1539
207. A M Pinchuk, L N Markovskii, I M Kosinskaya *Zhur. Obshch. Khim.*, 1968, **38**
208. J C Guillemin, J M Denis *Synthesis*, 1985, 1131
209. V B Mochalin, T N Maksimova, N I Filenko, et al. *Zhur. Org. Khim.*, 1982, **18** 1202
210. C Bachard, H Driguez, J M Paton, et al. *J. Org. Chem.*, 1974, **39** 3136
211. K Otsuki, S Takemura, K Okamoto, Y Ueno *Chem. Pharm. Bull. (Japan)*, 1969, **17** 528
212. L A Oshin (Editor) *Spravochnik. Promyshlennye Khlororganicheskie Produkty* (Handbook on Industrial Organochlorine Products), Izd. Khimiya, Moscow, 1978, pp 386, 407, 469
213. N P Grechkin *Izv. Akad. Nauk SSSR, Otdel Khim. Nauk*, 1957, 1053
214. K A Petrov, F L Maklyaev, A A Neimisheva, N K Bliznyuk *Zhur. Obshch. Khim.*, 1960, **30** 4060
215. A Zwierzak, A Koziara *Angew. Chem.*, 1968, **80** 285
216. L N Markovskii, A M Pinchuk, T V Kovalevskaya *Zhur. Obshch. Khim.*, 1970, **40** 543

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Catalytic conversion of paraffinic hydrocarbons into isoparaffins and olefins

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ABSTRACT. The catalytic isomerisation, disproportionation, and dehydrogenation reactions of the C_4–C_{12}, C_4–C_8, and C_3–C_{18} hydrocarbons respectively are examined. The chemical composition, the methods of preparation of the catalysts, the effect of promoting agents, and the kinetics and mechanisms of the reactions are discussed. The principal characteristics of the existing and likely future processes leading to the synthesis of C_4–C_{12} isoparaffins and C_3–C_{18} mono-olefins are presented.
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I. Introduction

The isomeristion, dehydrogenation, and also disproportionation reactions of paraffinic hydrocarbons are linked together by the application of catalytic systems of the same type and by the existence of common features in their chemistry and technology. These reactions are carried out on heterogeneous catalysts in the presence of hydrogen, using individual paraffinic hydrocarbons or their narrow fractions as the starting materials. The limititation of the degree of conversion by the thermodynamic equilibrium necessitates the isolation and recirculation of the hydrocarbons which have not reacted.

Isomerisation and dehydrogenation constitute traditional methods for the selective conversion of paraffinic hydrocarbons[1,2] and during the last decade these have been the object of vigorous investigation, which is to a significant extent due to the appearance of new highly efficient catalysts.[3,4] The isomerisation and dehydrogenation reactions of lower paraffins are combined in the proposed technological schemes for the processing of hydrocarbons in order to attain the optimum yield of the branched olefins [Bursian (Ref.3, page 99), Zhorov (Ref.4, page 218), Pujado and Vora,[5] and Bursian et al.[6]]. The manufacture of scarce C_4–C_5 paraffinic hydrocarbons can be expanded by employing a new process involving the disproportionation of C_6–C_8 hydrocarbons.[7-9]

The need for isoparaffinic and olefinic hydrocarbons has been increasing continuously owing to the need to solve the general world problem of the pollution of the atmosphere and water. In all countries, the use of ethylated types of automobile petrols has been decreasing, the consequent reduction in the octane number of petrols being compensated for by increasing the amount of isomerisation and alkylation mixtures and oxygen-containing compounds as additives—see Bursian (Ref.3, page 157) and other investigators.[5,6] Ecological requirements are also responsible for the growth in the manufacture of biodegradable surfactants based on higher linear olefins (Refs.10, 11, page 11).

The hydrocarbon composition of the most promising (North Siberian) petroleums of the Soviet Union is distinguished by a fairly high content of C_4–C_{20} paraffinic hydrocarbons (~20 wt.%), the ratio of the iso- and normal hydrocarbons varying within the limits 0.3–0.8 (Ref.12, p.126). Paraffinic hydrocarbons are extracted from petroleum by processes involving fractionation (C_4–C_6 paraffins) and isolation by absorption on zeolites (C_{11}–C_{18} paraffins) (Ref.3, page 7).

The economic efficiency of the processes involving the isomerisation and dehydrogenation of paraffinic hydrocarbons is determined by the low consumption of metals and energy, the high selectivity of the reactions, reaching 97–99%, the technological simplicity, and the waste-free technology.

In particular, platinised alumina containing halogen promoting agents[1-3] and metal-containing zeolites[3,4,13] are used as isomerisation catalysts. Metallozeolite catalysts are extremely effective also in the paraffin disproportionation reactions.[14] Non-acid polymetallic aluminoplatinum catalysts are used for the dehydrogenation of higher paraffins to olefins.[10,15] Catalysts based on chromium oxide have come to be widely used in the preparation of lower olefins by the dehydrogenation of paraffins.[16-18]

A series of large-scale industrial processes are based on the application of isomerisation and dehydrogenation reactions. The catalytic isomerisation of paraffinic C_4–C_{12} hydrocarbons increases the available raw material resources for the manufacture of isoprene rubber, ensures the preparation of high-octane components of AI-93 petrol and of reactive diesel C_3–C_5 paraffinic hydrocarbons—the source of mono-olefins used in the synthesis of monomers for isoprene and butadiene fuels and oils with a low setting temperature,[3] and dehydrogenation of natural rubbers.[16-18] The dehydrogenation of C_8–C_{18} hydrocarbons is used to obtain linear olefins which are necessary for the manufacture of plasticisers and components of surfactants characterised by high biodegradability.[10,15]

II. Isomerisation of paraffinic hydrocarbons

The isomerisation of paraffinic hydrocarbons in the presence of aluminium chloride was discovered in 1933 by Nenitzescu and Dragan. In 1935, Moldavskii demonstrated the possibility of

accelerating the isomerisation of paraffins in the presence of aluminium chloride by adding hydrogen chloride, which resulted in the practical application of this reaction (Ref.19, page 512).

The vapour-phase isomerisation of paraffinic hydrocarbons under hydrogen pressure was subsequently achieved at 350–500 °C in the presence of bifunctional catalysts—the oxides and sulphides of Group VI elements as well as Group VIII metals on carriers with acidic properties (alumina promoted by halogens and aluminosilicates).[1-4]

The fluorine-promoted aluminoplatinum catalyst became the first widely used catalyst of an industrial isomerisation process.[3,4,15,20]

1. Thermodynamics, kinetics, and mechanism

The isomerisation reaction of paraffinic hydrocarbons proceeds without change in volume and the thermodynamic equilibrium depends virtually only on temperature. Theoretical corrections for the non-ideality of the gas[21] under the usual isomerisation conditions do not exceed 1% (Ref.4, page 11). The data on the composition of the equilibrium mixtures of isomeric paraffins are well known.[1-4,22] A common characteristic is the increase in the content of branched isomers as the temperature is reduced.

The form of the kinetic equation and the isomerisation mechanism depend on the type of catalyst and the experimental conditions. At the same time, comparison of the various existing equations (Table 1) shows that the reaction is found in all cases to be of first order with respect to the hydrocarbon and is inhibited by hydrogen. The optimum hydrogen partial pressure is determined by the nature of the catalyst (Ref.3, pages 18–28).

The study of the kinetics of the isomerisation of paraffinic hydrocarbons as well as the mechanism of the poisoning of catalysts by poisons acting on various active centres of bifunctional isomerisation catalysts established that the rate-limiting stage of the reaction is the conversion of the intermediate unsaturated products on acid centres of the catalysts (Ref.3, page 18; Ref.31, page 347; Ref.32, page 38).

In the limiting cases of high and low partial hydrogen pressures, the rate of isomerisation can be limited by the rates of dehydrogenation of paraffins and hydrogenation of olefins on the metallic centres of catalysts respectively (Ref.3, page 28). In contrast to aluminium chloride, in the presence of bifunctional aluminoplatinum catalysts the rate of isomerisation of C_4–C_6 paraffins increases with increase in their molecular weight; the isomerisation of C_7 and higher hydrocarbons takes place non-selectively on all the catalysts investigated with the cracking reaction predominating.[1]

The relative rates of interconversions of hexanes in the presence of metal halide salts and an aluminoplatinum catalyst have been measured in a number of studies (Ref.33–35, page 171; Ref.36, page 99) and it has been established that the migration of the methyl group along the paraffinic hydrocarbon chain takes place at the highest rate.

In the isomerisation of C_5–C_6 mixtures on the platinum/mordenite catalyst, n-hexane is found to have a strong influence on the rate of isomerisation of n-pentane.[28] This effect, which can be explained by the preferential adsorption of n-hexane on the active centres of H-mordenite, is reflected in the inverse dependence of the rate of isomerisation of n-pentane on the partial pressure of n-hexane (Table 1).

The activation energies for isomerisation reactions on various catalysts diminish with increase in the activity of the latter, which is manifested by a decrease in the process temperature (Table 1).

The side reactions involving hydrogenolysis, cracking, and disproportionation accompanying the main isomerisation reaction of paraffinic hydrocarbons leads to a decrease in the selectivity and

Table 1. Kinetics of the n-pentane and n-hexane isomerisation reactions on different catalysts.

Catalyst	p, MPa	T, °C	Kinetic equation	α, mol%	E, kJ mol^{-1}	Refs.
$Pt—Al_2O_3$	0.77–2.77	372	$r=\frac{k(p_{n\text{-}C_5}/p_{H_2})}{1+m(p_{n\text{-}C_5}/p_{H_2})}$	4–18	—	[23]
$Pt—Al_2O_3—F$	3.5	360–485	$r=(k_1p_{n\text{-}C_5}-k_2p_{iso\text{-}C_5})/p_{H_2}$	12–56	172	[24]
$Pt—Al_2O_3—F$	0.1	420–480	$r=kp_{n\text{-}C_5}p_{H_2}^{b}$	18–35	—	[25]
$Pt—Al_2O_3—Cl$	0.9–4.1	130–160	$r=\left\{k_{true}\left(\frac{[n\text{-}C_5]_0}{[H_2]}\right)^{0.125}-0.0000197t\right\}\times$ $\times\{K_e[n\text{-}C_5]_0-(K_e+1)[iso\text{-}C_5]\}$	0–20	46	[26]
H—M *	0.5–0.6	200–227	$r=k(p_{n\text{-}C_5}/p_{H_2})$	0–10	129	[27]
Pt—H—M **	0.79–2.17	241	$K_{C_6}=134/(1+0.294p_{C_6})^2p_{H_2}$	—	148	[28]
»	»	»	$K_{C_6}=366/(1+0.124p_{C_6})^2p_{H_2}$	—	—	[28]
Pd—Ca—Y	0.1–5.0	300–360	$r=k(p_{n\text{-}C_5}/p_{H_2})$	3–15	—	[29]
$HF—SbF_5$	1.0	from −20 to +20	$r=\{k_1[n\text{-}C_6]-k_2[iso\text{-}C_6]\}\frac{[SbF_5]}{[n\text{-}C_6]}$	—	60	[30]

Notation: α is the degree of conversion, m the adsorption coefficient, r the rate of reaction, k the reaction rate constant, K_e the equilibrium constant, and p the pressure.

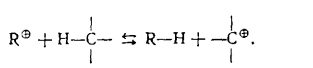
* H–M represents the hydrogen-form of mordenite.

**Isomerisation of the C_5 + C_6 mixture; C_5 content 15–75 mol %.

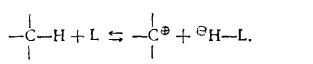
stability of the catalyst. Hydrogenolysis takes place on metallic centres and cracking and disproportionation take place on acid centres.

In order to restrict the side reactions under the conditions of isomerisation on bifunctional catalysts, the optimum ratio of the concentration of the metal and the acidity of the carrier, regulated by the chemical composition of the latter and the selection of the partial hydrogen pressure, is established. The rates of the cracking and disproportionation reactions are maximum in the absence of hydrogen and, with increase in its partial pressure, they gradually diminish to a definite limit and then increase (Ref. 3, page 35).

The principal question concerning the mechanism of the isomerisation reaction is the mechanism of the formation of the carbonium ion. Such ions can be formed as a result of intermolecular hydride transfer:[37]

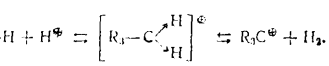


There exists also another view,[35,38] according to which carbonium ions are formed as a result of the abstraction of a hydride ion from the paraffin molecule by a Lewis acid:



In this case the recombination of a proton and a hydride ion can lead to the formation of gaseous hydrogen.

The isomerisation of paraffinic hydrocarbons in superacid media[39,40] proceeds via the protonation of paraffinic hydrocarbons at the σ-bond, whereupon a non-classical carbonium ion with a two-electron three-centre bond is formed and its subsequent cleavage leads to the formation of the usual tricoordinate carbonium ion and hydrogen:



A mechanism according to which the isomerisation proceeds via the formation of cyclic carbonium ions has been proposed.[1,40]

The isomerisation of paraffins on bifunctional catalysts of the aluminofluoroplatinum and metallozeolitic types takes place in accordance with the classical scheme[41] via stages involving the formation of unsaturated compounds on the metallic centres (M) of the catalyst, their further conversion via the carbonium ion mechanism on the acid centres (A) into the corresponding iso-olefin, and the rehydrogenation of the latter on the metallic centres:

$$\text{paraffin} \overset{M}{\rightleftarrows} \text{olefin} \overset{A}{\rightleftarrows} \text{iso-olefin} \overset{M}{\rightleftarrows} \text{isoparaffin}.$$

This scheme was confirmed by numerous experimental studies and mathematical analysis.[42] There exists also a different point of view on the mechanism of the reactions of paraffinic hydrocarbons on bifunctional catalysts, according to which a special role is attributed to the metal (Ref.31, pages 327, 347). The different ideas about the isomerisation mechanism (catalysis by metals, bifunctional catalysis, and catalysis by acids) are not mutually exclusive and their relative contributions depend on the nature of the catalyst and the reaction conditions.

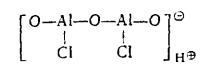
2. Catalysts

As already mentioned, paraffin isomerisation catalysts can be divided into three groups:

(a) platinum on halogenated alumina; (b) Group VIII metals on zeolites; (c) "superacids" (the fluorides of Group V and VI elements).

The study of the isomerisation of paraffinic hydrocarbons on these catalysts established a series of characteristic features. The most important include the dependence of the activity of the catalyst on its acidity. In the case of aluminoplatinum catalysts promoted by halogens, the acidity and activity increase with increase in the amount of fluorine and chlorine up to a certain limit (Ref.3, pages 17, 70). The acidity and activity also increase up to a definite value with increase in the modulus and degree of removal of sodium.[13] The maximum activity and acidity are shown by the SbF_5–HF system among metal fluorides.[43]

There exist a series of hypotheses concerning the structure of the active centres of the isomerisation catalyst promoted by chlorine or fluorine. According to one of them,[1] the acidity of alumina treated with HCl increases if the chloride ion substitutes one of a pair of hydroxy-groups, whereupon the hydrogen of the other hydroxy-group becomes capable of dissociation in the form of a proton by virtue of the presence of the electronegative chlorine atom in its immediate vicinity. The structure of the active centre of chlorine-substituted alumina can be represented by a formula according to which the halogenated alumina is an acid having mobile hydrogen ions:



The enhancement of the acidity when halide ions and hydroxy-groups are accommodated on neighbouring aluminium atoms has been postulated.[44]

The mechanism of the gas-phase activation of the aluminoplatinum catalyst by halogens and organochlorine compounds (especially carbon tetrachloride) in the absence of water has been discussed.[15,45–48] It has been suggested that organochlorine compounds react with the surface hydroxy-groups and the sections of the η-alumina surface generated on dehydroxylation; the oxygen of the oxygen-containing groups is then replaced by chlorine and active centres with the properties of acid Lewis centres are formed.

The interaction of CCl_4 with pairs of dehydroxylated surface sites on the γ-Al_2O_3 surface leads to the formation of centres with an enhanced acidity.[45] The requirements which must be met by the structures of alumina and the chlorinating agent have been formulated (Ref.3, page 66). It has been suggested that the active centres of the chlorinated η-alumina represent complexes whose composition includes chloride, oxygen, and aluminium ions as well as a proton. The chemisorbed hydrogen chloride, whose presence is ensured by the small amounts of water on the catalyst surface, serves as the source of protons. Centres which are active in the isomerisation reaction of paraffinic hydrocarbons are generated when platinised alumina is treated with aluminium chloride as a result of the formation on the surface of aluminium oxide chlorides stabilised by added hydrogen chloride (Ref.3, page 73).

The formation of acid active centres as a result of the introduction of up to 2 wt.% of fluorine into the aluminoplatinum catalyst proceeds via the substitution of the hydroxy-groups on neighbouring aluminium atoms by fluorine;[49] when the content of fluorine is above 2 wt.%, it substitutes isolated hydroxy-groups, which increases

the strength of the existing acid centres without increasing their concentration. The proton centres on the surface of fluorinated alumina can be formed on chemisorption of water.

The influence of fluorine on the isomerising, hydrogenating, and cracking functions of the aluminoplatinum catalyst has been investigated (Figs. 1 and 2) (Ref.3, page 48).

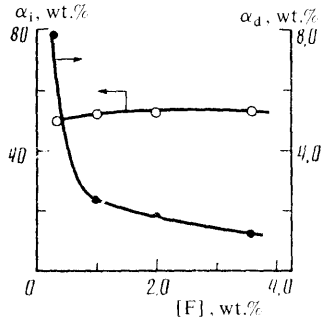


Figure 1. Dependence of the yield of the n-pentane conversion products on the fluorine content [F] in the aluminoplatinum catalyst (Ref.3, page 49); T = 380 °C; p = 3.5 MPa; α_i and α_d are the yields of isopentane and the decomposition products respectively.

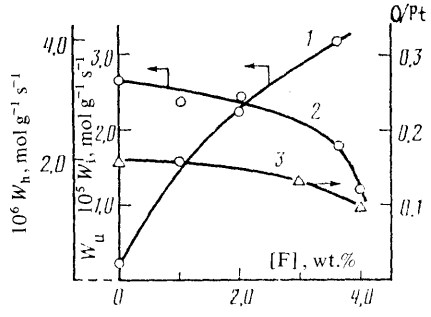


Figure 2. The influence of fluorine on the activity of the aluminoplatinum catalyst in the n-pentane isomerisation (curve *1*) and benzene hydrogenation (curve *2*) reactions and on the chemisorption capacity of platinum (curve *3*) (Ref.3, page 48); W_i and W_h are the rates of isomerisation and hydrogenation respectively.

The increase in the isomerising activity when aluminoplatinum catalysts are promoted by fluorine (Fig. 2) is associated with increase in the Lewis acidity and the appearance of Brønsted acidity. The simultaneous decrease in the activity of the catalyst in the reactions involving the hydrogenation of benzene and the hydrogenolysis of paraffins indicates a change in the state of the platinum, which has been confirmed by an IR spectroscopic study of the adsorption of carbon monoxide (Ref.3, page 49). The fluorination of the catalyst increases significantly the CO vibration frequency, which indicates an increase in the electron deficiency in the platinum. The latter can be explained by the strengthening of the electron-accepting centres of the carrier with which platinum interacts.

The introduction of sulphur into an aluminoplatinum catalyst promoted by fluorine suppresses the hydrogenolysis reaction in the course of the isomerisation of n-pentane without altering the isomerising activity of the catalyst (Ref.3, page 55).

The IR spectroscopic study of the adsorption of CO on the sulphur-treated catalyst showed that the maximum of the band corresponding to the CO adsorbed on platinum undergoes a hypsochromic shift in the presence of sulphur and that its position is independent of the degree of surface coverage of platinum by carbon monoxide (Ref.3, page 49). This finding indicates the inhomogeneity of the platinum in the non-sulphur-treated catalyst. On treatment with sulphur, the latter forms a strong bond with some of the platinum centres (the least electron-deficient centres), while the electron-deficient platinum centres remain free after heat treatment in the presence of hydrogen. The increase in the electron deficiency of platinum as a result of promotion by fluorine and sulphur weakens the Pt–C bond in the chemisorption of hydrocarbons and suppresses the hydrogenolysis reactions, whose rate is determined by the chemisorption stage.

The studies which have been carried out have served as a basis for the selection of the chemical composition of the catalysts of the high-temperature isomerisation of paraffinic hydrocarbons (IP-62, IP-62-M, and IP-82). Their platinum content is 0.45–0.55 wt.%, the fluorine content in γ-alumina is 3.5 ± 0.5 wt.%, and the sulphur content is 0.2 wt.%.[3,4,15,20]

The discovery of a new method for the introduction of chlorine into the carrier by the gas-phase chlorination of the catalyst with organic chlorides is of fundamental importance for the synthesis of bifunctional aluminoplatinum isomerisation catalysts (Ref.3, page 74; Refs.15,20,50,51). The gas-phase chlorination procedure, which consists in treating the aluminoplatinum catalyst at 250 to 300 °C with an inert gas containing carbon tetrachloride, makes it possible to obtain a catalyst whose acid strength approaches that of aluminium chloride, which creates the possibility of carrying out the isomerisation of paraffinic hydrocarbons in the absence of a metal at 50–100 °C. The introduction of platinum ensures the stability of the catalyst.

The isomerisation of paraffins on metallozeolitic catalysts was first described by Rabo et al.[52] and has been widely used by Minachev and co-workers.[13] Faujasite in the calcium- and H-forms and zeolites of the type of mordenite and ZSM in the H-forms are used for this reaction. Catalysts with a high activity, making it possible to achieve the isomerisation at 230–270 °C, can be obtained by maintaining a number of conditions; they must have a definite value of the silicate modulus (not less than 4.5 for faujasite, 12–18 for mordenite, and 40 for ZSM), adsorption capacity, and degree of crystallinity. The required acidity is obtained by removing sodium by ion exchange or de-alumination. H-Mordenite exhibits the highest activity and selectivity in the paraffin isomerisation reactions; the metal is introduced to increase the stability of the catalyst.[53]

The possibility of isomerising paraffinic hydrocarbons on Group V and VI metal fluorides in the presence of HF in hydrogen was first demonstrated by Oeldrik.[54] The reaction takes place at a higher rate and with a high selectivity at 20–50 °C and a hydrogen pressure of 0.5 MPa in the liquid phase in the presence of the MF_5–HF complex. The TaF_5–HF system is the most stable and the SbF_5–HF system is the least stable.

The nature of the active centres on "superacid" catalytic systems of the type of MF_x–HF has been examined.[43] The sharp increase in the acidity of hydrogen fluoride following the addition of SbF_5 is explained by the formation of the more acid ion H_2F^+. The low nucleophilicity of superacids, promoting the stabilisation of carbonium ions, is due to the stablisation of the F^- and FSO_3^- ions as a consequence of the formation of complex anions in which antimony has a coordination number of 6. The instability of the given catalytic system is associated with the formation of polymeric compounds and their dissolution in the catalyst.

The selectivity and stability of the catalytic system depend on the ratio of the rates of formation of carbonium ions and of their alkyl rearrangement and hence are determined to a significant extent by the properties of the initial hydrocarbon. Thus the isomerisation of n-butane can be achieved at an acceptable rate and with an acceptable selectivity in the presence of aluminium chloride and chlorine-promoted aluminoplatinum catalysts. In the presence of fluorine-promoted aluminoplatinum catalysts and metallozeolitic catalysts, it proceeds with a lower selectivity, while it hardly occurs at all in the presence of metal fluorides, with the exception of the MoF_6–HF and AsF_5–HF systems, which nevertheless exhibit some activity.[43] The lack of activity of the SbF_5–HF system in the isomerisation of n-butane can be explained by the fact that the secondary butyl cation can rearrange to a tertiary butyl cation only via the formation of an intermediate carbonium ion with a very high energy (in contrast to the pentyl and hexyl cations, whose rearrangement proceeds via the formation of secondary carbonium ions). The isomerisation of n-butane on the $AlCl_3$–HCl, AsF_5–HF, and MoF_6–HF systems can be explained by the rearrangement of the butyl cation via a preliminary carbonium ion dimerisation stage, where the product rearranges and is cleaved without the formation of primary cations.[33]

High-silica zeolites (H-mordenite, ZSM-5), promoted by Group VI and VIII elements, are the most effective in the isomerisation of higher n-paraffins (Ref.3, pages 63, 118; Ref.4, page 142).

In practice, isomerisation catalysts are always used at an appreciable hydrogen pressure which promotes the desorption of the unsaturated intermediate compounds and ensures high stability.

One of the most important questions associated with the isomerisation of paraffinic hydrocarbons is that of the poisoning of the catalysts as well as the protection of the latter against the action of poisons. Sulphur and nitrogen compounds, carbon oxides, and water are some of the poisons. As a result of the reactions of sulphur and nitrogen compounds in hydrogen on platinum catalysts, hydrogen sulphide and ammonia are formed respectively.

Bearing in mind the bifunctional nature of the isomerisation catalysts, model reactions characterising the functions of the catalyst are selected to investigate the influence of the poisons on the properties of the metal and carrier.

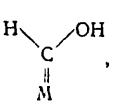
Sulphur compounds are poisons for all the catalysts investigated in the reactions occurring preferentially on metallic centres (hydrogenation and dehydrogenation). Nitrogen compounds do not have such a pronounced effect on the dehydrogenating activity at comparable concentrations but they do poison selectively the acid centres of the carrier, which is indicated by the change in the activity of the catalysts in the isomerisation reactions.[55]

The poisoning action of hydrogen sulphide is due to its interaction with platinum involving the formation of fairly stable sulphides. The toxicity of sulphide sulphur is determined by the presence of an unshared electron pair.[56] The comparatively weak influence of nitrogen is associated with the conversion of ammonia in the presence of water into the ammonium ion, which has a "non-toxic" fully shielded structure (Ref.31, page 307, Ref.56). The influence of sulphur and nitrogen compounds on the isomerising properties of platinum and palladium catalysts depends on the nature of the carrier. Thus sulphur compounds suppress the isomerisation of n-hexane on the Pd–CaY catalyst but do not influence the isomerising properties of the fluorine-promoted aluminoplatinum catalyst.[55] The latter indicates the absence of influence by sulphur on the slow stage in the isomerisation of paraffinic hydrocarbons—the structural isomerisation of olefins.

The poisoning of the aluminofluoroplatinum catalyst by sulphur (at concentrations in excess of 0.01 wt.%) is due to its effect on the rate of the paraffin dehydrogenation stage, which determines in the given instance the rate of isomerisation. Another possible cause is the action of sulphur on the acid centres of the alumina (Ref.3, page 88). There are data indicating the influence of carriers on the sensitivity of the deposited platinum to poisoning by sulphur. In the case of a stable (irreversible) adsorption of sulphur on platinum without a carrier, the ratio of the surface S and Pt atoms is 0.5.[57–59] Such adsorption fully deactivates the metal (and leads to the absence of adsorption of CO, H_2, O_2, acetylene, ethylene, and benzene at temperatures below 400 °C).[59] For the same or even a higher degree of surface coverage by sulphur, the platinum on alumina is capable of adsorbing CO, H_2, and O_2[60–64] and retains its activity in the reactions involving the hydrogenation of aromatic hydrocarbons[60] and the isomerisation of n-pentane.[64] In the adsorption of CO on platinum converted into a sulphide, there is a possibility of the formation of groups of the type CO–Pt–S.[61] Presumably bridged sulphide Pt_2S is also formed on massive platinum, while on more isolated deposited platinum centres the linear PtS structure predominates.[65] As the degree of surface coverage of platinum by sulphur is 0.5, isolated adsorption centres should be retained in this case on the surface of the aluminoplatinum catalyst, which agrees with the absence from the IR spectra of "sulphided" catalysts of the band due to the bridge-type form of adsorption of CO[63] and with the independence of the position of the maximum due to the linear CO–Pt form of adsorption from the degree of surface coverage of the Pt–Al_2O_3–F (Ref.3, pages 49,57; Ref.64) and Pt–Al_2O_3[66] catalysts.

The mechanism of the poisoning effect of sulphur on the Pt–Al_2O_3–Cl catalyst for low-temperature isomerisation should differ fundamentally from that examined above. In this case, the toxicity of sulphur is due to the dissociative adsorption of H_2S on the donor–acceptor centres of chlorinated alumina (Ref.3, page 88; Ref.67, pages 50–55).

The effect of carbon oxides on the different functions of platinum and palladium catalysts on alumina and of zeolitic catalysts has also been studied.[68] The dehydrogenating activity of all the catalysts fell in the presence of carbon monoxide regardless of the nature of the carrier, which indicates a direct interaction of CO with the metal of the catalyst. The toxicity of carbon monoxide is due to the formation of adsorption complexes with platinum. In the presence of carbon monoxide, the degree of chemisorption of hydrogen on the metal surface increases, which can be attributed to the formation of the complexes



the toxicity of CO in relation to platinum decreasing as a consequence of its hydrogenation to methane. However, for a

constant supply of the poison, the detoxification phenomenon may not be observed. Presumably, the poisoning of the platinum catalyst by carbon oxides is associated with their simultaneous action on the metal and the carrier–alumina or zeolite. The poisoning effect of CO and CO_2 on alumina is due to the formation and adsorption of water on its acid centres. The effect of carbon monoxide on platinum or palladium has been explained by the competitive adsorption of hydrocarbons and carbon oxides on the metal surface. Since carbon monoxide is adsorbed more strongly, its presence in hydrogen even in small amounts suppresses the dehydrogenation of cyclohexane and the isomerisation of n-pentane (Ref.3, page 90).

The study of the poisoning of platinum and palladium catalysts by water has shown that in this case the properties of the carriers are of decisive importance in the isomerisation of paraffinic hydrocarbons (Ref.3, page 91). The poisoning by water is thus caused by its interaction with the acid centres of the carrier. The rehydration of the catalysts based on alumina results in the formation of new hydroxy-groups which reduce the concentration of the active centres of the Al_2O_3 surface. In zeolite-containing systems, this phenomenon is observed at much higher water concentrations and the palladium-zeolite isomerisation catalyst is therefore relatively resistant to poisoning by water.[68] The metallozeolitic isomerisation catalysts (Pt–CaY, Pd–CaY) are relatively insensitive even to poisoning by nitrogen compounds[55] and carbon dioxide.[68]

The characteristic features observed in the study of the influence of poisons on the rates and selectivities of the reactions occurring on platinum and palladium catalysts established the permissible content of the poisoning impurities in the raw material and hydrogen and have led to the recommendation of measures for the protection of catalysts against the action of these impurities.[3]

3. Industrial application

Depending on the catalyst employed, the isomerisation of paraffinic hydrocarbons takes place with high yields at temperatures in the range 20–370 °C, hydrogen pressures in the range 0.5 to 3.5 MPa, space velocities at which the raw material is supplied in the range 2.0–3.0 h^{-1}, and a hydrogen: hydrocarbon molar ratio of 2–3 (Table 2).

Isomerisation reactions of paraffinic hydrocarbons of several types are used nowadays in industry, the differences between them being determined by the properties of the catalyst employed (Table 2).

In the high-temperature isomerisation reactions of pentane–hexane fractions, metal–fluorine-promoted alumina and metal–aluminosilicate systems are used as catalysts. The attainable degree of isomerisation of n-pentane in one pass at temperatures in the range 360–400 °C amounts to 50–55% and the octane number of the isomerisation reaction mixture resulting from the pentane–hexane fraction reaches 75 measured purely by the research method (RM) (Ref.3, page 76).

The application of high-silica zeolites of the type of mordenite[3,4,13] has served as the basis of a moderate-temperature isomerisation process for the pentane–hexane fraction, which is carried out at 230–260 °C; the isomerisation reaction mixture obtained after a single pass of the raw material has an octane number of 80–82 (RM).

The isomerisation reactions of n-butane, n-pentane, and of the pentane–hexane fraction at temperatures in the range 140–180 °C on aluminoplatinum catalysts modified by organochlorine compounds or aluminium chloride have been developed to the greatest extent. The vast majority of industrial plants use the technology of the low-temperature isomerisation of the pentane–hexane fraction via the "one pass" scheme with formation of an isomerisation reaction mixture having an octane number of 83–84 (RM).

If it is necessary to obtain individual isoparaffins, the part of the paraffinic hydrocarbons which have not reacted must be returned to the process. When n-butane and n-pentane are isomerised, recirculation is economically useful and is generally used. In the isomerisation of pentane–hexane fractions, which contain a large number of hexane isomers having similar boiling points but different octane characteristics, the usefulness of the recirculation of n-hexane

Table 2. Conditions in the isomerisation of n-pentane (P) and n-hexane (H) in the presence of different catalysts.[3,69]

Catalyst	$Pt–Al_2O_3–F$		Pd–Ca–H–Y		Pt–H–M		$Pt–Al_2O_3–Cl$		$HSbF_6$	$HTaF_6$
	P	H	P	H	P	H	P	H	P	H
Temperature, °C	370	360	330	320	260	260	140	140	50	20
Pressure, MPa	3.5	3.5	3.0	3.0	2,0	2,0	3.0	3.0	0,5	0,5
Rate of supply of raw material (space velocity), h^{-1}	2—3	2—3	2,0	2,0	2.0	2.0	2,0	3	2,5	2,5
H_2 : hydrocarbon molar ratio	2	2	3	3	2	3	2	2	0	0
Degree of conversion per pass, wt.%	52—55	70	57	75	57	73	75	87	84	94
Yield of C_1–C_4 (P) or C_1–C_6 (H), wt.%	1,5—2	2,5	1.8	2 9	1 2	3.4	0.5	1	0,5	0,5—2.5
2,2-Dimethylbutane content in C_6, wt.%	—	9.1	—	12 8	—	14.6	—	25.2	—	46.1
Octane number of product (according to RM) formed per pass*	75		76		80		83		89	

*In the experiment using the pentane–hexane fraction with the ratio C_5: C_6 = 1 : 1.

and of its low-octane monosubstituted isomers is determined by the required octane number of the isomerisation reaction mixture. The energy expenditure on the recirculation increases with increase in the octane number of the isomerisation reaction mixture. There is a corresponding increase in the intrinsic cost of the isomerisation reaction mixture as well, which depends also on the method of isolation of the paraffinic hydrocarbons—fractionation or extraction on molecular sieves; the latter method is much more economical.[3]

One of the ways of increasing the antiknocking capacity of the isomerisation reaction mixtures obtained from the hexane fraction involves their processing by selective hydrocracking on metallo-zeolitic catalysts. The selective hydrocracking of normal paraffinic hydrocarbons takes place in this process; the selectivity of the action of the catalyst, determined by the molecular sieve effect of zeolites of the type of erionite and ZSM, can be explained by the difference between the critical diameters of molecules of different structure (Ref.3, pages 145, 174).

The isomerisation of C_7 and higher paraffins (combined with partial hydrocracking) is used to improve the characteristics of diesel fuels and oils. A number of corresponding Soviet and foreign technological processes are known in which 98% conversion of the raw material is attained in one pass.[3,4]

More than 80 plants for the isomerisation of n-butane, n-pentane, and pentane–hexane fractions are functioning at the present time throughout the world. The tendency towards a decrease in the content of tetraethyl-lead and of aromatic hydrocarbons in automobile petrols has promoted an increase in the number of isomerisation plants being built and in the planning stage[70] and an expansion of the manufacture of the corresponding catalysts.[71]

III. Disproportionation of paraffinic hydrocarbons

The disproportionation of paraffinic hydrocarbons, which takes place in the simplest case in accordance with the equation

$$2C_nH_{2n+2} \leftrightarrows C_{n-x}H_{2n+2-2x} + C_{n+x}H_{2n+2+2x}, \quad (1)$$

was first observed[72] as a side reaction in the isomerisation of paraffinic hydrocarbons in the presence of aluminium chloride. Later this reaction was studied by Moldavskii and co-workers.[73–75]

The conversion of n-pentane at 50–90 °C resulted in the formation of 25–40% of products heavier than C_5 compounds and of up to 30–50% of light hydrocarbons (mainly butanes).[74] The products for the interaction of copper and lead sulphates with hydrogen chloride, which were regarded as HCl donors, were used as activating additives. It was shown later that the promoting effect of metal sulphates and chlorides is manifested also in the absence of HCl under anhydrous conditions and is evidently caused by the formation of molecular complexes between aluminium chloride and the promoting salts.[76,77] The study of the disproportionation of C_5–C_7 paraffins on aluminium chloride at temperatures up to 100 °C established that, together with copper salts, those of zinc, cadmium, gallium and a series of Group VI–VIII elements exhibit the properties of promoting agents.[78]

The disproportionation in the presence of aluminium chloride is accompanied by the extensive isomerisation of the products obtained and by polymerisation side reactions leading to the deactivation of the catalyst, which restricts the applicability of the catalytic system in question.

The deficit of C_4 and C_5 hydrocarbons which arose in the 1970's, combined with the availability of superfluous C_6–C_8 paraffins, stimulated the interest of investigators in this reaction. It was established that extensive (more than 50%) disproportionation of paraffinic hydrocarbons can be achieved at a pressure above 1 MPa in the presence of high-silica zeolites (mordenite and type ZSM zeolites),[7,79–81] as well as bifunctional catalysts containing Group VI and VIII metals and a non-acid carrier.[82,83] In the latter case, the process proceeds without the isomerisation of the products of the kind which occurs on aluminium chloride and zeolites.

On zeolitic catalysts, the paraffin disproportionation products are undoubtedly formed via repeated intermediate reactions, as a result of which the composition of the products does not correspond to the equivalent contents of paraffins which are lighter and heavier than the initial hydrocarbon.

This type of process makes it possible to obtain the light homologues closest to the initial paraffinic hydrocarbons virtually without the formation of low-molecular-weight C_1 and C_2 products, the appearance of such products being inevitable in the usual hydrogenolysis. Thus the conversion of n-butane into propane with a selectivity of about 90% has been achieved on H-mordenite:[80]

$$3C_4H_{10} + H_2 = 4C_3H_8.$$

Table 3. Proportions of the products of the disproportionation of C_5–C_7 paraffins on the H-mordenite catalyst[9] [T = 320–340 °C, p = 5 MPa, rate of supply of raw material (space velocity) 1 h^{-1}, molar ratio hydrogen : raw material = 0.5].

Products*	n-Pentane	n-Hexane	n-Heptane	Products*	n-Pentane	n-Hexane	n-Heptane
C_1	4.8	1.2	1.5	C_5	—	26.8	14.7
C_2	9.3	2.5	1.9	C_6	15.7	—	6.6
C_3	21.0	30.6	36.8	C_7	—	1.1	—
C_4*	49.2	37.8	38.0	C_8	—	—	0.5

*iso : n ≃ 2 : 1.

According to the results of Bursian et al.,[9] the predominance of light paraffins in the disproportionation products on the metallo-mordenite catalyst becomes more pronounced on passing from n-pentane to n-hexane, which can be explained by the vigorous hydrocracking of heptanes (Table 3). Indeed, n-heptane undergoes hydrocracking under the conditions investigated with formation of equimolecular amounts of propane and butanes. Thus the reaction of n-hexane can be described by the overall equation

$$2C_6H_{14} + H_2 = C_3H_8 + C_4H_{10} + C_3H_{12}. \quad (2)$$

In this sense, this process can be regarded as bimolecular hydrocracking.[9] The significant role of disproportionation in the hydrocracking of paraffins on metallozeolitic catalysts had been pointed out previously.[84] Approximately 70% of paraffinic C_4 and C_5 hydrocarbons have a branched structure. Together with the main reaction, side reactions involving the unimolecular hydrocracking of the raw material and the C_4 and C_5 products take place

to a slight extent: the yield of the C_1 and C_2 products does not exceed 5 mol % relative to the hexane which has reacted, while the yield of propane is close to the stoichiometric value corresponding to Eqn. (2).

There exist different points of view concerning the mechanism of the disproportionation of paraffinic hydrocarbons. Some workers[7,77,81] believe that it takes place via a condensation fragmentation mechanism, i.e. without the formation of low-molecular-weight alkylating agents. According to other workers,[75,85] the reaction takes place via a transmethylation mechanism.

According to the results of Kogan et al.[86] and Zhdanov et al.,[87] considerable amounts of C_7–C_{10} alkylbenzenes are formed in the reaction of C_5 and C_6 paraffins on H-mordenite and H-ZSM-5 zeolite in the presence of benzene at 300–380 °C and a pressure of 3.5 MPa (the degree of alkylation of benzene exceeds 50%), which is regarded as confirmation, in principle, of the transalkylation mechanism.[75,85] However, from the same data[86,87] one can conclude that the intermolecular transfer of the C_2, C_3 fragments plays the most significant role because the main primary alkylation products are ethylbenzene (on H-mordenite) and propylbenzene (on H-ZSM-5).

Analysis of the few data available[7,79–83] shows that metal-containing high-silica zeolites are the most promising catalysts of the disproportionation of C_6 and C_7 paraffins with formation of isoparaffinic C_4 and C_5 hydrocarbons. The reaction is carried out at a hydrogen pressure of 3–10 MPa, temperatures in the range 300–450 °C, and with the raw materials supplied at a space velocity of 0.5–2 h^{-1}. For the vigorous occurrence of the disproportionation reaction, it is essential to maintain a higher partial pressure of the hydrocarbon than in hydrocracking.

In a study of the disproportionation of mixtures of isobutane and n-hexane on a metallozeolitic catalyst with formation of isopentane [the reverse of reaction (1)], it was shown that, with increase in the isobutane : n-hexane molar ratio from 0.5 to 2.7, the yield of isopentane increases from 14.3 to 49.3 wt.%.[7] The data on the hydrocracking of n-hexane presented in the above study[7] for comparison show that the disproportionation ensures a more favourable composition of the reaction products (an increased content of isopentane and isohexanes).

The industrial application of paraffinic hydrocarbon disproportionation processes will make it possible to increase the manufacture of the acutely deficient C_4 and C_5 paraffins by processing their nearest homologues without the formation of the C_1 and C_2 light products, which are of little value, and, as can be seen from Eqn. (2), will significantly restrict the consumption of hydrogen compared with hydrocracking.

IV. Dehydrogenation of paraffinic hydrocarbons on aluminoplatinum catalysts

The dehydrogenation of C_4 and C_5 paraffinic hydrocarbons was first achieved on oxide catalysts. This led to the creation of large-scale industrial processes involving the dehydrogenation of butanes and isopentane on chromium oxide catalysts promoted by the addition of alkali metals (Ref.11, pages 147, 157; Ref.17). The dehydrogenation of higher n-paraffins to the corresponding mono-olefins was also initially investigated on aluminochromium catalysts.[18] Subsequently, in order to increase the selectivity and stability of aluminochromium catalysts, the reaction was carried out in hydrogen on catalysts promoted by lithium or potassium.[88,89]

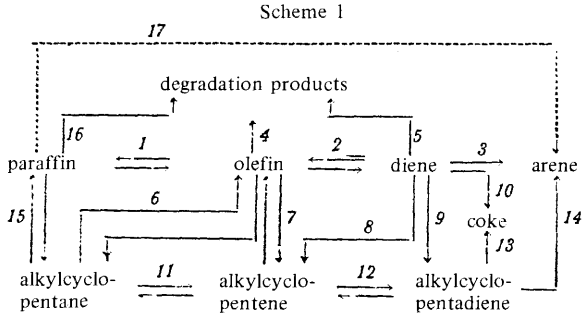
In connection with the development of the industrial manufacture of polymetallic reforming catalysts and the growth of the requirement for higher linear mono-olefins in order to obtain surfactants and detergents, at the end of the 1960's the dehydrogenation of C_8–C_{18} n-paraffins on an industrial scale began to be carried out on platinum polymetallic catalysts.[10,90] The number of patents for the dehydrogenation of lower paraffins, starting with propane, as well as ethylbenzene on platinum increased.[15] Data concerning the development of similar processes for the dehydrogenation of C_3–C_5 paraffins to mono-olefins appeared in the 1980's.[5,6,8,90] The main advantages of the platinum catalysts, namely their ability to effect the reaction at a high rate and with a high selectivity (90–95%), make them especially valuable in the light of modern requirements for the intensification of technology and the economic use of raw materials.[91,92] Nevertheless, it follows from reviews and monographs,[17,18,93–96] that the characteristic features of the dehydrogenation of paraffinic hydrocarbons to olefins or metallic catalysts have been little described in the literature compared with the dehydrogenation on oxides.

1. Thermodynamics, kinetics, and mechanisms

According to data for equilibrium in the reaction involving the dehydrogenation of paraffins to mono-olefins, a degree of hydrogenation which is acceptable in practice (30–40% for light paraffins and 10–15% for higher paraffins) in hydrogen is attained at a pressure not exceeding 0.2–0.4 MPa (Table 4).

According to Kazanskii et al.[101] and Isagulyants et al.,[102] the set of the possible reactions of paraffinic hydrocarbons heavier than C_5 on platinum catalysts can be represented by the following Scheme:

Scheme 1



The main mono-olefin formation reaction (*1*) is catalysed by metallic centres and is the primary process relative to most of the side reactions (*2–14*), which occur both on the metal and on the carrier. This is the reason for the need to modify both components of the catalyst and for the significant restriction of the contact time.

Studies on the kinetics of the dehydrogenation of paraffins with formation of olefins on platinum were begun comparatively recently. The kinetic data for the dehydrogenation of C_{10}–C_{14} n-paraffins on catalysts promoted by the addition of lithium and tungsten,[103] tin,[104] and lead[105] agree with the consecutive parametrisation scheme (reactions *1–3* in Scheme 1).

The rate of formation of mono-olefins from higher n-paraffins (C_{10}–C_{12}) on an aluminoplatinum–tin catalyst at 430–470 °C and atmospheric pressure can be expressed by the equation[104]

$$r = (k_1 p_1 - k_2 p_2 p_{H_2})/(p_{H_2}^{1.5} + n_2 p_2 + n_3 p_3),$$

where p_1, p_2, and p_3 are the partial pressures of the paraffin, the mono-olefins, and the diolefins respectively and k_1, k_2, n_2, and n_3 are constants ($n_3 \gg n_2$).

Table 4. Equilibrium degrees of dehydrogenation of paraffins to mono-olefins*.

p, MPa	Initial H_2:RH molar ratio	Equilibrium degree of dehydrogenation (mol%) at different temperatures, °C			
Propane (Ref.22)**		477	527	577	627
0.1	0	14	25	41	59
0.1	1	4	11.5	26	47
0.2	0	9.5	17 5	30	46
0.2	1	2	6	16	32
Isobutane (Ref.97)**		427	527	627	727
0.1	0	14	42	78	95
0.1	1	3.5	29	71	93
0.2	0	9	32	66	91
0 2	1	1.5	17	56	87
n-Butane (Ref.98, 99)**		427	527	627	727
0.1	0	10	37	75	93
0.1	1	2 5	21	66	91
0.2	0	7.5	27	61	87
0.2	1	1	13	50	83
Isopentane (Ref.98)**		427	527	627	727
0.1	0	19	57	88	97
0.1	1	7	45	84	96
0.2	0	4.5	44	80	94
0.2	1	3.5	30	73	92
n-Dodecane (Ref.100)		440	460	480	500
0.2	1	12	19	28	38
0.2	8	8	12	19	28
0.4	1	7	11	17	24
0.4	8	4	7	11	16
n-Octadecane (Ref.100)		440	460	480	500
0.2	1	18	27	38	49
0.2	8	12	19	28	39
0.4	1	10	16	24	34
0.4	8	6	10	16	24

* The reaction products are equilibrium mixtures of mono-olefins with different positions of the double bond in the molecule.
** The equilibrium degrees of dehydrogenation are quoted in the literature source only for a pressure of 0.1 MPa in the absence of hydrogen; the remaining values have been calculated.

Aromatic hydrocarbons do not influence the rate of formation of olefins under the conditions investigated.

The kinetics of the dehydrogenation of isobutane on bimetallic aluminoplatinum catalysts (promoting agents—copper, cadmium, indium, tin, and selenium; 500–600 °C; 0.1 MPa) correspond to the equation[106]

$$r = k_1 p_1 \gamma/(p_2 + k_2 p_{H_2}^{0.5}),$$

where γ is the coefficient which allows for the reversibility of the reaction; for the significance of the other notation, see above.

The mechanism of the dehydrogenation reaction includes the following stages:[104,106,107]

(1) the adsorption of the paraffinic hydrocarbons with elimination of one hydrogen atom; (2) the elimination of a second hydrogen atom with formation of an adsorbed olefin; (3) desorption of the olefin; (4) desorption of hydrogen.

In the case of consecutive dehydrogenation to the diolefin and an aromatic hydrocarbon, additional stages involving the readsorption of the mono- and di-olefin and the desorption of the diolefin and the aromatic product appear. Appreciable differences as well as common features (first order with respect to the initial hydrocarbon, inhibition by the reaction products) are characteristic of the kinetics of the dehydrogenation of paraffins with different molecular weights. Thus, according to isotopic data, the slow stage in the dehydrogenation of isobutane is dissociative adsorption of the paraffin,[106] while in the dehydrogenation of higher paraffins the slow stage is the desorption of the products.[104]

The presence of promoting agents can induce significant differences in the kinetics and chemistry of the dehydrogenation reaction on platinum. On bimetallic catalysts (in contrast to the unpromoted catalyst), the aromatisation via pathways related kinetically to olefins (reactions *2*, *6*, and *7* in the Scheme) is inhibited with a corresponding increase in the contribution of the "latent" aromatisation pathway *17* without the desorption of the intermediate products.[108]

A kinetic equation has been obtained[109] for the rate of dehydrogenation of isopentane to isopentenes in the presence of water vapour on a platinotin catalyst deposited on a zinc–aluminium oxide spinel (546–589 °C, 0.1 MPa) with allowance for the deactivation of the catalyst by coke:

$$r = \frac{k_1 p_1}{(1 + b p_1)^2}\left(1 - \frac{p_1 p_{H_2}}{p_1 K_e}\right)\exp(-\alpha c_c),$$

where K_e is the dehydrogenation equilibrium constant, k_1 and b are constants, c_c is the concentration of coke in the catalyst, and α is a parameter; for the significance of other notation, see above.

2. Catalysts

Platinum paraffin dehydrogenation catalysts are highly dispersed multi-component systems deposited on a thermostable oxide carrier with a high surface area. The concentration of platinum and the promoting agents does not usually exceed 1 wt.%. The most widely used carrier is γ-alumina.[10,15] Previously such platinum catalysts were widely used in the low-pressure reforming process.[31,32]

When the dehydrogenation process is carried out in the presence of steam at a temperature of about 600 °C, extremely stable spinels based on alumina and containing magnesium[110] or zinc[111] are used as the carrier.

In order to suppress the acidity, alkali or alkaline earth metals are introduced into the catalyst and also the halogen (chlorine) is removed. Group IB–VIB elements are added mainly with the aim of modifying the platinum.

Lithium or potassium as well as germanium subgroup elements are most often used as the promoting agents.[15] The nature of the surface of the highly dispersed deposited platinum catalyst is usually considered in terms of clusters—non-crystalline species whose size is as a rule less than 1 nm.[112]

The state of the atoms and the character of their interaction in clusters and crystals differ significantly, which is due to the coordinative unsaturation of the majority of atoms in the former case. Complex clusters, incorporating either only metal atoms (clusters of the alloy type[112]) or the atoms of an active metal together with the low-valence cations of the promoting agent stabilised by interaction with the carrier,[95,113] are formed on the surfaces of polymetallic deposited catalysts. Depending on the particle size and the nature of the interaction of the active metal with the carrier and the promoting agents, a significant change in the specific activity and selectivity of the active metal can occur[95,114,115] owing to both the geometrical effect (dilution of the active metal by the inert component, decrease in the size of the clusters) and the electronic effect (modification of the active metal as a result of the electronic interaction with the promoting agents[116,117]). The main cause of the deactivation of platinum dehydrogenation catalysts under the reaction conditions is coke deposition. Apart from the blocking of the surface of the metal and of the carrier pores by coke,[118] contact between platinum and the hydrocarbon medium diminishes the surface area of the metal as a result of its crystallisation[119] or the formation of a spinel with aluminium oxide.[120]

These effects evidently represent special forms of a general process involving the formation of the catalyst surface under the influence of the reaction mixture, which has been considered by Balandin,[121] Roginskii,[122] and Boreskov.[123]

Saturation by carbon alters the activity and selectivity of platinum in the hydrogenolysis, isomerisation, and dehydrocyclisation reactions of n-hexane[124] and in the dehydrogenation of cyclohexene (Ref.125, page 487). The degree of the poisoning of the catalyst by coke is not determined exclusively by its concentration and may differ significantly depending on the coke formation conditions and the nature of the catalytic reaction. The causes of the variation in the toxicity of coke may be (a) a difference in the structure of the coke deposits[125,126] (in particular the influence of the ordered and disordered layers of coke may be significantly different[125]), (b) a change in the quantitative distribution of coke between the metal and the carrier when the coke formation conditions are altered,[127] and (c) selective poisoning of the metallic centres catalysing the given reaction (deuterium exchange, dehydrogenation, and hydrogenolysis[128,129]).

The most important feature of modern polymetallic catalysts is their increased stability under coke formation conditions. The causes of the resistance to coke of catalysts of this kind is believed to be a decrease in the intensity of coke deposition as a result of the poisoning of the strong acid centres by the promoting agents (when tin is introduced[130,131]), saturation of the intermediates—precursors of coke (rhenium[132,133]), or hydrogenation of the carbon deposits (iridium[134]). At the same time, data have been obtained in recent years which indicate a sharp limit to the saturation of platinum by carbon in deposited dehydrogenation catalysts promoted by the zinc, gallium, and germanium subgroup elements, without the reduction in the overall coke concentration.[15,65,66,135–142] A similar effect involving protection against coke is caused, according to IR spectroscopic data for CO[135,136,138] and data for the chemisorption of benzene,[66] by the weakening of the adsorption of the reactants on platinum associated with the migration of the precoke intermediates onto the carrier, i.e. with the accumulation of coke outside the surface of the active metal.

The rhenium–sulphur system affords analogous protecting properties in relation to coke,[15,65] which has been explained by the high stability of rhenium sulphides.[65] A dependence of the promoting effect of rhenium on the presence of sulphur in platinum catalysts has been observed.[143,144]

The ideas examined here make it possible to explain the retention of the high effectiveness of bimetallic aluminoplatinum dehydrogenation catalysts even for a coke content exceeding 10% of the mass of the catalyst (Ref.31, pages 355, 358; Ref. 32, page 101; Refs.145–148).

3. Technological processes involving the dehydrogenation of paraffinic hydrocarbons

The dehydrogenation of higher n-paraffins is carried out in a stationary bed of a non-acid polymetallic aluminoplatinum catalyst with the raw material supplied at high space velocities (20–40 h^{-1}), in the presence of a small excess hydrogen pressure (0.3–0.4 MPa), and at a temperature 450–500 °C. The degree of conversion per pass is ~10 wt.%, which necessitates the repeated recirculation of the unreacted paraffins.[10,15,149,150] The low degree of dehydrogenation makes it possible to carry out the process in a single adiabatic reactor.

The "Pacol" process developed by the UOP Corporation (USA), characterised by the above features, has found application in industry.[149,150] The synthesis of mono-olefins by this method is promising because of the exclusively high (not less than 90%) selectivity and economy of the process. An additional valuable product is also the hydrogen-containing gas with a purity of 96 vol.%, whose yield relative to the initial raw material is 2–2.7 wt.%. The catalytic dehydrogenation reaction mixture can be used directly for the alkylation of benzene with isolation of the unreacted paraffins in the stage involving the fractionation of the alkylation products. When olefins are used to synthesise higher alcohols using the oxo synthesis, the catalytic reaction mixture is directed from the dehydrogenation plant to the stage in which olefins are isolated by adsorption (the "Oleflex" proces), where a concentrate containing 90–95% of the linear mono-olefins is obtained. By 1983, 22 "Pacol" plants were in operation or were being built[150] with an output of 25 000–100 000 tonnes of olefins per year. The development of a forced version of the process with a conversion of 13–14.5% per pass has been reported.[150]

It follows from Table 5 that Soviet technological processes have analogous basic parameters. An increase in the degree of conversion from 10–11% to 16–17% makes it possible to reduce the number of circulations of the unreacted raw material by a factor of 1.5 and to diminish the energy expenditure, in agreement with the conclusions reached by Vora et al.[150] In industrial practice, the catalyst is replaced by a fresh portion after a single raw material cycle, the old one being directed to the platinum extraction stage.

The possibility of the selective dehydrogenation of C_3–C_5 paraffinic hydrocarbons to mono-olefins on promoted aluminoplatinum catalysts with an up to 15 day reaction cycle was demonstrated at the beginning of the 1980's.[90,97,151] In an isothermal reactor with a fixed catalyst bed, where the raw materials were supplied at a rate of 1000 h^{-1} (with respect to the gas), a 30–40 wt.% conversion of C_4 and C_5 paraffins was achieved with a selectivity up to 91–92.5 wt.% with respect to mono-olefins. These parameters are significantly better than in the fluidised chromium

oxide catalyst bed (Table 6). The coke content in the catalyst at the end of the cycle reaches 12–15 wt.% (0.007–0.012 wt.% relative to the raw material passed through the system).

Table 5. Characteristics of the dehydrogenation reactions of C_{11}–C_{14} paraffinic hydrocarbons on a polymetallic aluminoplatinum catalyst.[15]

Parameters	Regime	
	normal	severe
Pressure, MPa abs.	0.4—0.5	0.3
Conversion, wt.%	11.2	17.8
Selectivity in formation of n-monoolefins, wt.%	90	85*
Duration of reaction cycle, days	30	20

Note. Temperature 460–500 °C, rate of supply of liquid raw material (space velocity) 20–30 h^{-1}, molar ratio hydrogen : raw material = 8 : 1.
** Without the hydrogenation of dienes.

The considerable interest in the synthesis of C_3–C_5 olefins by the paraffin dehydrogenation method is due to their wide application in petrochemistry, mainly for the preparation of synthetic rubber monomers and polyolefins[15–17] and to the considerable growth of the extraction of the raw material—liquefied petroleum gases.[152] Three new processes have been developed for this purpose during a short period.[153]

In the "Oleflex" process of the UOP Corporation (USA), a unit of three adiabatic reactors, analogous to the reactor for the "Pacol" process, is used with intermediate heating of the stream to compensate for the endothermicity of the reaction (~130 kJ mol^{-1}). The process is carried out in a fluidised bed of a polymetallic platinum catalyst (of the type of the catalyst for the "Pacol" process) with continuous regeneration. Coke formation does not exceed 0.02 wt.% relative to the raw material.[97] The working cycle of the catalyst, withstanding more than 250 regenerations,[97] is 3–14 days.[153] For a 45% conversion of isobutane, the selectivity for the formation of isobutene was 87.5% and that for the dehydrogenation of isopentane, taking into account the formation of isoprene, was 77.5 wt.%.[97]

In the "Star" process of the Philips Company, carried out in an isothermal tubular reactor with a fixed catalyst bed in the presence of steam,[153] a promoted platinum catalyst based on a thermostable spinel is also used judging from the patents of this Company.[17,111]

According to Choudhury's communication,[153] for an 8 h working catalyst cycle the selectivity in the dehydrogenation of isobutane reaches 95 mol % with ~50% conversion, which agrees with patent and research data for the dehydrogenation of paraffins on catalysts of this kind under similar conditions.[111,154] The "Oleflex" and "Star" processes are being tested on a semi-industrial scale.[153]

Thus, among the three new C_3 and C_4 paraffin dehydrogenation processes, two are based on the use of polymetallic platinum catalysts, which indicates the maintenance of the tendency towards the expansion of their applications noted previously.[15]

References

1. Al A Petrov *Kataliticheskaya Izomerizatsiya Uglevodorodov* (Catalytic Isomerisation of Hydrocarbons), Izd. Akad. Nauk SSSR, Moscow, 1960, 214 pp
2. F E Condon *Kataliz v Neftekhimicheskoi i Neftepererabatyvayushchei Promychlennosti* (Catalysis in the Petrochemical and Petroleum-processing Industry), Gostoptekhizdat, Moscow, 1961, Book 2, p. 48
3. N R Bursian *Tekhnologiya Izomerizatsii Parafinovykh Uglevodorodov* (Technology of the Isomerisation of Paraffinic Hydrocrbons), Izd. Khimiya, Leningrad, 1985, 191 pp
4. Yu M Zhorov *Izomerizatsiya Uglevodorodov* (Isomerisation of Hydrocarbons), Izd. Khimiya, Moscow, 1983, 301 pp
5. P R Pujado, B V Vora *Chem. Econ. Eng. Rev.*, 1983, **15**(5) 16
6. N R Bursian, P N Borutskii, S B Kogan, et al. *Khim. Tekhnol. Topl. Masel*, 1987(7), 4

Table 6. Parameters of the dehydrogenation reactions of butanes and isopentane on different catalysts.[16,151]

Parameter	n-Butane		Isobutane		Isopentane	
	a	b	a	b	a	b
Temperature, °C	545—560	570—600	540—570	580—620	530—560	550—610
Pressure, MPa	0.2	0.1—0.2	0.25	0.1—0.2	0.2	0.1—0.2
Hydrogen : raw material molar ratio	0.75:1	—	1:1	—	2:1	—
Rate of supply of raw material (space velocity) (with respect to gas), h^{-1}	1000	100—300	1000	100—300	700	100—300
Degree of conversion per pass, wt.%	31	41—43	40	44—48	30	43—45
Yield of olefins relative to raw material which has reacted, wt.%	92.5	72—76	91.1	77—82	92.0	68—74
Selectivity, % of theoretical	96.0	75—79	94.5	80—85	94.5	70—76

Note. Catalysts: a) aluminoplatinum; b) K-5 aluminochromium.

7. A M Tsybulevskii, P M Pak, V I Berezhnaya *Khim. Tekhnol. Topl. Masel*, 1980(12), 10
8. N R Bursian, N K Volnukhina, S B Kogan, D S Orlov *XII Mendeleevskii S'ezd po Obshchei i Prikladnoi Khimii: Referaty Dokladov i Soobshchenii* (The XIIth Mendeleev Congress on General and Applied Chemistry: Abstracts of Reports and Communications), Izd. Nauka, Moscow, 1980, Part 4, p. 36
9. N R Bursian, V K Daragan, S B Kogan, G A Lastovkin *Khim. Tekhnol. Topl. Masel*, 1986(10), 6
10. B R Serebryakov, T K Plaskunov, V R Ansheles, M A Dalin *Vysshie Olefiny. Polizvodstvo i Primenenie* (Higher Olefins. Manufacture and Applications) (Edited by M A Dalin), Izd. Khimiya, Leningrad, 1984, 264 pp
11. I R Chernyi *Proizvodstvo Syr'ya dlya Neftekhimicheskikh Sintezov* (The Manufacture of Raw Material for Petrochemical Syntheses), Izd. Khimiya, Moscow, 1983, 336 pp
12. *Nefti SSSR* (Petroleums in the USSR), Izd. Khimiya, Moscow, 1974, Vol. 4, 390 pp
13. Kh M Minachev, Ya I Isakov *Metallsoderzhashchie Tseolity v Katalize* (Metal-containing Zeolites in Catalysis), Izd. Nauka, Moscow, 1976, p. 85
14. Kh M Minachev, D A Kondrat'ev *Uspekhi Khim.*, 1983, **52**(12) 1921 [English translation in *Russ. Chem. Rev.*, 1983(12)]
15. N R Bursian, S B Kogan, V Sh Gruver, P N Borutskii *Platinovye Promotirovannye Katalizatory v Protsessakh Izomerizatsii i Degidrirovaniya Parafinovykh Uglevodorodov* (Platinum-promoted Catalysts in the Isomerisation and Dehydrogenation Reactions of Paraffinic Hydrocarbons), Izd. TsNIITENeftekhim, Moscow, 1981, 50 pp
16. S K Ogorodnikov *Spravochnik Neftekhimika* (Handbook of the Petroleum Chemist) (Edited by S K Ogorodnikov), Izd. Khimiya, Leningrad, 1978, Vol. 2, p. 349
17. G R Kotel'nikov, L V Strunnikova, V A Patanov, V A Arapova *Katalizatory Degidrirovaniya Nizshikh Parafinovykh, Olefinovykh i Alkilaromaticheskikh Uglevodorodov* (Catalysts for the Dehydrogenation of Lower Paraffinic, Olefinic, and Alkyl-substituted Aromatic Hydrocarbons), Izd. TsNIITENeftekhim, Moscow, 1978, 81 pp
18. V K Skarchenko *Degidrirovanie Uglevodorodov* (Dehydrogenation of Hydrocarbons), Izd. Naukova Dumka, Kiev, 1981, 328 pp.
19. F Asinger *Chemie und Technologie der Paraffin-Kohlenwasserstoffe* (Russian translation from German edited by V I Isagulyants), Gostoptekhizdat, Moscow, 1959, Vol. 1, 623 pp.
20. N R Bursian *Spravochnik Neftepererabotchika* (Handbook of the Petroleum Processing Chemist) (Edited by G A Lastovkin, et al.), Izd. Khimiya, Leningrad, 1986, p. 178
21. A S Kazanskaya, V A Skoblo *Raschety Khimicheskikh Ravnovesii* (Calculations of Chemical Equilibria), Izd. Vys. Shkola, Moscow, 1974, 287 pp
22. A A Vvedenskii *Termodinamicheskie Raschety Neftekhimicheskikh Protsessov* (Thermodynamic Calculations for Petrochemical Processes), Gostoptekhizdat, Leningrad, 1960, 576 pp
23. J H Sinfelt, H Hurwitz, J C Rohrer *J. Phys. Chem.*, 1960, **64** 892
24. N R Bursian, N K Volnukhina, I A Volkov, A A Polyakov *Kataliticheskie Prevrashcheniya Parafinovykh Uglevodorodov* (Catalytic Reactions of Paraffinic Hydrocarbons), Izd. **VNIINeftekhim, Leningrad, 1976, p. 75**
25. E M Davydov, M S Kharson, S L Kiperman *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 2687
26. A S Aleksandrov, N R Bursian, N S Gurfein, et al. *Khim. Tekhnol. Topl. Masel*, 1976(10), 5
27. Kh M Minachev, V I Garanin, V V Kharlamov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1970, 835
28. J I Spivey, Ph Bryant *Ind. Eng. Chem. Process. Des. Dev.*, 1982, **21** 750
29. V I Garanin, Kh M Minachev, T A Isakova *Neftekhimiya*, 1972, **12** 501
30. R Bonifay, B Torek, M Hellin *Bull. Soc. Chim. Fr.*, 1977(11/12), 1077
31. B C Gates, J R Katzner, G C A Schuit *Chemistry of Catalytic Processes* (Russian translation from English edited by A F Plate), Izd. Mir, Moscow, 1981, 552 pp (McGraw-Hill Series in Chemical Engineering)
32. G N Maslyanskii, R N Shapiro *Kataliticheskii Riforming Benzinov* (Catalytic Reforming of Petrols), Izd. Khimiya, Leningrad, 1985, 222 pp.
33. D M Brouwer, J M Oeldrik *Recl. Trav. Chim.*, 1968, **87** 721
34. G B Marin, F G Froment *Chem. Eng. Sci.*, 1982, **37** 759
35. J E Germain *Catalytic Conversion of Hydrocarbons* (Russian Translation from English edited by A B Shekhter), Izd. Mir, Moscow, 1972, 310 pp
36. Al A Petrov *Khimiya Alkanov* (The Chemistry of Alkanes), Izd. Nauka, Moscow, 1974, 243 pp
37. F E Condon *Catalysis* (Edited by P B Emmett), Reinhold, New York, 1958, Vol. 6, p. 83
38. T H Milliken, G A Mills, A G Oblad *Disc. Faraday Soc.*, 1950, **8** 279
39. G A Olah *J. Am. Chem. Soc.*, 1972, **94** 808
40. F Fajula *Catalysis by Acids and Bases*, Elsevier, Amsterdam, 1985, p. 361
41. G A Mills, H Heinemann, T H Milliken, A G Oblad *Ind. Eng. Chem.*, 1953, **45** 134
42. P Weis *Catalysis. Polyfunctional Catalyst and Complex Reactions* (Translated into Russian), Izd. Mir, Moscow, 1965, p. 3
43. N R Bursian, D S Orlov, A N Shakun *Kataliz na Sverkhkislotakh* (Catalysis on Superacids), Izd. TsNIITENeftekhim, 1979, 51 pp
44. J B Peri *J. Phys. Chem.*, 1965, **69** 211, 231
45. J Basset, F Figueras, M V Mathieu, et al. *J. Catal.*, 1970, **16** 53
46. N R Bursian, N K Volnukhina, I A Volkov, et al., *Kataliticheskie Prevrashcheniya Parafinovykh Uglevodorodov* (Catalytic Reactions of Paraffinic Hydrocarbons), Izd. VNIINeftekhim, Leningrad, 1976, p. 36
47. L N Izmailova, E I Kotov, P N Borutskii, N R Bursian *Kinet. Katal.*, 1978, **19** 390
48. Yu A Bitenazh, N R Bursian, P N Borutskii, et al. *Nauchnye Osnovy Prigotovleniya Katalizatorov. Tezisy Dokladov Vsesoyuznogo Soveshchaniya* (Scientific Principles of the Preparation of Catalysts. Abstracts of Reports at an All-Union Conference), Izd. IK Sibir. Otd. Akad. Nauk SSSR, Novosibirsk, 1983, p. 222
49. T V Antipina, V A Chernov *Vestn. Moskov. Gos. Univ., Ser. 2*, Khimiya, 1962, **3** 22
50. A G Goble, P A Lawrence *Preprints of the Proceedings of III International Congress on Catalysis* , North-Holland, Amsterdam, 1965, p. 328

51. N R Bursian, G V Stavrova, USSR P. 189 804; *Byull. Izobret.*, 1967(1)
52. J A Rabo, F E Pickert, B L Mays *Ind. Eng. Chem.*, 1961, **53** 733
53. Ya I Isakov, Kh M Minachev *Uspekhi Khim.*, 1982, **51**(12) 2069 [English translation in *Russ. Chem. Rev.*, 1982(12)]
54. J M Oeldrik, B. P. 981 311
55. N R Bursian, Yu A Shavandin, N K Volnukhina, G V Stavrova *Kinet. Katal.*, 1971, **12** 769
56. E B Maxted *Kataliz. Voprosy Teorii i Metody Issledovaniya* (Catalysis. Problems of the Theory and Methods of Investigation), Inostr. Lit., Moscow, 1955, p. 100
57. E Bechtold *Ber. Bunsenges Phys. Chem.*, 1966, **70** 713
58. Y Berthier, M Perderean, J Oudar *Surf. Sci.*, 1973, **36** 225
59. T E Fischer, S R Kelemen *J. Catal.*, 1978, **53** 24
60. C R Apesteguia, T F Garetto, C E Brema, J M Parera *Appl. Catal.*, 1984, **10** 291
61. C R Apesteguia, C E Brema, T F Garetto, et al. *J. Catal.*, 1984, **89** 52
62. M Mendez, D Duprez, C Apesteguia, J Barbier *React. Kinet. Catal. Lett.*, 1983, **23** 397
63. M-V Mathieu, M Primet *Appl. Catal.*, 1984, **9** 361
64. N R Bursian, V Sh Gruver, M M Filippov, et al. *Zh. Prikl. Khim. (Leningrad)*, 1986, **59** 595
65. P Biloen, J N Helle, H Verbeek, et al. *J. Catal.*, 1980, **63** 112
66. N R Bursian, B B Zharkov, S B Kogan, et al. *VIII International Congress on Catalysis*, DECHEMA, Frankfurt am. Main, 1984, Vol. 2, p. 481
67. A V Mashkina *Geterogennyi Kataliz v Khimii Organicheskikh Soedinenii Sery* (Heterogeneous Catalysis in the Chemistry of Organic Compounds of Sulphur), Izd. Nauka, Novosibirsk, 1977, 338 pp
68. N R Bursian, Yu A Shavandin, N K Volnukhina, P N Borutskii *Zh. Prikl. Khim.*, 1974, **47** 1335
69. N R Bursian, N K Volnukhina, G V Stavrova, et al. *Vazhneishie Protsessy Pererabotki Uglevodorodnogo Syr'ya* (The Most Important Processes in the Processing of Hydrocarbon Raw Material), Izd. TsNIITENeftekhim, Moscow, 1979, p. 37
70. R A Corbett *Oil and Gas J.*, 1986, **84(12) 71**
71. G L Hofmann *Neft', Gaz i Neftekhimiya za Rubezhom*, 1987(2) 85
72. V Grignard, R Stratford *Compt. Rend.*, 1924, **178** 2148
73. B L Moldavskii, M V Kobyl'skaya, S E Livshits *Zh. Obshch. Khim.*, 1935, **5** 1791
74. B Moldavskii, T Nizovkina *Zh. Obshch. Khim.*, 1940, **10** 1183
75. B Moldavskii, E Nebylova, T Nizovkina *Zh. Obshch. Khim.*, 1944, **14** 343
76. Y Ono, T Tanabe, N Kitajima *Chem. Lett.*, 1978(6), 625
77. Y Ono, T Tanabe, N Kitajima *J. Catal.*, 1979, **56** 47
78. N R Bursian, S B Kogan, D S Orlov, E I Zhemchugova *Zh. Prikl. Khim. (Leningrad)*, 1986(7), 1570
79. US P. 3 812 199
80. *Oil and Gas J.*, 1977, **75**(40) 64
81. G Gianetto, G Perot, M Guisnet *Proceedings of the International Symposium on Zeolites in Catalysis (Siofok)*, Acta Physica et Chemica Szegediensis, Szeged, 1985, p. 467
82. US P. 3 773 845
83. US P. 3 793 251
84. A P Bolton *The Chemistry of Zeolites and Catalysis on Zeolites* (Edited by J Rabo) (Translated into Russian), Izd. Mir, Moscow, 1980, Vol. 2, p. 431
85. H K Beyer, F Reti, J Horvath *Acta Chim. Acad. Sci. Hung.*, 1982, **109** 199
86. S B Kogan, V K Daragan, N R Bursian *Neftekhimiya*, 1984 **24** 32
87. S P Zhdanov, N N Feokistova, N I Kozlova, et al. *Proceedings of the International Symposium on Zeolites in Catalysis (Siofok)*, Acta Physica et Chemica Szegediensis, Szeged, 1985, p. 129
88. E A Timofeeva, V E Ivankovskii, G V Isagulyants *Neftekhimiya*, 1977, **17** 58
89. E A Timofeeva, V E Ivankovskii, G V Isagulyants *Neftekhimiya*, 1980, **20** 50
90. R C Berg, B V Vora, J R Mowry *Oil Gas J.*, 1980, **78**(45) **191**
91. N V Lemaev *Khim. Promst. (Moscow)*, 1986(9), 3
92. A I Lukashev *XII Mendeleevskii S'ezd po Obshchei i Prikladnoi Khimii* (The XIIth Mendeleev Congress on General and Applied Chemistry, (Izd. Nauka, Moscow, 1984, p. 94
93. C L Thomas *Catalytic Processes and Proven Catalysts* (Translated into Russian), Izd. Mir, Moscow, 1973, 385 pp
94. T P Kornienko *Kataliticheskie Svoistva Veshchestv* (Catalytic Properties of Substances) (Edited by V A Roiter), Izd. Naukova Dumka, Kiev, 1977, Vol. 4, p. 147
95. Yu I Ermakov, V A Zakharov, B N Kuznetsov *Zakreplennye Kompleksy na Okisnykh Nositelyakh v Katalize* (Immobilised Complexes on Oxide Carriers in Catalysis), Izd. Nauka, Novosibirsk, 1980, 246 pp
96. O V Bragin, A L Liberman *Prevrashcheniya Uglevodorodov na Metallsoderzhashchikh Katalizatorakh* (The Reactions of Hydrocarbons on Metal-containing Catalysts), Izd. Khimiya, Moscow, 1981, 264 pp
97. B V Vora, T Imai *Hydrocarb. Process.*, 1982, **61** 171
98. O D Sterligov, T G Olfer'eva, N F Kononov *Uspekhi Khim.*, 1967, **36**(7) 1200 [English translation in *Russ. Chem. Rev.*, 1967(7)]
99. Yu S Khodakov, Doctoral Thesis in Chemical Sciences, Institute of Organic Chemistry, USSR Academy of Sciences, Moscow, 1976, 371 pp
100. N R Bursian, I A Vasil'ev, S B Kogan, et al. *Neftepererab. Neftekhim.*, 1978(12), 51
101. B A Kazanskii, V S Fadeev, V V Gostunskaya *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1971, 677
102. G V Isagulyants, M I Rozengart, Yu G Dubinskii *Kataliticheskaya Aromatizatsiya Alifaticheskikh Uglevodorodov* (Catalytic Aromatisation of Aliphatic Hydrocarbons), Izd. Nauka, Moscow, 1983, 160 pp
103. T L Krylova, N V Nekrasov, N A Gaidai, et al. *Kinet. Katal.*, 1980, **21** 1487
104. Z A Sadykhova, N V Nekrasov, V R Gurevich, S L Kiperman *Kinet. Katal.*, 1981, **22** 396
105. Z A Sadykhova, N V Nekrasov, V R Gurevich *Kinet. Katal.*, 1984, **25** 593
106. Lyu Kam Lok, N A Gaidai, S L Kiperman, et al. *Khimicheskaya Kinetika v Katalize. Kineticheskie Modeli Organicheskikh Reaktsii* (Chemical Kinetics in Catalysis. Kinetic Models of Organic Reactions), Izd. IOKh-IKhF Akad. Nauk SSSR, Chernogolovka, 1985, p. 112

107. Lyu Kam Lok, N A Gaidai, B S Gudkov, et al. *Kinet. Katal.*, 1986, **27** 1371
108. S B Kogan, N M Podkletnova, A M Moroz, et al. *Khimicheskaya Kinetika v Katalize. Kineticheskie Modeli Organicheskikh Reaktsii* (Chemical Kinetics in Catalysis. Kinetic Models of Organic Reactions), Izd. IOKh-IKhF Akad. Nauk SSSR, Chernogolovka, 1985, p. 120
109. B S Bal'zhinimaev, A A Ivanov, N A Pakhomov, G R Kotel'nikov *Kinetika-3. Materialy III Vsesoyuznoi Konferentsii. Kalinin* (Kinetics-3. Proceedings of the IIIrd All-Union Conference. Kalinin), 1980, Vol. 1, p. 46
110. US P. 3 842 139
111. US P. 4 191 846
112. J H Sinfelt *J. Catal.*, 1973, **29** 308
113. S R Adkins, B H Davis *J. Catal.*, 1984, **89** 371
114. G K Boreskov *Teoreticheskie Problemy Kataliza* (Theoretical Problems of Catalysis), Izd. IK Sibir. Otd. Akad. Nauk SSSR, Novosibirsk, 1977, p. 113
115. N R Bursian *Nanesennye Metallicheskie Katalizatory Prevrashcheniya Uglovodorodov. Materialy Vsesoyuznoi Konferentsii* (Deposited Metallic Catalysts for the Conversion of Hydrocarbons. All-Union Conference Proceedings). Izd. IK Sibir. Otd. Akad. Nauk SSSR, Novosibirsk, 1978, Part 1, p. 30
116. W M H Sachtler, R A Santen *Adv. Catal.*, 1977, **26** 69
117. A A Slinkin *Kinet. Katal.*, 1981, **22** 71
118. R A Buyanov *Zakoksovanie Katalizatorov* (Saturation of Catalysts by Coke), Izd. Nauka, Novosibirsk, 1983, 208 pp
119. N R Bursian, S B Kogan, G I Semenov, E A Levitskii *Kinet. Katal.*, 1974, **15** 1608
120. V A Ushakov, E M Moroz, N R Bursian, et al. *Kinet. Katal.*, 1978, **19** 805
121. A A Balandin, V V Patrikeev *Zh. Prikl. Khim (Leningrad)*, 1942, **15** 139
122. S Z Roginskii *Geterogennyi Kataliz* (Heterogeneous Catalysis), Izd. Nauka, Moscow, 1979, 416 pp
123. G K Boreskov *Kinet. Katal.*, 1980, **21** 5
124. P P Langhorst, H C de Jongste, V Ponec *Catalyst Deactivation. Proceedings of International Symposium*, Elsevier, Amsterdam, 1980, p. 43
125. G A Somorjai *Chemistry in Two Dimensions*, Cornell Univ. Press, Ithaca–London, 1981, 515 pp
126. G A Somorjai *Surf. Sci.*, 1979, **84** 496
127. M A Tanatarov, N M Shaimardanov, M E Levinter *Kinet. Katal.*, 1975, **16** 1313
128. J Barbier, P Marecot, V Martin, et al. *Catalyst Deactivation. Proceedings of International Symposium*, Elsevier, Amsterdam, 1980, p. 53
129. J H Sinfelt *Novoe v Issledovanii Poverkhnosti Tverdogo Tela* (Advances in the Study of the Surfaces of Solids), Izd. Mir, Moscow, 1977, No. 1, p. 285
130. V K Duplyakin, A S Beyi, V S Alfeev, M E Levinter *Nanesennye Metallicheskie Katalizatory Prevrashcheniya Uglevodorodov. Materialy Vsesoyuznoi Konferentsii* (Deposited Metallic Catalysts for the Conversion of Hydrocarbons. All-Union Conference Proceedings), Izd. IK Sibir. Otd. Akad. Nauk SSSR, Novosibirsk, 1978, Part 1, p. 35
131. R Bacaud, P Bussiere, F Figueras, I P Mathiev *Catalyst Preparation. Proceedings of I International Symposium*, Elsevier, Amsterdam, 1976, p. 509
132. Yu M Zhorov, G M Panchenkov, Yu N Kartashev *Kinet. Katal.*, 1981, **22** 1341
133. R J Bertolacini, R I Pellet *Catalyst Deactivation. Proceedings of International Symposium*, Elsevier, Amsterdam, 1980, p. 73
134. J C Rasser, W H Biendorf, J J F Scholten *J. Catal.*, 1979, **59** 211
135. N R Bursian, Z S Volkova, V Sh Gruver, et al. *Nanesennye Metallicheskie Katalizatory Prevrashcheniya Uglevodorodov. Materialy Vsesoyuznoi Konferentsii* (Deposited Metallic Catalysts for the Conversion of Hydrocarbons. All-Union Conference Proceedings), Izd. IK Sibir. Otd. Akad. Nauk SSSR, Novosibirsk, 1978, p. 191
136. O M Oranskaya, I V Semenskaya, S B Kogan, et al. *Primenenie Opticheskoi Spektroskopii v Adsorbtsii i Katalize* (Application of Optical Spectroscopy in Adsorption and Catalysis), Izd. IOKE Akad. Nauk Kazakh. SSSR, Alma-Ata, 1980, p. 65
137. F M Dautzenberg, J N Helle, P Biloen, W M H Sachtler *J. Catal.*, 1980, **63** 119
138. S B Kogan, N M Podkletnova, O M Oranskaya, et al. *Kinet. Katal.*, 1981, **22** 663
139. S B Kogan, N M Podkletnova, A S Ilyasova, N R Bursian *Zh. Prikl. Khim (Leningrad)*, 1983, **56** 1832
140. J Völter, U Kürschner *Appl. Catal.*, 1983, **8** 167
141. G Lietz, J Völter, M Dobrovolszky, Z Paal *Appl. Catal.*, 1984, **13** 77
142. B B Zharkov T M Klimenko, N P Fedyanin, et al. *Zh. Prikl. Khim. (Leningrad)*, 1984, **57** 2555
143. G N Maslyanskii, B B Zharkov *Khim. Tekhnol. Topl. Masel*, 1977(1), 16
144. R W Coughlin, K Kawakami, A Hassan *J. Catal.*, 1984, **88** 150
145. L R Aalund *Oil Gas J.*, 1971, **69**(51) 43
146. NPRA Q. and A. *Oil Gas J.*, 1973, **71**(15) 88
147. B B Zharkov, R N Shapiro, V V Shipikin *Spravochnik Neftekhimika* (Handbook of the Petroleum Chemist), (Edited by S K Ogorodnikov), Izd. Khimiya, Leningrad, 1978, Vol. 2, p. 134
148. A P Fedorov, E A Shkuratova, G N Maslyanskii, B B Zharkov *Khim. Tekhnol. Topl. Masel*, 1984(9), 15
149. R C Berg, R A Persak, G K Winter *Petrol. Int.*, 1978, **25**(9) 31
150. B V Vora, P R Pujado, J B Spinner, T Imai *Hydrocarb. Process.*, 1984, **63**(11) 86
151. N R Bursian, S B Kogan, G A Lastovkin, D S Orlov *Khim. Tekhnol. Topl. Masel*, 1981(10), 7
152. B V Vora, R C Berg, P R Pujado *Chem. Econ. Eng. Rev.*, 1983, **15**(4) 27
153. J Choudhury *Chem. Eng.*, 1984, **91**(13) 40
154. N A Pakhomov, R A Buyanov, E M Moroz, et al. *Nanesennye Metallicheskie Katalizatory Prevrashcheniya Uglevodorodov. Materialy Vsesoyuznoi Konferentsii* (Deposited Metallic Catalysts for the Conversion of Hydrocarbons. All-Union Conference Proceedings), Izd. IK Sibir. Otd. Akad. Nauk SSSR, Novosibirsk, 1978, p. 227

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The introduction of functional groups into unsaturated systems by carbonyl compounds in the presence of manganese(III) acetate

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ABSTRACT. **The review is devoted to the reactions of unsaturated systems (alkenes, alkynes, arenes, alkadienes, and alkenynes) with carbonyl compounds (aldehydes, ketones, carboxylic acids, and α-, β-, γ-, and δ-dicarbonyl compounds) initiated by manganese(III) acetate. Attention is concentrated on the regio- and stereo-chemistry of the interaction, the pathways leading to the stabilisation of the intermediate radical-adducts, and also the assessment of the synthetic possibilities of reactions of the given type.**

The bibliography includes 91 references.

I. Introduction

The development of methods for the generation of free radicals with the aid of oxidation-reduction systems, especially the salts and oxides of variable-valence transition metals (Mn^{3+}, Co^{3+}, Cu^{2+}, Fe^{3+}, Ag^{2+}, Pb^{4+}, Ce^{4+}, Mn^{4+}, Ag^{+}, Cu^{+}, Fe^{2+}, and Cr^{2+}), has been a powerful stimulus to the development of the chemistry of such radicals.[1–4] Compared with the traditional method of radical generation, oxidation-reduction methods have a greater selectivity, in particular in relation to polyfunctional organic compounds. Furthermore, radicals which cannot be generated by classical methods can be obtained with their aid.[3]

The oxidation radical generation methods, proceeding via outer- and inner-sphere mechanisms, have now been investigated most widely.[4] The fundamental difference between them consists in the fact that the oxidant not only generates the radical from the addend in the initiation stage but reacts effectively with the radical-adduct formed when the radical adds to the organic substrate; as a result of this, the synthetic result of the reaction is different from that of the reaction initiated by classical methods.[5]

In the series of oxidants listed above, manganese(III) acetate is of special interest. The one-electron oxidation by the latter of the α-C–H bonds of carbonyl compounds generates α-oxo- and αα-dioxo-alkyl radicals, which react with unsaturated substrates when the latter are present in the reaction mixture. The subject of the present review is the consideration of reactions of precisely this type where monocarbonyl compounds—aldehydes, ketones, carboxylic acids, and α-, β-, γ-, and δ-dicarbonyl compounds—serve as the addend, the initiator is manganese(III) acetate, used separately or in combination with copper(II) acetate, and the unsaturated substrates consist of alkenes, alkynes, arenes, alkadienes, alkenynes, and alkadiynes. Attention will be concentrated on the regiochemistry of the generation of the oxoalkyl radicals, the regio- and stereochemistry of the interaction of the latter with the substrates, the pathways leading to the stabilisation of the intermediate radical-adducts, and the assessment of the synthetic possibilities of the reactions of the given type, including their use for the synthesis of natural products.

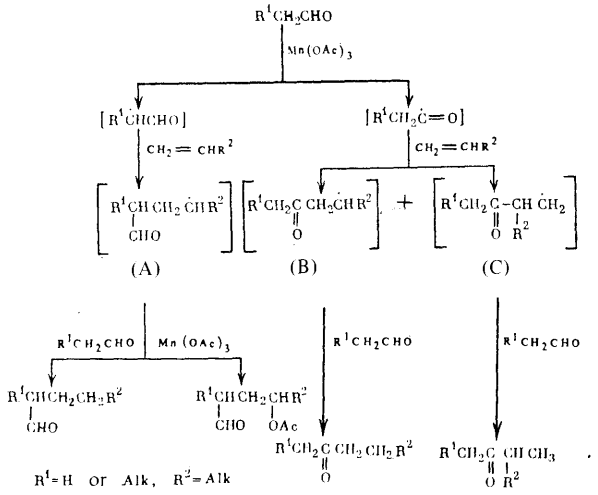
II. Reactions of alkenes with monocarbonyl compounds

1. Reactions with aldehydes

When aldehydes are oxidised by manganese(III) acetate, radicals of two types are formed—the α-formylalkyl radicals $R\dot{C}HCHO$ and the acyl radicals $RCH_2\dot{C}=O$, the type of the radical generated depending on the manganese(III) acetate concentration in the solution.[3,6] In a polar solvent (homogeneous conditions), the α-formylalkyl radicals are formed preferentially, while in the absence of solvent (heterogeneous conditions) the main product is acyl radicals, as for peroxide initiators.[7] It has been established that a primary isotope effect (k_H/k_D = 6) is observed for the reaction of CD_3CHO with $Mn(OAc)_3$, while in the reaction of CH_3CDO with $Mn(OAc)_3$ it is absent. This finding permits the conclusion that the direct interaction of the aldehyde with $Mn(OAc)_3$ yields the α-formylalkyl radicals, while the corresponding acyl radicals are apparently formed as a result of a secondary hydrogen atom transfer reaction.[3] It is also noteworthy that, in the oxidation of aldehydes without α-hydrogen atoms, for example, pivalaldehyde, acyl radicals are formed directly.[8]

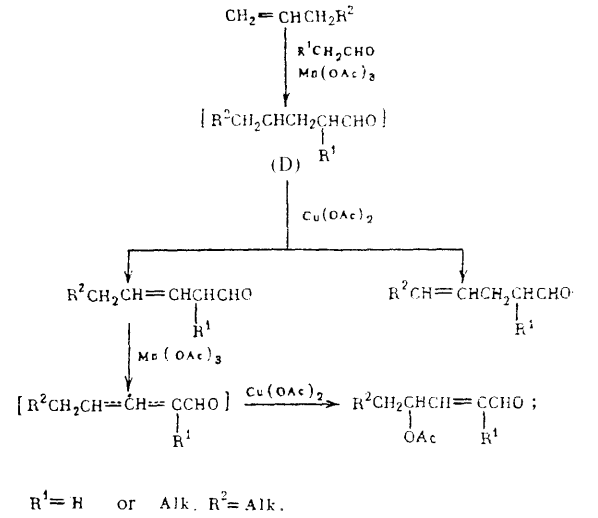
The addition of α-formylalkyl radicals to an alk-1-ene under homogeneous conditions affords radical-adducts of type (A), which are stabilised by the abstraction of a hydrogen atom or by oxidation with manganese(III) acetate via a ligand transfer mechanism.[1]

Radical-adducts of types (B) and (C) are formed under heterogeneous conditions and are stabilised by the addition of a hydrogen atom, which leads to isomeric saturated ketones:[9]



Depending on the structure of the aldehyde and the alkene, the ratio of the products listed in the above scheme is between 74:26 to 100:0 for homogeneous conditions and from 20:80 to 52:75 for heterogeneous conditions. This reaction has been proposed as a single-stage method of synthesis of higher α-alkyl-substituted aldehydes.[10]

The modification of the reaction of aldehydes with alkenes by the addition of catalytic amounts of copper(II) acetate proved to be extremely effective: the intermediate radical-adduct of type (D) was stabilised as a result of the oxidative elimination of β-protons, which led to γδ- and βγ-unsaturated aldehydes. Under the reaction conditions, the latter underwent further oxidation with formation of *trans*-4-acetoxyalk-2-enals:[11]

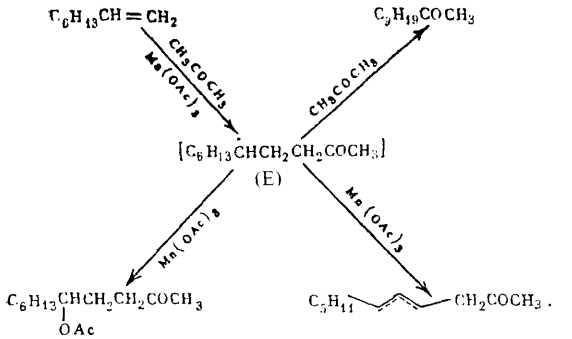


On passing from monosubstituted to 1,1-disubstituted alkenes, the chemistry of the reaction changes appreciably.[12] The main reaction products then become βγ- and γδ-unsaturated aldehydes also in the absence of copper(II) acetate. The authors explain this result by the nature of the intermediate radical-adducts, the difference between which is reflected quantitatively by the ratio of the rate constants for the oxidative elimination (k_{ox}) and abstraction of a hydrogen atom (k_{abs}). The ratio k_{ox}/k_{abs} is higher by 1–2 orders of magnitude for tertiary radical-adducts than for secondary radical-adducts. The reaction of aldehydes with β-pinene proceeds analogously, the intermediate radical-adducts undergoing skeletal isomerisation with the opening of the four-membered ring under these conditions.[13]

A mechanism, according to which the aldehyde reacts with the manganese(III) salt to form initially an oxallyl complex, has been proposed on the basis of kinetic data for the reactions of aldehydes with alkenes. The oxallyl complex decomposes reversibly with formation of α-formylalkyl free radicals, the regioselectivity of the alkylation of aldehydes by alkenes being determined by the equilibrium position.[14]

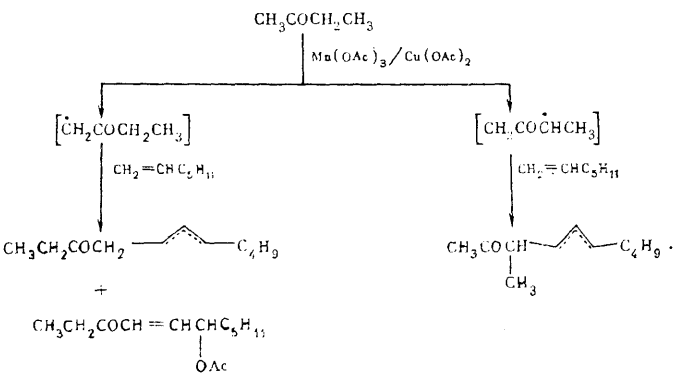
2. Reactions of ketones

The interaction of aliphatic and aromatic ketones with manganese(III) acetate leads to the formation of α-oxoalkyl radicals.[15–17] In the presence of unsaturated substrates, for example an alk-1-ene, the acetonyl radical, generated from acetone, affords the radical-adduct (E), which abstracts a hydrogen atom from the acetone or acetic acid molecule and undergoes oxidative elimination or substitution on treatment with manganese(III) acetate:[18,19]

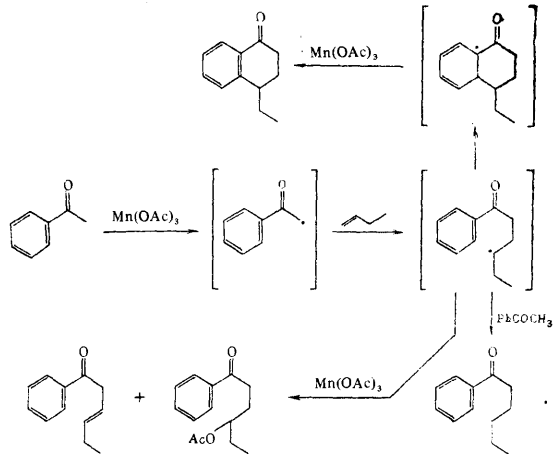


The authors established a direct proportionality between the ratio of the reaction products and the acetone concentration, and showed that, in the hydrogen atom transfer stage, acetone is four times more active than acetic acid. In addition, it was demonstrated that the addition of copper(II) acetate to the reaction mixture greatly increases the content of unsaturated ketones and γ-acetoxyketones as a result of the ability of $Cu(OAc)_2$ to oxidise alkyl radicals more effectively compared with $Mn(OAc)_3$.[5] The $Mn^{3+}/Ce^{4+}/Cu^{2+}$ relative reactivity of the ions in the oxidation of secondary radical-adducts was determined quantitatively as 1/12/350.[19]

The methylene group participates preferentially in the oxidation of ethyl methyl ketone, but the methyl group is also involved:[20]



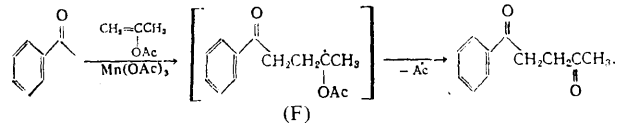
The interaction of aliphatic-aromatic ketones with alk-1-enes involves a new reaction pathway, together with those described above, namely intramolecular cyclisation leading to bicyclic compounds.[21] In particular, the reactions involving the cyclisation of acetophenone and but-1-ene yield a substituted tetralone:



The intramolecular cyclisation of δ-phenylalkyl radicals has been used to synthesise tetralin and indan derivatives.[21]

Cyclic ketones are oxidised by manganese(III) acetate, forming 2-oxocycloalkyl radicals, which interact with alkenes analogously to acyclic radicals.[20,22] It is remarkable that the ratio of the oxidative elimination products (βγ- and γδ-enones) depends on the ring size of the initial cycloalkanone.[22]

Enol ethers have also been involved in the reaction with ketones, which has made it possible to develop a single-stage method for the synthesis of 1,4-diketones—intermediates in the synthesis of jasmonoids.[23-25] For example, the addition of acetophenone to isopropenyl acetate leads initially to the radical-adduct (F), which is stabilised via the β-elimination of the acetyl radical with formation of a 1,4-diketone:[23]



(F)

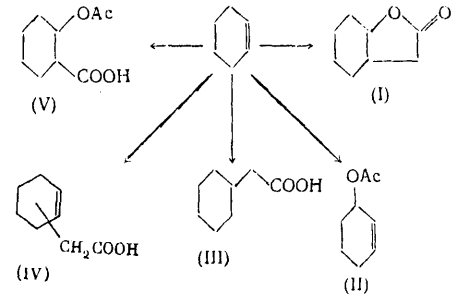
The analogous reactions of cyclohexanone, 2-octanone, and 3-methyl-2-heptanone have been investigated; the reaction involving asymmetric ketones results in the formation of a mixture of isomeric 1,4-diketones in accordance with two types of α-oxoalkyl radicals generated by the oxidation with manganese(III) acetate.[23] This reaction was subsequently extended by involving in it terpene ketones—nopinone, *cis*-verbanone, isonopinone, and isomenthone[24]—and has also been used in a key stage in the specific synthesis of 2-pentyl-2-cyclopent-1-enone—the precursor of dihydrojasmone and methyldihydrojasmonate.[25]

The telomerisation of ethylene with acetone, initiated by manganese(III) acetate, has also been investigated.[26-28] The products are 2-alkanones with a linear structure and isomeric 3-butyl-2-alkanones, formed as a result of the intermolecular rearrangement of the intermediate radical-adduct with 1,5-migration of a hydrogen atom. On catalysis by copper(II) acetate at an ethylene pressure of 100 atm, the main reaction pathway becomes the oxidative elimination of the telomeric radicals, leading to ω-unsaturated ketones.[27]

3. Reactions with carboxylic acids

The interaction of carboxylic acids with manganese(III) acetate is known to generate α-carboxyalkyl radicals.[3] The latter are capable of adding to the double bond of alkenes with formation of 3-carboxyalkyl radicals, which cyclise to alkan-4-olides in the presence of one-electron oxidants.[29-35] The formation of allyl acetates[30,32] as a result of the abstraction of the allyl hydrogen atom by the α-carboxymethyl radical and subsequent acetoxylation has been detected in a number of instances. It is notable that the selectivity of the lactonisation of the lactone:allyl acetate product ratio is 30:1 for methylstyrene and 50:1 for oct-1-ene.[32]

The lactonisation of alkenes by treatment with acetic acid and manganese(III) acetate is achieved in the presence of acetic anhydride[30] or potassium acetate.[32] The synthetic result of the application of two alternative methods is frequently the same,[30-32] but in the case of oct-1-ene the addition of potassium acetate leads to the corresponding lactone[32] whereas the main product resulting from the use of acetic anhydride is decanoic acid together with small amounts of decan-4-olide and 3- and 4-decenoic acids.[36] It is remarkable that the application of the same method involving the use of acetic anhydride by different investigators yielded different results. In the reaction involving cyclohexene, the formation of the lactone (I) and allyl acetate (II) has been detected by Bush and Finkbeiner.[30] Subsequently carboxymethylcyclohexane (III), carboxymethylcyclohexene (IV), and 1-acetoxy-2-carboxymethylcyclohexane (V) were also isolated:[37]

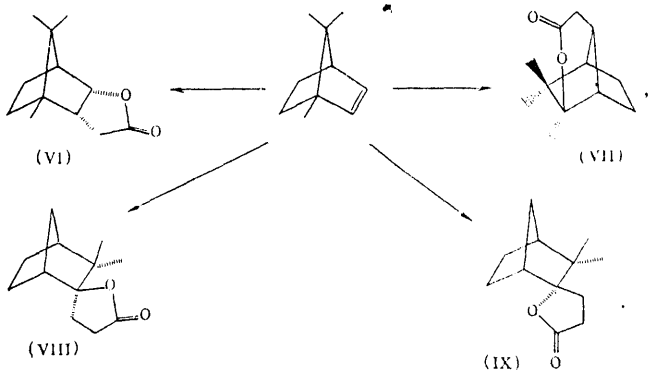


An analogous picture has been observed for cyclopentene, 1-methylcyclohexene, hex-1-ene, and 2-methylpent-2-ene.[37,38]

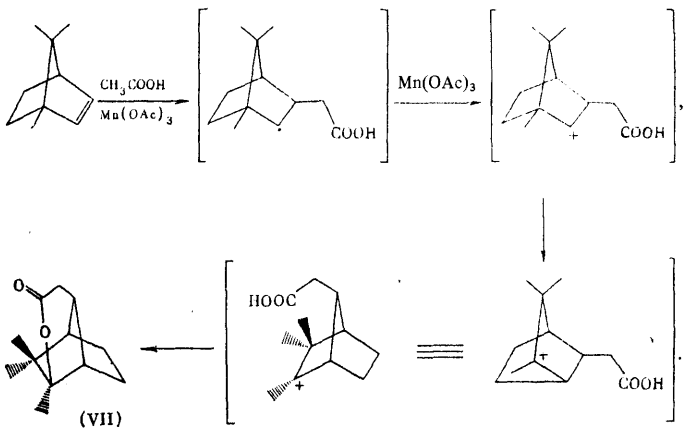
The monoterpenes *p*-menth-1-ene, 3-carene, α-pinene, bornene, and camphene have also been involved in the reaction with acetic acid initiated by manganese(III) acetate.[39-42] The products of the reactions for the first two compounds are lactones[39,40] but, on passing to α-pinene, the reaction chemistry changes appreciably.[41] The expected lactone is a minor reaction product, a mixture of the acetates of *cis*-pin-3-en-2-ol, myrtenol, and α-terpineol being mainly formed.[41] The last compound is produced as a result of the isomerisation of α-pinene via a carbonium ion mechanism under the influence of acetic acid.

The interaction of bornene with acetic acid affords a mixture of the isomeric lactones (VI)–(IX) and it has been demonstrated unambiguously that the formation of the *exo*- and *endo*-lactones (VIII) and (IX) is a result of the acid-catalysed rearrangement of

bornene to camphene and its subsequent interaction with acetic acid:[42]



The presence among the reaction products of the δ-lactone (VII), which is formed via the scheme presented below involving the Wagner–Meerwein rearrangement stage, is of separate interest:

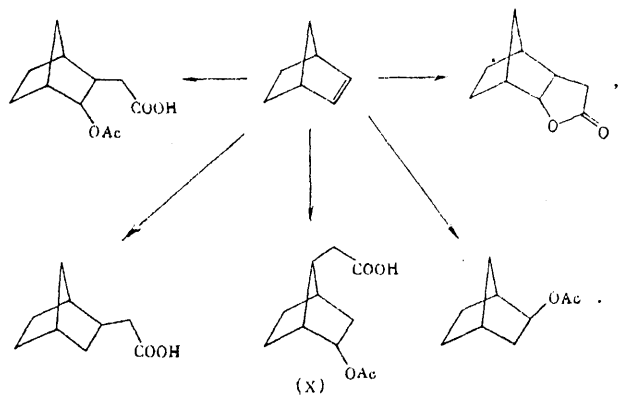


Since the Wagner–Meerwein rearrangement does not take place for radicals, the authors believe that this reaction indicates the intermediate formation of carbonium ions in the oxidation of radicals by manganese(III) acetate.[42]

Reactions of the above type have been modified by carrying them out in the presence of potassium bromide[43,44] and potassium or copper(II) acetates.[45,46] In the former case, the main reaction products are substituted allyl acetates while in the latter the main products are *trans*-alk-4-enoic acids.

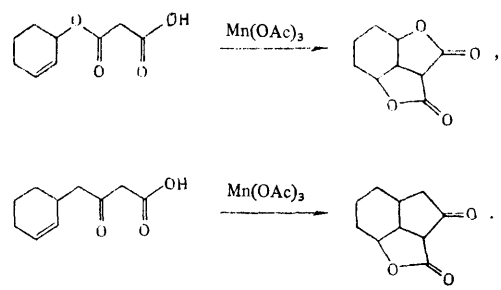
Detailed investigation of the reaction of alkenes with acetic acid has shown that (a) the use of manganese(III) acetate trihydrate is more effective in the synthesis of alkan-4-olides than the use of the anhydrous salt, that (b) acetic anhydride increases the rate of reaction as a consequence of its greater C–H acidity compared with acetic acid but the yields of alkan-4-olides are reduced as a result of the formation of unsaturated and α-acetoxy-substituted carboxylic acids, and that (c) potassium acetate increases the yield of alkan-4-olides by playing the role of a base facilitating deprotonation in the acetoxidation stage.[47] The study of the stereochemistry of the lactonisation reaction showed that the alkan-4-olides are mixtures of geometrical isomers and that their ratio varies within wide limits depending on the structure of the alkene—from 67:1 to 1:5.4.[47]

Like bornene, norbornene gives rise to a mixture of products on lactonisation, among which compound (X)—the result of the Wagner–Meerwein rearrangement of the intermediate cation—is formed in 1% yield.[47] On this basis, the authors claim that the reaction takes place almost fully via a radical mechanism and that there is no formation of intermediate carbonium ions in the oxidation of alkyl radicals by manganese(III) acetate:

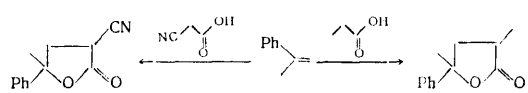


It is remarkable that this conclusion conflicts with the conclusion reached by Witkiewicz and Chabudzinski[42] that a carbonium ion is formed in an analogous reaction.

The lactonisation of alkenes by acetic acid has been used to synthesise jointed ketolactones and dilactones, which are intermediates in the synthesis of polycyclic compounds of natural origin:[48]



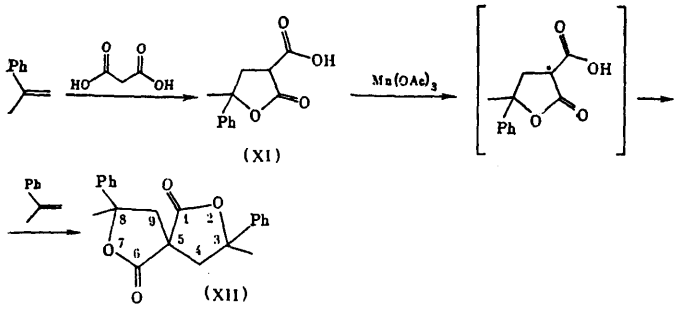
It has been reported that propionic[31,38,49] and cyanoacetic[31,50] acids also enter into the cycloalkylation reaction with alkenes and that the reaction involving α-methylstyrene results in the selective formation of 2-methyl- and 2-cyano-4-phenyl-lakan-4-olides:[31]



The interaction of camphene with cyanoaectic acid proceeds analogously.[50] On the other hand, the interaction of cyclohexene, cyclopentene, 1-methylcyclohexene, hex-1-ene, 2-methylpent-2-ene with propionic acid proceeds non-selectively.[38,49]

Malonic acid is the only dicarboxylic acid which has been introduced into the reaction with alkenes initiated by manganese(III) acetate;[51] the αα-dicarboxymethylradical adds in this reaction, in particular to α-methylstyrene with formation of the lactone (XI), which undergoes further oxidation and this leads to the

spirolactone (XII) in the form of a mixture of stereoisomers [3(*R*), 5(*R*), 8(*R*)-, 3(*S*), 5(*R*), 8(*S*)-, and 3(*R*), 5(*R*), 8(*S*)-]:



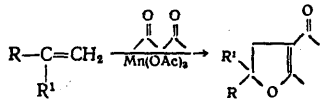
(XI)

(XII)

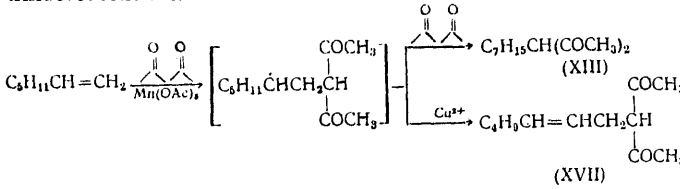
Manganese(III) acetate also initiates the interaction of carboxylic acid anhydrides with alkenes. The reaction products are saturated carboxylic acids.[52]

III. Reactions of alkenes with dicarbonyl compounds

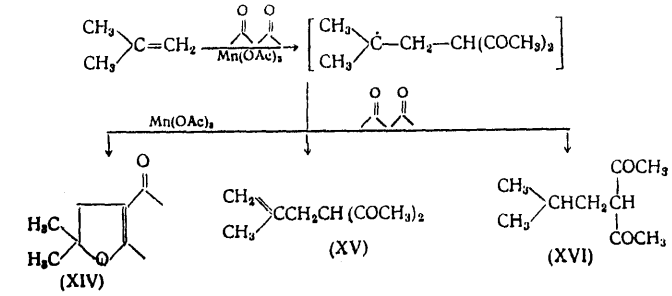
Acetylacetone is oxidised selectively by manganese(III) acetate at the methylene group of the acetylacetonyl.[53,54] When the above reaction is carried out in the presence of α-methylstyrene,[53] styrene,[53,54] 2-methylpent-2-ene,[53] and oct-1-ene,[53] it is accompanied by oxidative cyclisation to the 4,5-dihydrofuran derivatives:



The interaction of hept-1-ene with acetylacetone results in the formation of an adduct—3-acetyl-2-decanone (XIII), while the reaction of isobutene affords, together with dihydrofuran (XIV), also the diketones (XV) and (XVI) in proportions of 35:18:3.[54] In the presence of copper(II) acetate, the unsaturated diketone (XVII) is also obtained together with compound (XIII) (in proportions of 1:2). On the other hand, in the case of isobutene the effect of the introduction of $Cu(OAc)_2$ proved to be insignificant.[54] A detailed investigation of the reaction of hex-1-ene with acetylacetone showed that, depending on the reaction conditions, there is also a possibility of the formation of a 4,5-dihydrofuran derivative of type (XIV) together with an adduct of type (XIII).[55] The content of the dihydrofuran derivative increases with increasing acetic acid/acetylacetone ratio and manganese(III) acetate concentration and when water and trifluoroacetic acid are added:



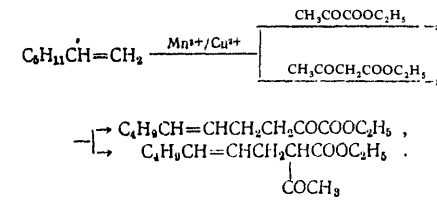
(XIII), (XVII)



(XIV), (XV), (XVI)

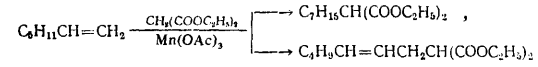
Cyclohexane-1,3-dione reacts with alkenes similarly to acetylacetone and the reaction products are substituted benzofurans.[53] Together with 1,3-diketones, the esters of carboxylic α-, β-, and γ-ketoacids and α-, β-, and γ-acetoxy-substituted aliphatic ketones have also been involved in the reaction with alkenes.[53,56,57] The selectivity in the formation of radicals on oxidation with manganese(III) acetate depends on the structure of the ketoesters. In the reaction of the acetoacetic ester, the radicals are generated from the methylene group, while in the reaction of the acetate of diacetonyl alcohol and ethyl pyruvate they are formed from the ethyl group. On the other hand, acetylpropyl acetate, methyl levulinate, and acetoxyacetone give rise to mixtures of isomeric radicals and, with decrease in the number of carbon atoms between the carbonyl and ester groups, the involvement of the methyl group in the oxidation increases appreciably.[57]

The nature of the products formed in the interaction of ketoesters with alkenes depends both on the structure of the latter and on the participation of copper(II) acetate in the reaction. In particular, styrene reacts with acetoacetic ester in the same way as with acetylacetone, forming 4,5-dihydrofuran derivatives.[53] The reaction of hept-1-ene with ethyl pyruvate and acetoacetic ester leads selectively to γδ-unsaturated ketoesters:[57]



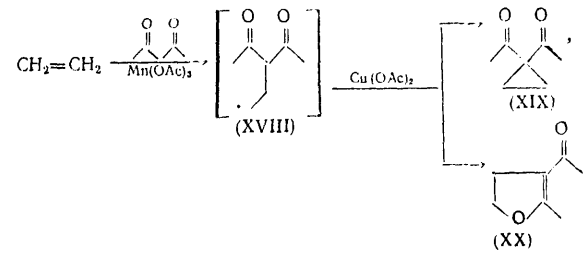
The remaining ketoesters listed above afford products with both linear and branched structures in which the double bond is in the βγ-and γδ-positions relative to the keto-group in their reactions with alkenes.[57]

Diethyl malonate has also been introduced into the reaction with alkenes initiated by manganese(III) acetate.[56,58] In the reaction with hept-1-ene, addition is observed; when the reaction is catalysed by copper(II) acetate, the main pathway becomes oxidative deprotonation:



The reaction proceeds similarly also with ethyl cyanoacetate and with diethyl butylmalonate.[56]

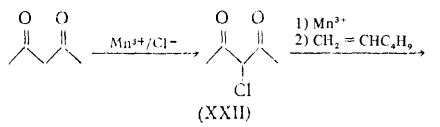
A new reaction pathway was discovered in the interaction of ethylene with β-dicarbonyl compounds.[59] The intermediate radical adduct (XVIII) undergoes oxidative 1,3-cyclisation on treatment with copper(II) acetate with formation of the *gem*-disubstituted cyclopropane (XIX) together with the dihydrofuran (XX):

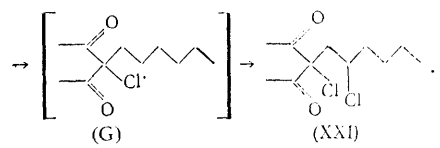


(XVIII), (XIX), (XX)

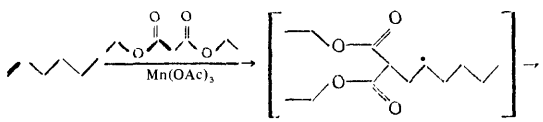
In contrast to reactions with acetylacetone and acetoacetic ester, in the interaction of ethylene with cyanoacetic and malonic esters the radical-adducts of type (XVIII) undergo oxidative elimination and prototropic isomerisation with formation of ethylidenecyanoacetic and ethylidenemalonic esters.[60]

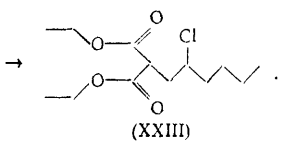
The reactions of alkenes with dicarbonyl compounds initiated by manganese(III) acetate have been modified by carrying them out in the presence of lithium chloride.[55,61] In this case, the products are either 1,3-dichloro- or monochloro-derivatives of β-dicarbonyl compounds. In particular, 3-acetyl-3,5-dichloro-2-nonanone (XXI) was isolated in the reaction of hex-1-ene with acetylacetone. The proposed reaction mechanism involved the formation of monochloroacetylacetone (XXII), the oxidative addition of the latter to the double bond of the substrate, and the subsequent chlorination of the radical-adduct (G):[55]





The mechanism of the reaction involving diethyl malonate differs from that illustrated above by the fact that lithium chloride participates in the reaction in the stage involving the oxidation of the intermediate radical-adduct and not in the radical generation stage, which leads to the monochlorosubstituted diester (XXIII):[61]

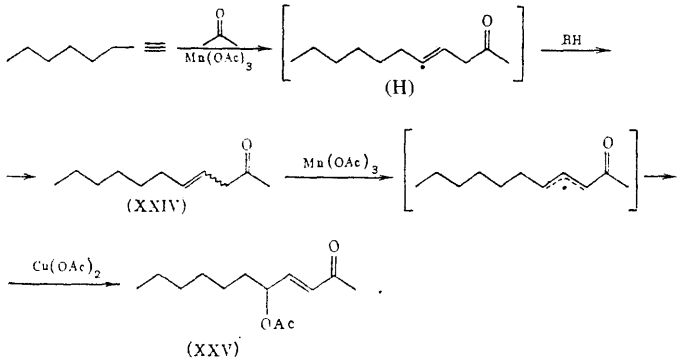




Chloromalonic ester can also be used in this reaction as the dicarbonyl compound.[62]

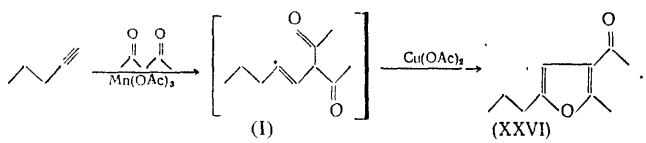
IV. Reactions of alkynes with carbonyl compounds

Alkynes have been investigated to an incomparably smaller extent than alkenes in reactions with carbonyl compounds initiated by manganese(III) acetate.[20,22,62,63] In particular, the interaction of oct-1-yne with acetone entails the initial formation of the vinyl radical-adduct (H), whose stabilisation as a result of the abstraction of hydrogen from the addend or the solvent leads to the βγ-unsaturated ketone (XXIV). The latter undergoes partial oxidation under the reaction conditions, being converted into *trans*-5-acetoxyundec-3-en-2-one (XXV):[20]



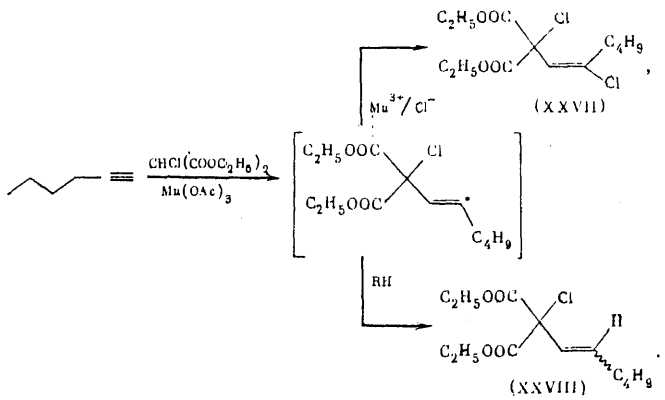
In the reactions with cyclic ketones, the primary products are βγ-unsaturated ketones, which are converted as a result of prototropic isomerisation into 2-substituted 2-cycloalkenones, in particular the analogues of dihydrojasmone.[22]

On passing from monocarbonyl to β-dicarbonyl compounds, a qualitatively new synthetic result has been achieved in reactions with alkynes. The vinyl radical-adduct (I), formed in the first stage of the reaction, undergoes oxidative cyclisation on treatment with copper(II) acetate, which leads to the furan derivative (XXVI):[63]



Acetylene, pent-1-yne, phenylacetylene, acetylacetone, and acetoacetic ester have been introduced into the above reaction.[63]

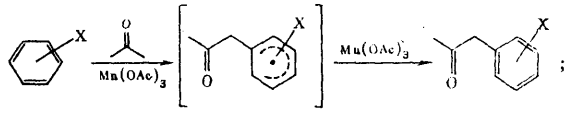
The reaction of chloromalonic ester with hex-1-yne has been investigated in the presence of the manganese(III) acetate–lithium chloride system[62] and it has been shown that the intermediate radical-adduct is stabilised by oxidative chlorination and addition of a hydrogen atom:



It has been established that the double bond in compound (XXVII) has the (*E*)-configuration, while the monochloro-derivative (XXVIII) is a mixture of geometrical isomers owing to the partial inversion of the vinyl group.[64]

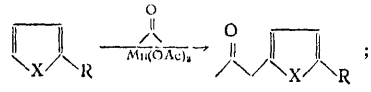
V. Reactions of arenes with carbonyl compounds

The oxoalkyl radicals generated in the oxidation of carbonyl compounds by manganese(III) acetate can interact with aromatic systems: benzene, its mono- and di-substituted derivatives, and naphthalene.[20,65–67] In the reaction with acetone, the intermediate radical-adducts are converted by oxidative elimination into *p*-, *m*-, and *o*-methylbenzyl ketones with the last predominating:[66,67]



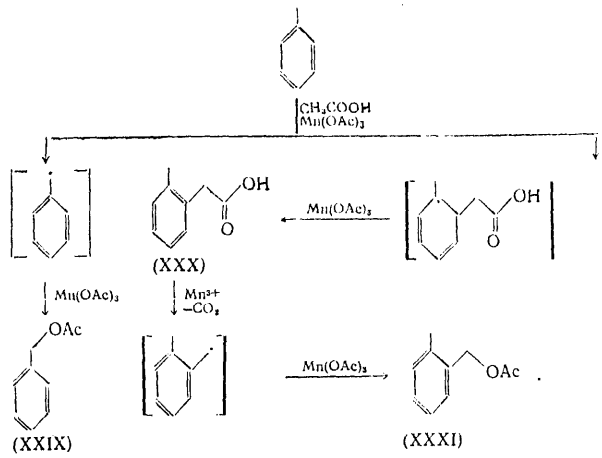
X = H, CH_3, CH_3O, Cl, CN, $COOC_2H_5$, F .

Furan, silvan, and thiophen also undergo homolytic substitution reactions with α-oxoalkyl radicals, but, in contrast to carbocyclic compounds, the reactions take place selectively via the α-carbon atom of the heteroaromatic ring:[66,68]



R = H, CH_3; X = O, S .

An analogous picture is observed in the interaction of the above heterocycles with acetylacetone.[68] The formation of benzyl acetate as a minor component has been detected in the reaction of toluene with acetone.[19] The same compound is one of the main products of the reaction of toluene with acetic acid.[69] Tolylacetic acid (XXX)—the result of the attack by the carboxymethyl radical on the aromatic nucleus—as well as methylbenzyl acetate (XXXI)—the product of the further oxidation of compound (XXX)—are formed under these conditions together with benzyl acetate (XXIX):



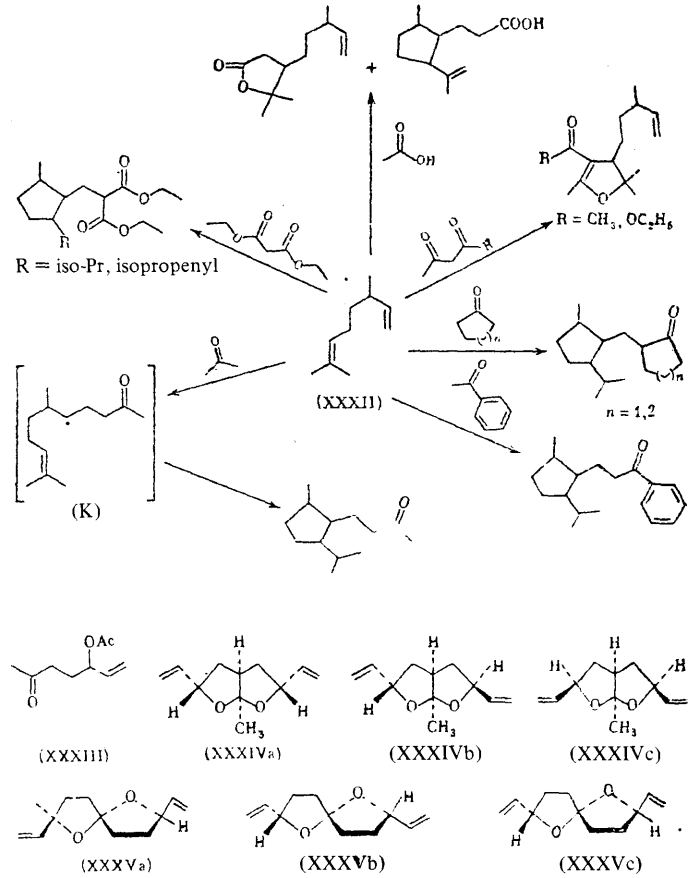
The interaction of arenes with nitromethane, leading to arylnitromethanes, is related to reactions of the type considered in this Section.[70,71]

VI. Reactions of alkadienes with carbonyl compounds

Alkadienes with isolated double bonds—octa-1,7-diene, 2,4-dimethylpenta-1,4-diene, and 2,5-dimethylhexa-1,5-diene—can interact with carbonyl compounds via both one and both double bonds,[72] which leads to 4-alkenylbutan-4-olides and bisbutan-4-olides in the reactions with acetic and cyanoacetic acids respectively. In the presence of double bonds substituted to different extents in the alkaldiene molecule, the regiochemistry depends on the nature of the carbonyl component.[73] In the reactions involving acetyl acetate and acetoacetic ester, radical attack is directed selectively to the C(6) atom of 3,7-dimethylocta-1,6-diene (XXXII), while in the reactions with cyclopentanone, cyclohexanone, acetophenone, diethyl malonate, and acetone the attack is directed to the C(1) atom. In contrast to this, the carboxymethyl radical generated from acetic acid adds to both the C(6) and the C(1) atoms.

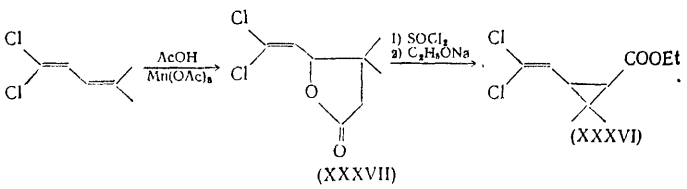
When a trisubstituted double bond is involved in the reaction, derivatives of a γ-lactone and 4,5-dihydrofuran are formed in the reactions involving acetic acid, acetylacetone, and acetoacetic ester, as in the analogous reactions of alk-1-enes.[29,31,53] The reaction involving a monosubstituted double bond leads to cyclopentane derivatives as a result of the intramolecular cyclisation of radical-adducts of type (K). The cyclopentane derivative is also the main product of the reaction of hexa-1,6-diene with acetic acid in the presence of manganese(III) acetate.[46]

An unexpected result has been obtained in the study of the reaction of acetone with butadiene.[74] It was found that the reaction products are 5-acetoxyhept-6-en-2-one (XXXIII), three isomeric 1-methyl-3,7-divinyl-2,8-dioxa-*cis*-bicyclo[3.3.0]octanes (XXXIV a–c), and three isomeric 2,7-divinyl-1,6-dioxaspiro[4,4]nonanes (XXXV a–c):



The authors proposed a mechanism involving the initial formation of compound (XXXIII), its subsequent oxidation by manganese(III) acetate, and interaction with a second butadiene molecule.[74]

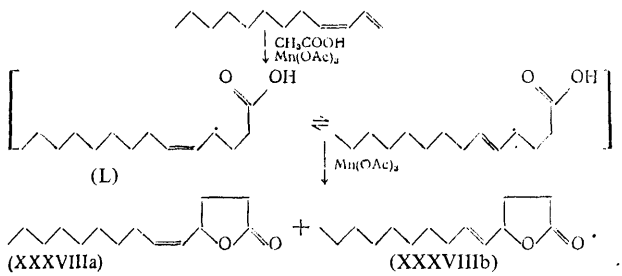
The reaction of an alkadiene with acetic acid, initiated by manganese(III) acetate, has been used as the key stage in the specific synthesis of pyrethroid (XXXVI); it involves the selective lactonisation of the tetrasubstituted alkadiene, leading to the lactone (XXXVII):[75]



(XXXVII) (XXXVI)

The analogous reaction of cyclopentadiene with acetic acid has also been described.[34]

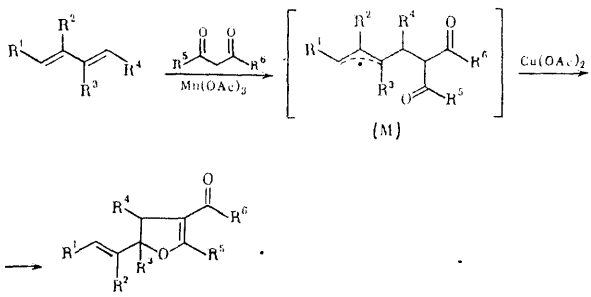
The data obtained in the stereochemical tests on the lactonisation reaction of *cis*-dodeca-1,3-diene are of individual interest.[76] It has been established that the reaction involves the inversion of the *cis*-double bond, leading to the *cis*- and *trans*-isomers of 5-tetradecen-4-olide (XXXVIIIa, b):



(XXXVIIIa) (XXXVIIIb)

The change in the configuration of the double bond apparently occurs in the *cis*-allyl radical-adduct (L). We may note that the lactones (XXXVIIIa, b) have been isolated from the females of the japanese beetle, the *cis*-isomer (XXXVIIIa) being the sex pheromone of the given species.[77]

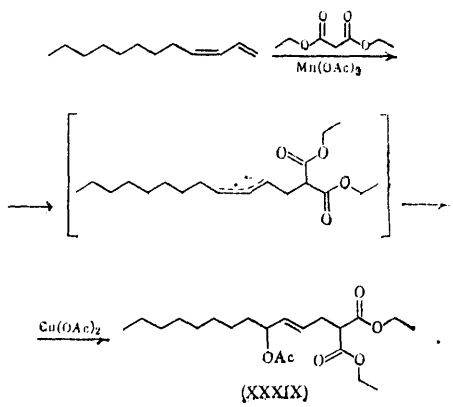
The oxidative addition of β-dicarbonyl compounds to conjugated alkadienes in the presence of manganese(III) and copper(II) acetates has also been investigated.[78–82] Butadiene, piperylene, isoprene, myrcene, methyl sorbate, crotonylideneacetone, cyclopentadiene, cyclohexadiene, bicyclopentadiene, 2,3-dimethylbutadiene, and vinylfuran were introduced as the unsaturated component, while acetylacetone, acetoacetic ester, dimedone, and diethyl acetonedicarboxylate were used as the carbonyl component. In all the cases examined, the products are derivatives of 4,5-dihydrofuran, formed as a result of the oxidative cyclisation of radical-adducts of type (M):



(M)

Reactions with isoprene and myrcene form mainly disubstituted double bonds. The activated dienes—methyl sorbate and crotonylideneacetone—react with acetylacetone preferentially via the α-carbon atom.[80]

The study of the stereochemistry of the reactions of conjugated alkadienes with β-dicarbonyl compounds has shown that *cis*-5-methylhexa-1,3-dien-5-ol and *cis*-dodeca-1,3-diene interact with acetoacetic ester and acetylacetone with partial inversion of the *cis*-double bond, while in the reaction of *trans*-5-methylhexa-1,3-dien-5-ol the configuration of the double bond is retained.[82] The degree of inversion varies depending on the structures of the unsaturated and carbonyl components: the inversion apparently occurs in the intermediate *cis*-allyl radical-adducts. The inversion of the *cis*-double bonds indicates unambiguously the formation of intermediate allyl radical-adducts, but the available experimental data did not permit a decision as to whether the inversion of the double bond of the allyl radical-adduct takes place in the coordination sphere of manganese(III) or outside it, i.e. after the decomposition of the π-allylmanganese(III) complex and the liberation of the free radical-adduct into the surrounding space,[80,82]



(XXXIX)

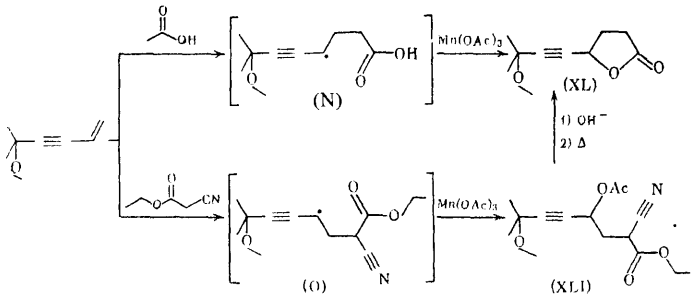
Derivatives of 4,5-dihydrofuran are obtained via the 1,2-cycloaddition of carbonyl compounds to alka-1,3-dienes. In contrast to this, the interaction of *cis*-dodeca-1,3-diene with malonic ester involves 1,4-addition with formation of the *trans*-ester (XXXIX) as a result of the stabilisation of the intermediate radical-adduct via the oxidative substitution mechanism.[82]

It has been reported that butadiene reacts with malonic ester, forming the products of both 1,2- and 1,4-addition.[81] On the other hand, in the reaction of the monoethyl ester of malonic acid cyclisation via the carboxy-group, leading to 5-vinylbutan-4-olide, takes place.[81]

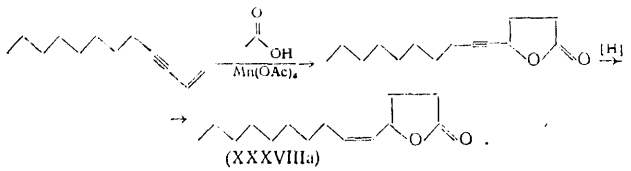
VII. Reactions of alkenynes and alkadiynes with carbonyl compounds

Conjugated alkenynes have also been involved as substrates in the interaction with carbonyl compounds initiated by manganese(III) acetate.[78,83–86] One of the motives which stimulated these investigations has been the development of the method of synthesis of 5-alkyn-4-olides—the key synthons in the synthesis of γ-butyrolactone derivatives, which are the sex pheromones of certain animals.[87–89] The lactonisation of the methyl ether of dimethylvinylethynylcarbinol was carried out by treatment with acetic acid or ethyl cyanoacetate in the presence of manganese(III) and copper(II) acetates.[85] In the former case, the reaction product was the lactone (XL), formed on cyclisation of the radical-adduct (N) via the carboxy-group. In the latter case, the radical-adduct (O) is stabilised via the 'oxidative substitution' mechanism, forming compound (XL), which is

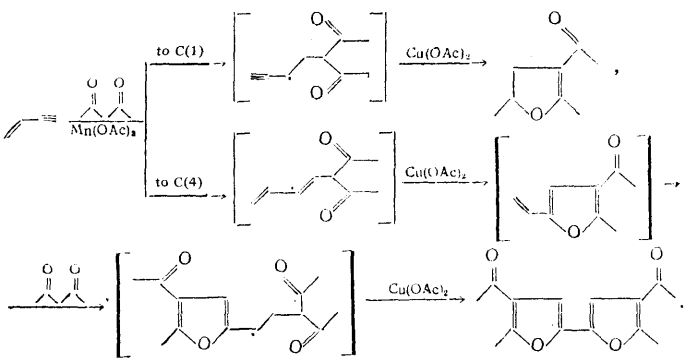
converted into the lactone (XL) as a result of alkaline hydrolysis and thermal decarboxylation-dehydration:



The method involving the direct lactonisation by treatment with acetic acid has been applied successfully in the synthesis of 5-alkyn-4-olides with different carbon skeletons, with the exception of the isoprenoid skeleton.[90] The reaction has been used as the key stage in the synthesis of (±)-*cis*-tetradec-5-en-4-olide (XXXVIIIa)—the racemate of the sex pheromone of the japanese beetle:[76]

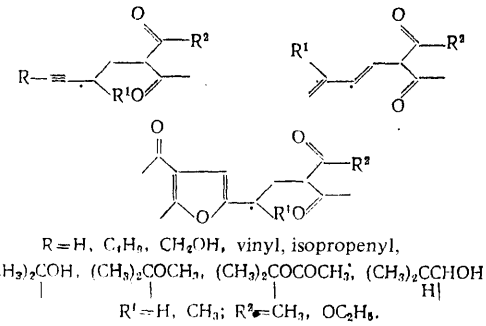


The regiochemistry of the interaction of conjugated alkenynes with β-dicarbonyl compounds in the presence of manganese(III) acetate and catalytic amounts of copper(II) acetate has been investigated[78,83,84,86] using but-1-en-3-yne (vinylacetylene) and its 2- and 4-alkyl or 2,4-dialkyl-derivatives as the substrate. In particular, it has been shown that the reaction of but-1-en-3-yne with acetylacetone is non-regioselective and leads to addition-cyclisation products with participation of the double and triple bonds:



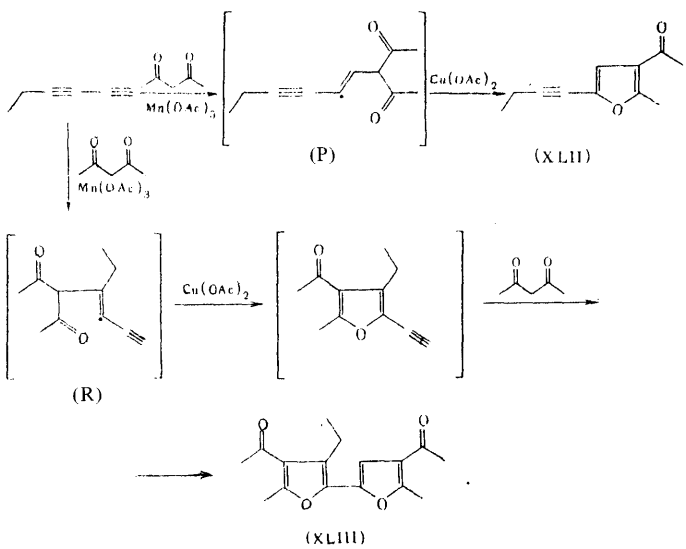
Vinylacetylene and isopropenylacetylene interact analogously with acetoacetic ester and, whereas in the former case the reactivities of both multiple bonds are comparable, in the reaction involving isopropenylacetylene an appreciable change in the regioselectivity of the process is observed with the preferential occurrence of the reaction via the double bond.[84] A similar picture has been observed for 4-substituted and 2,4-disubstituted derivatives of but-1-en-3-yne.[83,86]

The dihydrofuran and furan rings are formed in the reactions of conjugated alkenynes with β-dicarbonyl compounds as a result of the intramolecular cyclisation of secondary and tertiary propargyl, vinylpropargyl, dienyl, or α-furylalkyl radical-adducts on treatment with copper (II) acetate:



For comparison, one should note that the benzyl radical-adduct is also stabilised via cyclisation[53,54] whereas the alkyl radical-adducts, formed in the interaction of β-dicarbonyl compounds with alk-1-enes, undergo oxidative elimination on treatment with copper(II) acetate, affording γδ-unsaturated carbonyl compounds.[54,57] The set of these findings combined with data on the cyclisation of the allyl radical-adduct (Section VI) permitted the conclusion that alkyl radicals containing unsaturated groups in the α-position are stabilised, when the molecule contains at least one acetyl group, on treatment with copper acetate exclusively via the intramolecular cyclisation pathway.[84,90] It is to be expected that this postulate may have a predictive function in forecasting the structures of products of the type of reaction considered and also related processes.

The first study of the interaction of conjugated alkadiynes with β-dicarbonyl compounds initiated by manganese(III) acetate has been published recently.[91] It has been shown for the interaction of hexa-1,3-diyne with acetylacetone and acetoacetic ester that the reaction proceeds non-regioselectively with participation of both triple bonds. The intermediate radical-adducts (P) and (R) are stabilised by intramolecular cyclisation with formation of the furan derivatives (XLII) and the bifuryl derivatives (XLIII):



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Analysis of the literature data indicates a high synthetic potential of the reactions involving the introduction of functional groups into unsaturated systems by carbonyl compounds, initiated by manganese(III) acetate. Novel methods have been developed for the synthesis of compounds of different classes, including products of natural origin. Further development of this field should occur, tentatively, in the direction involving the use of new classes of substrates as the unsaturated components, a detailed investigation of the process mechanisms, and also a wider employment of reactions of this type in specific syntheses of substances of practical importance.

References

1. J K Kochi (Editor) *Free Radicals,* Wiley, New York–London–Sydney–Toronto, 1973, Vol. 1
2. F A Minisci *Acc. Chem. Res.,* 1975, **8** 165
3. M G Vinogradov *Zh. Vses. Khim. Ova im D I Mendeleeva,* 1979, 24 175
4. D C Nonhebel, J C Walton *Free-Radical Chemistry. Structure and Mechanism* (Translated into Russian), Izd. Mir, Moscow, 1977
5. G I Nikishin, E N Troyanskii *Zh. Vses. Khim. Ova im D I Mendeleeva,* 1979, **24** 169
6. G I Nikishin *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1984, 125
7. C Walling, E Heuser *Organic Reactions* (Translated into Russian), Izd. Mir, Moscow, 1966, Vol. 13, p. 130
8. G I Nikishin, M G Vinogradov, S P Verenchikov *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1969, 1835
9. G I Nikishin, M G Vinogradov, S P Verenchikov, et al. *Zh. Org. Khim.,* 1972, **8** 539
10. G I Nikishin, M G Vinogradov, G P Il'ina *Zh. Org. Khim.,* 1972, **8** 1401
11. G I Nikishin, M G Vinogradov, G P Il'ina *Synthesis,* 1972, 376
12. M G Vinogradov, G P Il'ina, A V Ignatenko, G I Nikishin *Zh. Org. Khim.,* 1972, **8** 1403
13. M G Vinogradov, G P Il'ina, G I Nikishin *Zh. Org. Khim.,* 1974, **10** 1153
14. M G Vinogradov, I P Kovalev, G I Nikishin *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1984, 384
15. M G Vinogradov, P A Direi, G I Nikishin *Zh. Org. Khim.,* 1976, **12** 527
16. M Okano, T Aratani *Bull. Chem. Soc. Jpn.,* 1976, **49** 2811
17. M G Vinogradov, P A Direi, G I Nikishin *Zh. Org. Khim.,* 1978, **14** 2043
18. M G Vinogradov, S P Verenchikov, G I Nikishin *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1971, 200
19. E I Heiba, R M Dessau *J. Am. Chem. Soc.,* 1971, **93** 524
20. M G Vinogradov, S P Verenchikov, T M Fedorova, G I Nikishin *Zh. Org. Khim.,* 1975, **11** 947
21. E I Heiba, R M Dessau *J. Am. Chem. Soc.,* 1972, **94** 2888
22. M G Vinogradov, N A Direi, G I Nikishin *Zh. Org. Khim.,* 1977, **13** 2498
23. R M Dessau, E I Heiba *J. Org. Chem.,* 1974, **39** 3457
24. M Chatzopoulos, J Montheard *C. R. Seances Acad. Sci.,* 1977, **C284** 133
25. N Fukayima, M Okano, T Aratani *Chem. Ind.,* 1980, 86
26. O N Petrenko, M G Vinogradov, S P Verenchikov, et al., *Zh. Org. Khim.,* 1978, **14** 1386
27. M G Vinogradov, O N Petrenko, S P Verenchikov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1979, 1420
28. M G Vinogradov, O N Petrenko, S P Verenchikov, G I Nikishin, *Zh. Org. Khim.,* 1980, **16** 714
29. G I Nikishin, Yu N Ogibin, E N Troyanskii *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1974, 483
30. J B Bush, H Finkbeiner *J. Am. Chem. Soc.,* 1968, **90** 5903
31. H Finkbeiner, J B Bush *Faraday Discuss. Chem. Soc.,* 1968, 150
32. E I Heiba, R M Dessau, W J Koehl *J. Am. Chem. Soc.,* 1968, **90** 5905
33. E I Heiba, R M Dessau, P G Rodewald *J. Am. Chem. Soc.,* 1974, **96** 7977
34. M Hoekman, G L Fagan, A D Webb, R E Kepner *Agr. Food Chem.,* 1982, **30** 920
35. US P. 3 758 513
36. B. P. 1 219 332
37. M Okano *J. Sci. Hiroshima Univ.,* 1976, **A40** 169; *Ref. Zh. Khim.,* 1977, 11Zh223
38. M Okano *Bull. Chem. Soc. Jpn.,* 1976, **49** 1041
39. K Witkiewicz, Z Chabudzinski *Rocz. Chem.,* 1976, **50** 1545
40. K Witkiewicz, Z Chabudzinski *Rocz. Chem.,* 1977, **51** 825
41. K Witkiewicz, Z Chabudzinski *Rocz. Chem.,* 1977, **51** 475
42. K Witkiewicz, Z Chabudzinski *Rocz. Chem.,* 1977, **51** 2155
43. J R Gilmore, J M Mellor *J. Chem. Soc.(C),* 1971, 2355
44. A Kasahara, R Saito, T Izumi *Bull. Chem. Soc. Jpn.,* 1973, **46** 2610
45. W J Klein *Rec. Trav. Chim.,* 1975, **94** 151
46. M Okano *Chem. Ind.,* 1972, 423
47. W E Fristad, J R Peterson *J. Org. Chem.,* 1985, **50** 10
48. E J Corey, M Kang, *J. Am. Chem. Soc.,* 1984, **106** 5384
49. M Okano *Chem. Lett.,* 1973, 165
50. K Witkiewicz, Z Chabudzinski *Bull. Acad. Pol. Sci. Ser. Sci. Chim.,* 1978, **26** 753
51. N Ito, H Nishino, K Kurosava *Bull. Chem. Soc. Jpn.,* 1983, **56** 3527
52. W J Klein *Rec. Trav. Chim.,* 1975, **94** 48
53. E I Heiba, R M Dessau *J. Org. Chem.,* 1974, **39** 3456
54. M G Vinogradov, T M Fedorova, G I Nikishin *Zh. Org. Khim.,* 1976, **12** 1175
55. M G Vinogradov, V N Dolinko, G I Nikishin *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1982, 2313
56. M G Vinogradov, T M Fedorova, G I Nikishin *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1974, 2384
57. M G Vinogradov, T M Fedorova, G I Nikishin *Zh. Org. Khim.,* 1975, **11** 1380
58. G I Nikishin, M G Vinogradov, T M Fedorova *J. Chem. Soc., Chem. Commun.,* 1973, 693
59. M G Vinogradov, O N Petrenko, S P Verenchikov, G I Nikishin *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1979, 1916
60. O N Petrenko, Abstract of Candidate's Thesis in Chemical Sciences, Institute of Organic Chemistry, USSR Academy of Sciences, Moscow, 1981
61. M G Vinogradov, V N Dolinko, G I Nikishin *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1984, 375
62. M G Vinogradov, V N Dolinko, G I Nikishin *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1984, 2065
63. M G Vinogradov, V N Dolinko, G I Nikishin *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1981, 700
64. W A Waters (Editor) *Free Radical Reactions,* Univ. Park Press, London, 1973

65. M G Vinogradov, S P Verenchikov, G I Nikishin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, 1674
66. R S Min, V S Aksenov, M G Vinogradov, G I Nikishin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 2292
67. M E Kurz, V Baru, P Nguyen *J. Org. Chem.*, 1984, **49** 1603
68. R S Min, V S Aksenov, M G Vinogradov, G I Nikishin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 2315
69. E I Heiba, R M Dessau, W J Koehl *J. Am. Chem. Soc.*, 1969, **91** 138
70. M E Kurz, T R Chen *J. Chem. Soc., Chem. Commun.*, 1976, 968
71. M E Kurz, T R Chen *J. Org. Chem.*, 1978, **43** 239
72. US P. 3 758 514
73. F J McQuillin, M Wood *J. Chem. Soc., Perkin Trans. I*, 1976, 1762
74. M G Vinogradov, M S Pogosyan, A Ya Shteinshneider, G I Nikishin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 842
75. V K Promonenkov, O A Korotkova *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1978, **23** 170
76. G G Melikyan, D A Mkrtchyan, K V Lebedeva, et al. *Khim. Prir. Soedin.*, 1984, 98
77. J H Tumlinson, M G Klein, R E Doolittle, et al. *Science*, 1977, **197** 789
78. G G Melikyan, D A Mkrtchyan, Sh O Badanyan *Khim. Geterotsikl. Soedin.*, 1980., 884
79. M G Vinogradov, N L Radyukina, M S Pogosyan, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 1949
80. M G Vinogradov, M S Pogosyan, A Ya Shteinshneider, G I Nikishin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 2077
81. M S Pogosyan, Abstract of Candidate's Thesis in Chemical Sciences, Institute of Organic Chemistry, USSR Academy of Sciences, Moscow, 1983
82. G G Melikyan, D A Mkrtchyan, V M Mkrtchyan, Sh O Badanyan *Khim. Geterotsikl. Soedin.*, 1985, 308
83. G G Melikyan, D A Mkrtchyan, Sh O Badanyan *Arm. Khim. Zh.*, 1981, **34** 1011
84. G G Melikyan, D A Mkrtchyan, Sh O Badanyan *Khim. Geterotsikl. Soedin.*, 1982, 19
85. G G Melikyan, D A Mkrtchyan, Sh O Badanyan *Arm. Khim. Zh.*, 1982, **35** 163
86. G G Melikyan, A B Sargsyan, Sh O Badanyan *Arm. Khim. Zh.*, 1986, **39** 228
87. W H Pirkle, P E Adams *J. Org. Chem.*, 1979, **44** 2169
88. U Ravid, R M Silverstein, L R Smith *Tetrahedron*, 1978, **34** 1449
89. Y Miyashita, K Mori *Agric. Biol. Chem.*, 1981, **45** 2521
90. D A Mkrtchyan, Abstract of Candidate's Thesis in Chemical Sciences, Institute of Organic Chemistry, Academy of Sciences of the Armenian SSR, Erevan, 1986
91. G G Melikyan, A B Sargsyan, Sh O Badanyan *Khim. Geterotsikl. Soedin.*, 1986, 562

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The electrochemistry of sandwich and bent sandwich transition metal complexes

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ABSTRACT. The result of electrochemical studies of homo- and hetero-ligand sandwich as well as bent sandwich biscyclopentadienyl complexes of transition metals are surveyed and described systematically. The existence of a linear relation between the redox potentials of these complexes and the gas-phase ionisation potentials of the corresponding metals and their ions is demonstrated. The electrochemical reactions catalysed by sandwich and bent sandwich complexes and the possibilities of the electrochemical synthesis of the above complexes and metal complex catalysts based on them are examined.
The bibliography includes 164 references.

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I. Introductions

Electrochemical studies on sandwich complexes (SC) of transition metals began to develop soon after the synthesis of ferrocene in 1951.[1] During the period which has elapsed since then, a large number of SC have been investigated by electrochemical methods. The application of polarography, cyclic voltammetry, and other methods have made it possible to obtain important information about the oxidation-reduction properties of these compounds in the condensed phase, i.e. about the reactivity of the SC in oxidation-reduction reactions. This information is extremely important for the correct understanding of the mechanisms of many reactions involving SC, the selection of optimum conditions in their synthesis and electrochemical synthesis, and the solution of important structural problems in the chemistry of the large class of complexes considered. Furthermore, the electrochemical methods provide valuable information about the distribution of electron density in the molecule and about the relative disposition of the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals.

Since the publication of the last reviews[2,3] on the electrochemistry of SC more than 10 years have elapsed and there has been so far no systematic consideration of bent sandwich complexes (BC) of the type Cp_2ML_n ($Cp = \eta^5\text{-}C_5H_5$ = cyclopentadienyl). There has been a significant increase in the number of publications in recent years on the electrochemical investigation of SC and BC. Individual studies in this field have been mentioned in reviews[4,5] and monographs.[6–8]

The author's aim has been to trace the principal characteristic features of the variation of the oxidation-reduction properties of SC and BC as a function of the nature of the metal and of its formal oxidation state and to find a parameter, common to SC and BC, which determines the reactivity of these complexes in oxidation-reduction reactions rather than the greatest possible accumulation of factual data.

The properties of the primary products of the electrochemical reactions of SC and BC are also examined in a number of instances. The review does not include studies dealt with in previous surveys[2,3] with the exception of cases which have been subjected to a repeated, more accurate analysis.

II. Electrochemical reactions of sandwich complexes

Sandwich complexes constitute a class of organometallic compounds in which the metal atom is located between two plane-parallel (or approximately parallel) aromatic π-ligands of the type $\eta^5\text{-}C_5H_5^-$, $\eta^6\text{-}C_6H_6$, $\eta^7\text{-}C_7H_7^+$, $\eta^8\text{-}C_8H_8^{2-}$, etc. The bond between the metal and the ligand is formed as a result of the overlap of the *d* orbitals of the metal and the π orbitals of the ligand. A characteristic feature of the SC is that their metal atom is surrounded by two bulky ligands and that its direct contact with solvent molecules is difficult. The latter prevents the appearance of specific solvation effects. As a result, the solvation effects in the redox reactions of SC are determined mainly by the electrostatic component, which is approximately the same for isostructural complexes bearing equal charges.[7,9,10] This makes it possible to investigate and compare electron transfer reactions in the series of SC in various solvents. The transfer reactions are usually uncomplicated by chemical reactions of the electrochemically generated species with the solvent molecules.

Quantum-chemical study of SC has shown[11-13] that the atomic orbitals (AO) of the metal make the main contribution to their HOMO and LUMO on which the changes of electron density as a result of the occurrence of oxidation-reduction reactions are localised (redox orbitals). Reactions occurring with a change in the formal oxidation state of the metal are therefore characteristic of SC.

1. Metallocenes

Reversible one-electron reactions according to the scheme

$$Cp_2M^{2+} \overset{e}{\rightleftarrows} Cp_2M^{+} \overset{e}{\rightleftarrows} Cp_2M \overset{e}{\rightleftarrows} Cp_2M^{-} \qquad (1)$$

are characteristic of the majority of compounds of this kind. The electron transfer in these systems is of the outer-sphere type[2,3] and the reversibility of the electrode reactions of the majority of metallocenes suggest that the transition from the oxidised form to the neutral form and further to the reduced form does not entail significant changes in the coordination sphere and geometry of the complexes, at least during the electrochemical measurements.

Depending on the nature of the metal and the solvent, the possibility of the electrochemical generation of members of the redox series (1) and their stability, especially the stability of Cp_2M^{2+} and Cp_2M^-, change significantly. As a result of the employment of solvents which are extremely stable in the anodic and cathodic potential regions, in which the reactive members of the redox series (1) are most stable, only in recent years has it been possible to identify the majority of the products of the redox reactions of metallocenes, which are possible in principle. We shall consider the electrochemical behaviour of metallocenes belonging to different Groups in the Periodic System.

Group IVB elements do not form stable metallocenes with a plane-parallel disposition of the rings.[14,15] Among the Group VB metallocenes, only vanadocene has been thoroughly investigated. It has been demonstrated by polarographic and cyclic voltammetric methods at Hg and Pt electrodes[16-18] that Cp_2V undergoes one-electron reversible reduction in tetrahydrofuran (THF) with the formation of the metastable anion Cp_2V^- and one-electron reversible oxidation with formation of the cation Cp_2V^+. Further oxidation of Cp_2V^+ to the dication Cp_2V^{2+} takes place irreversibly, which is believed[16,17] to be associated with the transition in the Cp_2V^{2+} generation stage from the plane-parallel to the bent sandwich structure (*EC*-process, where *E* and *C* represent respectively the electrochemical and chemical stages) as a result of the interaction with solvent molecules or other suitable ligands.

The electrochemical behaviour of the vanadocene analogues Cp_2Nb and Cp_2Ta has not been investigated because of their metastability.[19,20]

The electrochemistry of Group VIB metallocenes has been studied in detail in relation to Cp_2Cr. It has been shown by cyclic voltammetry at the Pt electrode[16,17] that chromocene is reduced reversibly in THF or acetonitrile to the Cp_2Cr^- anion with transfer of one electron. Preparative electrolysis at the limiting current Cp_2Cr reduction potentials does not, however, make it possible to obtain and characterise the Cp_2Cr^- anion in solution because of its low stability. It has also been shown that chromocene can undergo reversible one-electron oxidation to the unstable cation Cp_2Cr^+.[16,17,21]

Molybdenocene and tungstocene, whose stability is low (lifetime $\sim 10^{-2}$ s), have been generated and identified by cyclic voltammetry involving two-electron reduction of the corresponding metallocene dichlorides.[22,23] The potentials of the redox couples Cp_2Mo^0/Cp_2Mo^+ and Cp_2C^0/Cp_2M^+ are respectively −1.25 and −1.48 V.† These are the most readily oxidisable metallocenes among all those known. If E^0 = −0.68 V is adopted for the Cp_2Cr^0/Cp_2Cr^+ redox couple,[16] one may conclude that, within the framework of a single subgroup of the Periodic System, an increase in the atomic number of the metal facilitates the abstraction of an electron from the corresponding metallocene and not conversely, as had been postulated earlier in a review.[2]

†All the potentials in this review are quoted relative to the aqueous saturated calomel electrode.

Among the biscyclopentadienyl complexes of Group VIIB metals, only the manganese compound is known at present, although manganocene cannot be included among metallocenes because of its ionic character.[24] A substituted analogue of this compound [$(C_5Me_5)_2Mn$], in which the metal–ring bond is covalent and which has the metallocene structure, has been described.[25] It has been shown by cyclic voltammetry at a Pt electrode[25] that permethylmanganocene is reduced in acetonitrile to the $(C_5Me_5)_2Mn^-$ anion with transfer of one electron and is oxidised to the cation $(C_5Me_5)_2Mn^+$. Both processes are electrochemically reversible but the stability of the products has not been reported.

Like molybdenocene and tungstocene, rheniocene belongs to the class of relatively unstable metallocenes. These metallocenes are formed by the photolysis of the corresponding hydrides Cp_2MH in low-temperature matrices and their sandwich structure has been demonstrated by IR spectroscopy.[26-28] Rheniocene can be generated by cyclic voltammetry at a Hg electrode in THF by the two-electron reduction of the dimer $Cp_2Re-ReCp_2$ with the subsequent oxidation of the anion $[CpRe(\eta^3\text{-}C_5H_5)]^-$ formed under these conditions.[29] E^0 = −1.06 V for the Cp_2Re^0/Cp_2Re^+ redox couple.

Ferrocene, the first of the metallocenes synthesised, is undoubtedly the most thoroughly investigated representative of the Group VIIIB metallocenes. The Cp_2Fe^0/Cp_2Fe^+ redox couple is one of the most highly reversible systems. Numerous studies have been devoted to it.[2,3] In recent years, it has been possible to show, using solvents stable at high cathodic and anodic potentials, that ferrocene can be oxidised to the dication and can be reduced to the anion. In $AlCl_3$/1-butylpyridinium chloride melts (in 1 : 1 molar proportions), the $(C_5Me_5)_2Fe^+$ cation undergoes reversible one-electrochemical reduction at a carbon glass electrode to the stable dication $(C_5Me_5)_2Fe^{2+}$, which has been characterised by UV spectroscopy.[30] The electrochemical behaviour of the ferrocenium cation and of its permethylated analogue has also been investigated in liquid sulphur dioxide.[31] It has been shown by cyclic voltammetry at a Pt electrode that the reversible one-electron oxidation of Cp_2Fe^+ leads to the formation of the unstable dication Cp_2Fe^{2+}, the decomposition products of which partly block the electrode. The reversible one-electron oxidation of the decamethyl analogue under these conditions results in the formation of the high-spin dication $(C_5Me_5)_2Fe^{2+}$ (magnetic moment μ = 2.73 B.M.), which is stable at −30 °C.

The high purity of the solvent and electrochemical measurements at temperatures between −45° and −30 °C made it possible[32,33] to observe the reversible reduction of ferrocene to the relatively unstable anion Cp_2Fe^- at Pt and carbon glass electrodes in dimethylformamide (DMF) or dimethoxyethane. It has also been shown that an increase in temperature leads to the occurrence of the two-electron reduction of ferrocene via the *ECE*-mechanism involving the formation of an unidentified intermediate X:[32]

$$Cp_2Fe \overset{e}{\rightleftarrows} Cp_2Fe^- \rightarrow X \overset{e}{\rightarrow} 2Cp^- + Fe^0.$$

In order to elucidate the nature of X, a study has been made of the electrochemical reduction of substituted ferrocenes in DMF and THF under a CO atmosphere.[34] It is possible to identify the unstable anion $CpFe(CO)_2^-$, which interacts with MeI to form $CpFe(CO)_2Me$ or is oxidised at a Pt electrode to the radical $CpFe(CO)_2^{\cdot}$, which rapidly dimerises to the complex $[CpFe(CO)_2]_2$ with an Fe–Fe bond. These data led to the conclusion that the intermediate X is the $CpFe^{\cdot}$ + Cp^- mixture.

It has been noted[33] that the formal rate constant for the heterogeneous electron transfer to the ferrocene molecule ($k_e \cong 10^{-3}$ cm s^{-1}) is much lower than the analogous constant for the Cp_2Fe^0/Cp_2Fe^+ couple ($k_e > 10^{-1}$ cm s^{-1}). According to the authors,[33] this difference is due to the increase in the internal reorganisation energy on formation of Cp_2Fe^- as a result of the transition of one of the Cp rings from the planar η^5-conformation to the non-planar η^4-conformation, which makes it possible to retain the energetically most favourable 18-electron configuration of the metal atom in the anion. It is notable that this is not the only possible explanation of the decrease in k_e on passing from the Cp_2Fe^0/Cp_2Fe^+ redox system to Cp_2Fe^0/Cp_2Fe^-. In contrast to its oxidation, when ferrocene is reduced an electron is transferred to an antibonding MO which should undoubtedly entail an increase in the process activation energy and hence a decrease in k_e.

The kinetics of the heterogeneous electron transfer involving substituted ferrocenes and the Cp_2Co^+ ion in acetonitrile at a semiconductor (*p*-InP)/electrolyte interface have been investigated by cyclic voltammetry.[35] The above semiconductor is characterised by the presence of a forbidden gap and also a potential range at the limits of which the composition of the oxide layers changes as a result of electrode reactions involving the material of the electrode. Reversible electrode reactions are characteristic of alkylated ferrocenes, whose $Cp^*_2M^0/Cp^*_2M^+$ redox transition potential (Cp* is a substituted cyclopentadienyl) lies within this region, whereas irreversible electrode reactions are characteristic of the acylated ferrocene and Cp_2Co^+, whose potentials E^0 correspond to the limits of this region or are outside its limits. Furthermore, irreversible electrode reactions become characteristic also of complexes of the first type (with potentials E^0 lying outside the forbidden gap) when the potential at which the polarisation of the electrode changes moves outside the limits of the gap.

The electrochemical behaviour of heavier ferrocene analogues—ruthenocene and osmocene—has a number of characteristic features. Ruthenocene undergoes irreversible two-electron oxidation at a Pt electrode in acetonitrile, forming probably the dication.[2,3] Under the same conditions, the permethylated ruthenocene is oxidised reversibly to a stable cation which has been characterised by EPR spectroscopy ($e^3_{2g}a^2_{1g}$ electronic configuration), but its subsequent oxidation is irreversible.[36] The stepwise two-electron oxidation of Cp_2Ru, which is irreversible at each stage, has been observed by cyclic voltammetry in the $AlCl_3$/1-butylpyridinium chloride melt (with a molar ratio in excess of unity) at a carbon glass electrode.[37]

The oxidation of osmocene is characterised by the stepwise abstraction of two electrons, which is irreversible at each stage.[2,3] The preparative one-electron oxidation of Cp_2Os leads to the formation of a cation, which has been isolated as the salt $Cp_2Os^+BF_4^-$.[2] The difference in the electrochemical behaviour of ferrocene, ruthenocene, and osmocene is associated with the fact, according to Gale et al.,[30] that, with increase in the atomic number of the metal, the stability of the half-occupied d_5 electronic configuration of the singly charged cation diminishes and the formation of doubly charged cations becomes preferable. It is also noteworthy that the redox reactions of Cp_2Ru and Cp_2Os should be studied on solid electrodes, since on mercury these reactions are complicated by the formation of the corresponding organomercury compounds $(Cp_2M)_2Hg$.[2,3]

The cobaltocenium cation, formed as a result of the reversible one-electron oxidation of cobaltocene, is an isoelectronic analogue of ferrocene.[2,3,38,39] Cobaltocene can also undergo reversible one-electron reduction to the Cp_2Co^- anion.[38–41] In aqueous solutions, Cp_2Co^- is stable in an alkaline medium (pH > 8), while in an acid medium it is protonated at the ligand with formation of cyclopentadiene(cyclopentadienyl)cobalt, which is in its turn oxidised chemically at pH < 4 by the protons of the medium with liberation of H_2 and the formation of Cp_2Co^+.[39] It has been suggested that in acid media the $(C_5H_4COOR)_2Co^+$ (R = H or Me) ions can undergo electrochemical reduction at the substituent with formation of the corresponding aldehyde and alcohol derivatives. In non-aqueous media, the electrochemically generated Cp_2Co^- is protonated by phenols at the ligand with formation of $CpCo(\pi\text{-}C_5H_6)$ but without the formation of the hydride.[41]

The electrochemical behaviour of the heavier cobaltocene analogue—rhodiocene—has also been investigated.[42] It has been shown by polarographic and cyclic voltammetric methods at Hg and Pt electrodes that the Cp_2Rh^+ cation is reduced in acetonitrile in accordance with the scheme

$$Cp_2Rh^+ \overset{e}{\rightleftarrows} Cp_2Rh \overset{e}{\rightleftarrows} Cp_2Rh^-$$
$$\downarrow$$
$$(Cp_2Rh)_2$$

The intermediate rhodiocene is unstable under the conditions of preparative electrolysis and dimerises. Irreversible electrochemical oxidation of the dimer is accompanied by the regeneration of the Cp_2Rh^+ cation. There are no reliable data for the redox reactions of iridiocene and its ions.

Nickelocene, which is reduced most readily among all the known metallocenes, is the last as regards the position of the metal in the Periodic System among the class of metallocenes investigated.[16,17] However, the mechanism of this process is fairly complex. Under the conditions of the preparative electrochemical reduction of Cp_2Ni, a series of products are formed, one of which has been identified as $CpNi(\eta^3\text{-}C_5H_7)$.[17] At a reduced temperature (–58 °C) in DMF, nickelocene undergoes one-electron reduction to the anion Cp_2Ni^-, which is stable under these conditions, the electrode reaction being characterised by a slow charge-transfer stage. According to the author,[17] this is associated with the fact that the electron transfer is accompanied by a change in the solvation shell and/or in the structure of the complex (transition to a "slipped sandwich structure"). The electrochemically generated Cp_2Ni^- reacts with carbon monoxide[43] via the *CEC*-mechanism with decomposition of the sandwich structure:

$$Cp_2Ni^- \rightarrow Cp^- + CpNi \xrightarrow{CO,e} [CpNi(CO)]^- \xrightarrow{3CO} Cp^- + Ni(CO)_4.$$

Apart from the reduction reaction, the electrochemical oxidation reactions of nickelocene, which are electrochemically reversible, have been investigated. Thus the one-electron oxidation of Cp_2Ni in THF, DMF, and acetonitrile at a Pt electrode[16,17] and in the Al/1-butylpyridinium chloride melt at a carbon glass electrode[44] lead to the formation of the Cp_2Ni^+ cation. The subsequent oxidation of Cp_2Ni^+ in acetonitrile at a Pt electrode[45] and in the melt mentioned above[44] is also reversible and is completed by the formation of the Cp_2Ni^{2+} dication, which has been characterised by UV spectroscopy.[44] The dication interacts extremely readily with nucleophiles.

Thus extensive experimental data have accumulated on the redox reaction of metallocenes. Together with the Cp_2M^0/Cp_2M^+ redox transition known previously, the possibility of the Cp_2M^0/Cp_2M^- and Cp_2M^+/Cp_2M^{2+} redox transitions has been demonstrated for a series of metallocenes. The experimentally established forms of the metallocenes are presented in Table 1.

In earlier studies,[8,16] a similar Table resembled in its form an inverted triangle whose height was determined by the number of the known metallocenes or their ions with the d^6 electronic configuration, which is associated with the high stability of these 18-electron complexes. By virtue of the vigorous investigations the metastable metallocenes derived from the transition metal at the beginning of the series and the highly reactive Cp_2M^- and Cp_2M^{2+} ions, the form of Table 1 has changed significantly at the present time.

Table 1. Classification of the experimentally detected metallocenes and their ions in terms of the electronic configuration of the metal in Cp_2M.

d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9
V^+	V Cr^+ Mo^+ W^+	V^- Cr Mo W Mn^+ * Re^+ Fe^{3+} Ru^{3+}	Cr^- Mn * Re Fe^+ Ru^+	Mn^-,* Fe Ru Co^+ Rh^+ Ni^{2+}	Fe^- Co Rh Ni^+	Co^- Rh^- Ni	Ni^-

*Data for $(C_5Me_5)_2Mn$ are presented.

2. Homo- and hetero-ligand sandwich complexes with other π-ligands

Redox reactions involving a change in the formal oxidation state of the metal are characteristic of all the homo- and hetero-ligand SC as well as metallocenes.[2,5,8,46]

Diarenemetals. The metal in these neutral complexes is formally zerovalent and $(arene)_2M^0/(arene)_2M^+$ transitions are therefore characteristic of these compounds. Examples of such systems are provided by the $(arene)_2Cr$ complexes (where arene = C_6H_6, C_6Me_6, $C_6H_5-C_6H_5$, etc.)[2,47,48] and $(C_6H_6)_2Mo$.[2]

The electrochemical behaviour of the cationic complexes $(C_6H_6)_2Fe^{2+}$, $(C_6Me_6)_2Fe^{2+}$,[49] $(C_6Me_6)Ru^{2+}$,[50] and $(C_6Me_6)Co^{2+}$ [51] has also been investigated. It has been shown by polarographic and cyclic voltammetric methods at Hg and carbon glass electrodes in proton-donating and aprotic media that all of these complexes undergo multistage electrochemical reduction, reversible at each stage, according to the scheme

$$(arene)_2M^{2+} \overset{e}{\rightleftharpoons} (arene)_2M^{+} \overset{e}{\rightleftharpoons} (arene)_2M.$$

It has been shown for $(C_6Me_6)Ru^{2+}$ [50] that the replacement of CH_2Cl_2 by the more strongly coordinated acetonitrile leads to a greater change in the relative solvation energy (E_S) in the $(arene)_2Ru^{2+}$ transition, as a result of which the dication is electrochemically reduced to the neutral complex in a single two-electron stage. It is of interest that the reduction of $(C_6Me_6)Ru^{2+}$ is described by the *EEC*-scheme, where the chemical stage represents the transition from (η^6-arene)$_2$Ru to (η^6-arene)Ru(η^4-arene). Here it is appropriate to consider also the fundamental problem of oxidation-reduction reactions—the problem of the consecutive or multistage transfer of two electrons. If an oxidation-reduction reaction of this type is represented by the scheme

$$A \pm e \underset{}{\overset{E_1^0}{\rightleftharpoons}} A^{-(+)} \pm e \overset{E_2^0}{\rightleftharpoons} A^{2-(2+)},$$

it becomes evident that the quantity $\Delta E^0 = E_1^0 - E_2^0$ reflects the change in the gas-phase ionisation potential I_D in the transition from A to A^+ (for oxidation) or the change in the electron affinity in the transition from A to A^- (for reduction) and, furthermore, the change ΔE_S in the transition from $A^+(A^-)$ to $A^{2+}(A^{2-})$. The quantity ΔE^0, which is significantly smaller than ΔI_D, is determined by the greater solvation energies of A^{2+} and A^{2-} compared with A^+ and A^-. As a result, solvation effects can lead to a transition from the multistage ($1e^- + 1e^-$) mechanism to the apparently single-stage ($2e^-$) mechanism, as happens in the case considered above.[50] On the other hand, the true two-electron transfer, determined by the fact that the transfer of the second electron is energetically more favourable than that of the first, is observed only when the transfer of the first electron is accompanied by structural changes in the SC (*ECE*-process). The AO of the metal usually make the main contribution to the HOMO and LUMO of the sandwich complexes, as a result of which the HOMO and the LUMO have the *d* character. This leads to a relatively weak electronic influence of the substituents in the π-ligands on the quantities E_1^0 and E_2^0.[52] For example, E^0 changes only by approximately 0.2 V for the $(C_6H_{6-x}Me_2)Cr(CO)_3/C_6H_{6-x}Me_x)Cr(CO)_3^-$ redox couples in the transition from $x = 0$ to $x = 6$.[53,54] It is therefore difficult to suppose that the introduction of substituents into the π-ligand can induce the $1e^- + 1e^- \rightarrow 2e^-$ transition. Explicit reversible two-electron processes (the difference between the potentials of the cathodic and anodic peaks on cyclic voltammograms, amounting to 30 mV, can serve as an electrochemical sign of their occurrence) are observed only for certain SC and semi-sandwich complexes. As an example, one may quote the reduction of $(arene)Cr(CO)_3$,[54] where the operation of the $2e^-$ mechanism is a consequence of the $\eta^6 \rightarrow \eta^4$ haptoisomerisation of the arene ligand in the radical-anion stage. An analogous $2e^-$ process, accompanied by a change in the hapto-binding of the ligand, is also characteristic of the reduction of $Cp(\eta^6\text{-}C_6Me_6)Ir^{2+}$.[55] In all these cases, the structural changes occurring in the stage involving the formation of the one-electron reduction products lead to species which are reduced more readily than the initial complexes.

The $(arene)_2Cr^0/(arene)_2Cr^+$ redox couples together with ferrocene[56] have been recommended by IUPAC as internal standards and "pilot" ions for the comparison of the potentials $E_{1/2}$ measured in different solvents. The greater radius and spherical shape of the molecule, the solubility of both redox forms, the high reversibility of the redox reaction, the virtually complete absence of specific solvation effects as a consequence of the shielding of the metal by bulky ligands, and the insignificant change in the electrostatic components of ΔE_S in the transition from one solvent to another [as a consequence of the low surface charge of the complexes], make the $(arene)_2Cr^0/(arene)_2Cr^+$ systems, together with transition metal heteropolyanions[57] and tris(bipyridyl) complexes,[58] more promising as standard redox systems than the metallocenes.[10]

There are data indicating the possibility of the adsorption of $(arene)_2Cr^+$ on a Hg electrode in an aqueous medium.[59] It has been suggested that the adsorption is due to the positive charge of the complex, the "squeezing out" effect, the presence of an unpaired electron, the π-electronic interaction of the cation with the electrode, and the influence of the supporting electrolyte anion.

Metallocarbaboranes. As in other SC, in these complexes the transition metal is linked to dicarbaboryl ligands by π-bonds.[60,61] The study of the electrochemical behaviour (d.c. and a.c. polarography, cyclic voltammetry, and preparative electrolysis) of the dicarbaboryl complexes of iron,[60] cobalt,[38,60] rhodium,[42] nickel,[38,60] palladium,[62] copper[62] and gold[62] in aprotic media showed that, in contrast to the Cp ligands, the dicarbaboryl ligand [Cb = η^6-(3)-1,2-$C_2B_9H_{11}$] stabilises the metal in both the highest and lowest oxidation states. The overall scheme for the redox reactions of these complexes can be represented in the following form:

$$Cb_2M \overset{e}{\rightleftarrows} Cb_2M^- \overset{e}{\rightleftarrows} Cb_2M^{2-} \overset{e}{\rightleftarrows} Cb_2M^{3-}$$

The only exception in the series of dicarbaboryl complexes is platinum dicarbaboride, which has been shown [by cyclic voltammetry in dimethyl sulphoxide (DMSO) and DMF] to undergo the reversible two-electron Cb_2Pt^0/Cb_2Pt^{2-} transition with the subsequent quasi-reversible Cb_2Pt^{2-}/Cb_2Pt^{3-} transition at more cathodic potentials.[63] The two-electron character of the Cb_2Pt^0/Cb_2Pt^{2-} electrode process is probably associated with the transfer of the first electron to the antibonding LUMO and possibly with the solvation effects of the highly coordinating solvents in which the measurements were performed.

Ti, V, and Cr complexes, as well as Mn, Fe, and Co complexes, with another dicarbaboryl ligand $Cb^- = \eta^6$-(4)-1,6-$C_2B_{10}H_{12}$ have also been synthesised and characterised electrochemically.[64,65] The reversible redox transitions

$$Cb'_2M^- \overset{e}{\rightleftarrows} Cb'_2M^{2-} \overset{e}{\rightleftarrows} Cb'_2M^{3-}$$

are characteristic of these complexes too. Metallocarbaboranes can also be recommended as standard redox systems, although they are less readily available.

Other homoligand sandwich complexes. It has been shown by voltammetric and coulometric methods at Pt electrodes that bis(azaboralinyl)metal complexes [η^5-$C_3H_3B(Me)NR]_2M$ (R = H, Et, Bu, or $SiMe_3$; M = Co or Fe) in THF and CH_2Cl_2 undergo reversible one-electron oxidation to the corresponding cations, whose stability depends on the nature of R and M.[66]

Bis(cyclo-octatetraene)uranium $(COT)_2U$ is oxidised in THF, acetonitrile, benzonitrile, and CH_2Cl_2 at Hg, Pt, and carbon glass electrodes at temperatures below 10 °C in a single reversible two-electron stage to the dication via the *ECE*-mechanism, according to which the transfer of the first electron leads to the formation of the unstable cation $(COT)_2U^+$, which undergoes rapid structural and/or solvation changes with formation of a new more readily oxidisable cation.[67] With increase in temperature or with decrease in the rate of scanning of the potential, the electrochemically generated dication reacts with the initial "uranocene", forming the dimeric dication $(COT)_4U_2^{2+}$, which is capable of irreversible one-electron oxidation with elimination of cyclo-octatetraene and the formation of $(COT)_3U_2^{3+}$.

Mixed-ligand sandwich complexes. The heteroligand SC resemble in their electrochemical properties their homoligand analogues. They too are characterised by reversible one-electron reactions, which proceed with a change in the formal oxidation state of the metal. It has been established by polarographic, cyclic voltammetric, and preparative electrolysis methods in non-aqueous media that the redox transitions

$$[CpMCb]^+ \overset{e}{\rightleftarrows} CpMCb \overset{e}{\rightleftarrows} [CpMCb]^- \overset{e}{\rightleftarrows} [CpMCb]^{2-},$$
M = Fe (Ref.38), Co (Ref.45), Ni (Ref.60);

$$[CpMCb']^- \overset{e}{\rightleftarrows} [CpMCb']^{2-} \overset{e}{\rightleftarrows} [CpMCb']^{3-},$$
M = Fe (Ref.64), Co (Ref.64), Ti (Ref.65);

$$[(arene)MCp]^{2+} \overset{e}{\rightleftarrows} [(arene)MCp]^+ \overset{e}{\rightleftarrows} (arene)MCp \overset{e}{\rightleftarrows} [(arene)MCp]^-,$$
M = Fe (Refs.2, 51), Co (Ref.55), Ir (Ref.68), Rh (Ref.69);

$$(COT)\,TiCb \overset{e}{\rightleftarrows} [(COT)\,TiCb]^- \text{ (Ref.65)};$$

$$(COT)\,TiCp \overset{-e}{\rightleftarrows} [(COT)\,TiCp]^+ \text{ (Ref.70)};$$

$$(\eta^5\text{-L})\,Ti\,(COT) \overset{e}{\rightleftarrows} [(\eta^5\text{-L})\,Ti\,(COT)]^-,$$
L = indene, fluorene (Ref.70);

$$(\eta^5\text{-}C_7H_7)\,MCp \overset{-e}{\rightleftarrows} [(\eta^5\text{-}C_7H_7)\,MCp]^+,$$
M = V (Ref.71), Cr (Ref.72).

are possible. The study of the electrochemical synthesis of η^4-arenemetal complexes by the electrochemical reduction of the corresponding η^6-arene complexes as well as the electrochemical investigation of $\eta^6 \rightleftarrows \eta^4$ hapto-isomerisation—the postulated key stage in the catalytic hydrogenation of arenes,[73] ligand substitution reactions,[74] and isomerisation of complexes[75]—by polarography, cyclic voltammetry, and preparative electrolysis showed[55] that in non-aqueous media (CH_2Cl_2, acetonitrile, DMF, etc.) the complex $[(C_5Me_5)M(C_6Me_6)]^{2+}$ is reduced in two one-electron stages when M = Rh, whereas with M = Ir it is reduced in one two-electron stage, to the corresponding neutral complexes which consist, according to ^1H NMR data, of compounds having the structure $(\eta^5\text{-}C_5Me_5)M(\eta^4\text{-}C_6Me_6)$. It has been suggested that the $\eta^6 \rightarrow \eta^4$ hapto-isomerisation ($k \cong 10^3$ s^{-1}; stabilisation energy ~38 kJ mol^{-1}), leading to the thermodynamic stabilisation of these complexes, takes place in the stage involving the transfer of the second electron and is accompanied by the transition from the relatively unstable 20-electron complex to the stable 18-electron complex. The $\eta^6 \rightleftarrows \eta^4$ hapto-isomerisation is facilitated on passing from 3*d* metals to 4*d* and 5*d* metals. It has been shown for the redox transitions

$$[(C_6Me_6)\,Rh\,(C_6Me_6)]^{2+} \overset{e}{\rightleftarrows} [(C_5Me_5)\,Rh\,(C_6Me_6)]^+ \overset{e}{\rightleftarrows} (C_5Me_5)\,Rh\,(C_6Me_6)$$

that an increase in the Gutman's donor number of the solvent from 0 to 30 lowers $\Delta E^0 = E^{2+}/E^+ - E^+/E^0$ from 0.37 to 0.09 V as a result of the greater influence of the solvation effects on E^{2+}/E^+, but hardly affects the kinetics of the hapto-isomerisation. The oxidative cleavage of polyolefin cobalt SC (COT)CoCp and (COD)CoCp (whhere COD = cyclo-octadiene) in strongly (acetonitrile) and weakly (CH_2Cl_2) coordinating solvents has been investigated electrochemically.[76] In acetonitrile, these complexes undergo irreversible electrochemical oxidation accompanied by the cleavage of the polyolefin–metal bond, which can be described by the scheme

$$LCoCp \xrightarrow{-e} \underset{(A^+)}{[LCoCp]^+} \xrightarrow{+nMeCN} L + [CpCo\,(MeCN)_3]^+ \xrightarrow{-0.5e} \rightarrow 0.5Cp_2Co^+ + 0.5Co^{2+} + 3MeCN, \quad L = COT, COD. \qquad (2)$$

On the other hand, in CH_2Cl_2 the transfer of the first electron is reversible, while the A^+ cation is more stable (it has been characterised by its EPR spectrum in relation to the compound where L = COD), although it does undergo further reaction according to formula (2). The possibility of the isomerisation 1,5-COT ⇄ 1,3-COT in the cation A^+ has been discussed.

In order to investigate the possibility of carrying out electrochemically the reaction involving the abstraction of a hydride ion from $[CpM(\eta^6\text{-}C_7H_8)]^+$ (where M = Fe or Ru; $\eta^6\text{-}C_7H_8$ = η^6-cycloheptatriene) accompanied by its conversion into $[CpM(\eta^7\text{-}C_7H_7)]^{2+}$, which is possible in principle, by the cyclic voltammetric method in acetonitrile, a study has been made of the electrochemical oxidation of $[CpM(\eta^6\text{-}C_7H_8)]^+$.[77] Despite the fact that the electrochemical oxidation does indeed involve the coordinated cycloheptatriene with its conversion into $\eta^7\text{-}C_7H_7^+$, the passivation of the electrode by the products of the decomposition of the complexes prevents the preparative electrochemical synthesis of $[CpM(\eta^7\text{-}C_7H_7)]^{2+}$. It has also been noted that, for $E < -1$V, the complexes $[CpM(\eta^7\text{-}C_7H_7)]^{2+}$ undergo one-electron reduction, specific with respect to the method, which is, however, electrochemically irreversible.

The redox properties of mono- and di-phosphaferrocenes have been investigated[78] in CH_2Cl_2, $H_2\overline{COCOOCH}Me$, acetonitrile, DMF, and other non-aqueous solvents. Like ferrocene, these SC undergo reversible one-electron reduction to relatively unstable anions and one-electron oxidation to cations, whose stability depends significantly on the nature of the solvent. Analysis of the EPR spectra of the phosphaferrocenium cations permitted the conclusion that the unpaired electron is predominantly localised on the metal atom. The character of the change in the redox properties on passing from Cp_2Fe to phosphaferrocenes (the anodic shifts of E^0 on reduction and oxidation are respectively 0.39 and 0.19 V) is due to the change in the energy of the redox MO on replacement of the CH group in the Cp ligand by the phosphorus ligand.

The standard potentials of the redox reaction of the majority of homo- and hetero-ligand SC have been compiled in tables in a number of communications.[23,79,80]

Dinuclear sandwich complexes. It has been shown by cyclic voltammetry[81] that the dications $\{(\eta^{10},\mu^2\text{-}C_{10}H_8)[(\eta^6\text{-}C_6R_6)Fe]^2\}^{2+}$ (R = H or Me; $C_{10}H_8$ = fulvalene), designated henceforth by B^{2+}, are capable of the redox transitions

$$B^{2+} \overset{e}{\rightleftarrows} B^{+} \overset{e}{\rightleftarrows} B^{0} \overset{e}{\rightleftarrows} B^{-} \overset{e}{\rightleftarrows} B^{2-}$$

which are separated on the potential scale, with the intermediate formation of the mixed-valence complexes [Fe(2+) Fe(1+)](B^+) and [Fe(1+) Fe(0)](B^-). The complexes B^+ and B^0 have been characterised in terms of their magnetic susceptibility and also by EPR and NMR spectra. The electron exchange between the Fe nuclei in B^+ takes place at a rate $> 10^9$ s^{-1} at 4.2 K, the fulvalene ligand being involved in this process.

The oxidation-reduction properties of monometallic and dimetallic cyclophane complexes of ruthenium[50,82] and iron[83] in non-aqueous media (THF, CH_2Cl_2, CH_3COCH_3, DMF, etc.) have been investigated by cyclic voltammetry, chronoammetry, and preparative electrolysis. Together with the $\eta^6 \rightleftarrows \eta^4$ hapto-isomerisation of the arene ligand, accompanying the multistage two-electron reduction of the dications $[(\eta^6\text{-}C_6Me_6)Ru(\eta^6\text{-}L)]^{2+}$ (L = cyclophanes),[50,82] the complex $[(CpFe)_2(\eta^6\text{-}L)]^{2+}$ is reduced via two stages with similar potentials.[83] This process leads to the formation of the relatively unstable [Fe(2+)Fe(1+)] and [Fe(1+)Fe(1+)] complexes, which decompose with ejection of the cyclophanes and the formation of the solvated CpFe fragment, which disproportionates to ferrocene and Fe^0. It has been suggested[83] that the low stability of the neutral cyclophane complexes compared with CpM(arene) is due to the smaller degree of overlap of the orbitals of the cyclophane ligand and the AO of the metal as a result of the steric strain in the cyclophane structure.

We shall now consider metallocenophanes having the general formula $[(\eta^5\text{-}C_5H_4)CH_2]_2M^1M^2$, where M^1M^2 = FeFe, FeRu, or RuRu.[84]. In benzonitrile, the compound with $M^1 = M^2$ = Fe undergoes oxidation, specific with respect to each of the ferrocene fragments, in two reversible one-electron stages, which indicates the absence of appreciable interactions between these fragments. Such interaction is also absent from the complex with M^1 = Fe and M^2 = Ru, which undergoes a quasi-reversible one-electron oxidation specific with respect to the ferrocene fragment and irreversible two-electron oxidation specific with respect to the ruthenocene fragment. For $M^1 = M^2$ = Ru, both metallocene fragments probably interact strongly with one another, as a consequence of which the complex undergoes quasi-reversible two-electron oxidation at potentials displaced to the cathodic region by 0.54 V compared with the ruthenocene oxidation potentials. Analysis of the ^1H NMR spectra of the oxidation products has led to the conclusion that the oxidation involves a single ruthenocene fragment.[84]

The electrochemistry of bis(fulvalene)dimetal complexes $(C_{10}H_8)_2M_2$ (M = V, Cr, Fe, Co, or Ni) has been investigated in acetonitrile.[85] It has been shown by cyclic voltammetry at a Pt electrode that most of these complexes are capable of redox transitions:

$$(C_{10}H_8)_2M_2^0 \overset{e}{\rightleftarrows} [(C_{10}H_8)_2M_2]^+ \overset{e}{\rightleftarrows} [(C_{10}H_8)_2M_2]^{2+}.$$

Redox transitions with a change in the formal oxidation state of the metal are also characteristic of triple decker SC[86-88] and there is a significant increase in the number of possible redox transitions as a result of the increase in the numbers of metal atoms.

Examples of such systems are

$$[CpCo(\eta^5\text{-}C_2B_3H_5)CoCp]^{2+} \overset{e}{\rightleftarrows} [CpCo(\eta^5\text{-}C_2B_3H_5)CoCp]^{+} \overset{e}{\rightleftarrows}$$
$$\rightleftarrows [CpCo(\eta^5\text{-}C_2B_3H_5)CoCp]^{0} \rightleftarrows [CpCo(\eta^5\text{-}C_2B_3H_5)CoCp]^{-} \overset{e}{\rightleftarrows}$$
$$\rightleftarrows [CpCo(\eta^5\text{-}C_2B_3H_5)CoCp]^{2-} \quad \text{(Ref.87)}$$

and

$$[CpCo(COT)]^{2+} \overset{e}{\rightleftarrows} [CpCo(COT)]^{+} \overset{e}{\rightleftarrows} [CpCo(COT)]^{0} \overset{e}{\rightleftarrows} [CpCo(COT)]^{-} \text{ (Ref.88).}$$

The behaviour of other polynuclear SC in redox reactions has been described in a number of communications.[2-8,61,86,89-91]

In concluding the consideration of the oxidation-reduction reactions of SC, we may note that the author's aim was not the unrealistic task of providing exhaustive information about all the investigations in this large field. In particular, the question of the electronic effects of substituents on the redox properties of SC, with which one can become acquainted from other publications,[2-6,90] has been hardly dealt with. Whenever possible, later studies are quoted in which earlier publications on the same topic are mentioned. The author's aim was to demonstrate that the quantitative characteristics of the oxidation-reduction reactions of the class of complexes considered are determined primarily by the nature of the metal atom involved. The discovery of a quantitative relation between the redox properties of SC and the corresponding metals would make it possible, without resorting to additional physicochemical studies, to estimate beforehand, from tabulated data for metals, the redox properties of the corresponding complexes. This problem of

predicting the reactivities of metal complexes from the properties of the metal involved (even for individual classes of complexes and individual types of reactions) is of fundamental importance.

3. Linear relations between the redox potentials of sandwich complexes and the gas-phase ionisation potentials of metals

A model has been proposed[79] permitting the estimation of the contribution of the energies of the *d* orbitals of the metal to the redox orbitals of the complexes. This model has been used to discover the trends in the behaviour of the redox potentials of octahedral and pseudo-octahedral complexes, in particular metallocenes. However, the variation of the quantities E^0 as a function of the number of the *d* electrons of the metal, the charge of the complex, the type of the ligand environment, the character of the spreading of the redox MO, the electron pairing energy, etc. has been examined at a purely descriptive level. Attempts have been made to find a correlation between the quantities $E_{1/2}$ for metallocenes and the gas-phase ionisation potentials of metals (IP), but these were limited, since the comparison was carried out only for a single Cp_2M^0/Cp_2M^- redox transition and for a limited range of metals (V, Cr, Fe, Ni).[17] An attempt has also been made to find a correlation[16] between the potentials $E_{1/2}$ of the Cp_2M^0/Cp_2M^+ (M = V, Cr, Fe, Co, or Ni) redox transitions and the ionisation potentials of the complexes in the gas phase, but for certain metallocenes an appreciable deviation from the linear relation predicted by the equation[6,92]

$$E_{1/2} = 0.92\,I_D - 6.20.$$

was observed. Although the ionisation potentials have now been measured for a large number of SC,[13] such correlation is hardly suitable for the prediction of the redox properties, especially if one is dealing with complexes which have not yet been synthesised or which are unstable, for which the values of I_D are unknown. Furthermore there are no reliable literature data for the second, third, and subsequent ionisation potentials of the complexes, while the values of IP for the metals are readily available.[93]

A completely different approach has been proposed in studies[23,80,94] in which the existence of a linear relation between the standard potentials *of all possible redox transformations* of SC [see, for example, Eqn.(1) for metallocenes] and the IP of the corresponding metals has been established and justified. The existence of such a relation is due to the fact that the main contribution to the HOMO and LUMO of sandwich complexes comes from the AO of the metals[11-13,93] and the potentials E^0 for the electron transfer reactions in the series of SC, involving precisely the HOMO and LUMO,[2,3] should in fact reflect the change in the state of oxidation of the metal, whose measure is the IP.[23] Furthermore, the SC retain their plane-parallel structure regardless of the formal oxidation state of the metal and the solvation energy of the components of the redox couples, for example, Cp_2M^x/Cp_2M^{x-1}, depend little on the nature of the metal, since the manifestation of the effects of specific solvation is prevented by the bulky ligand environment in the SC. As a result, the solvation effects in the redox transition of SC are associated mainly with the electrostatic component E_S, which is approximately the same for equally charged isostructural complexes.[9,57,94] The change in E_S on transition from, for example, Cp_2M^x to Cp_2M^{x-1} makes approximately the same contribution to E^0 for different metals. Furthermore, the predominantly electrostatic character of the influence of E_S on the potentials E^0 for SC permits a comparison of the redox potentials of the SC measured in different solvents.[23] The set of these quantities leads to a significantly linear relation between E^0 and IP for all possible redox reactions of homo- and hetero-ligand SC.[23,80,94] However, in certain cases, for example, for individual di(arene)metal complexes,[47,48] whose redox reactions occur with electron transfer to the ligand, such a linear relation does not hold.

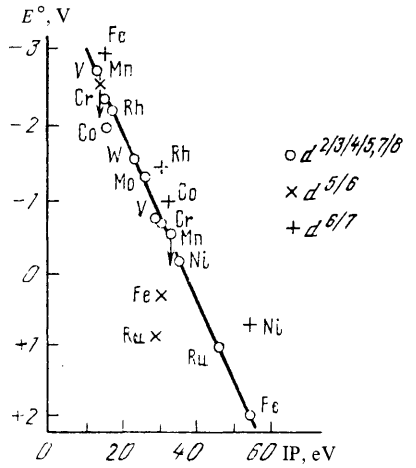


Figure 1. Dependence of E^0 for the d^x/d^{x+1} transitions in the series of metallocenes on the corresponding gas-phase ionisation potentials of the metals.[23] The values of E^0 for $(C_5Me_5)_2Mn$ are quoted in the case of manganocene; the arrows indicate the shift of E^0 taking into account the effects of the substituents.

Figs. 1 and 2 present the E^0–IP relations for metallocenes and metallocarbaboranes respectively. The parallel variation of the potentials E^0 and the corresponding IP is clearly seen (E^0 increases with IP), but certain points deviate significantly from the straight line. All these deviations refer to the redox transitions involving the most stable 18-electron configuration of the complex. The deviation of the quantities E^0 for the d^5/d^6 redox transitions in the direction of more positive potentials, which might have been expected from the IP of the metals, is not fully understood if account is taken of the order in which the redox orbitals of the metallocenes are filled with electrons. However, such deviations are characteristic only of iron subgroup metallocenes and are in all probability caused by the extraordinary stability of the metallocenes of this subgroup. As regards the d^6/d^7 redox transitions, it is clear, since in this case the electron is transferred to the antibonding e_1^* orbital of the SC,[11-13,95] that the potentials E^0 for these electronic transitions must deviate consistently in the direction of more negative potentials, because electron transfer to the given orbital requires an additional energy expenditure in order to overcome the splitting energy in the crystal field of the ligand. The splitting between non-bonding (a_{1g}) and antibonding (e_{1g}^*) orbitals can probably be estimated from the degree of deviation of the E^0 in the case of the d^6/d^7 redox transitions.

It is seen from Figs. 1 and 2 that the same slope of the E^0–IP relations, amounting to approximately 0.1 V eV^{-1}, is characteristic of SC of three different types. This makes it possible to predict the

redox properties of different SC from the IP of their metals, *provided that E^0 is known for at least one of the redox transitions of one of the complexes of the given type*. In fact, this is equivalent to the creation of a single redox scale for transition metal SC, which is especially important for SC which have been weakly characterised electrochemically, have not yet been synthesised, or are so unstable that their electrochemical investigation is impossible. This approach permits the expression of the potential of any possible redox transitions of hetero- and homo-ligand SC by the simple equation

$$E^0 = \sum_{i=1,2} a_i + 0.1 \text{ IP}.$$

The constants a_i have been calculated[23] for the principal types of π-ligands (in V): −2.08 for Cp, −0.73 for η^6-C_6H_6, +1.52 for η^7-C_7H_7, −3.61 for η^8-COT, −2.05 for Cb, and −1.70 for Cb′. Fig. 3 illustrates graphically the validity of the proposed approach (the E^0–IP relations calculated from the constants a_i found previously are shown by dashed lines).

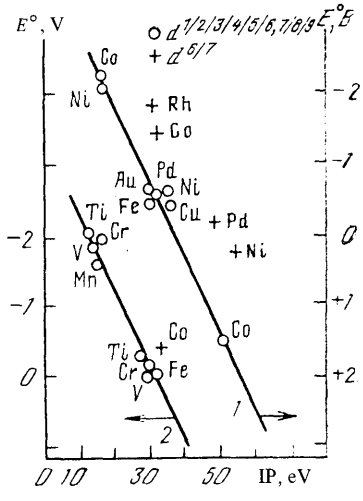


Figure 2. Dependence of E^0 for the d^x/d^{x+1} redox transitions in the series of metallocarbaboranes Cb_2M (line *1*) and Cb'_2M (line *2*) on the corresponding gas-phase ionisation potentials of the metals.[23]

The existence of a linear relation between the reactivity of SC in oxidation-reduction reactions and the ionisation potentials of the metals makes it possible to investigate systematically the regions of the thermodynamic stability of compounds of this type as a function of the nature of the metal, to understand the causes of the two-electron character of the oxidation-reduction reactions of certain complexes uncharacteristic of SC, to select the optimum conditions for the synthesis and investigation of the physicochemical characteristics of SC, to assess the possibility of the synthesis of various SC, to determine the redox properties of both relatively unstable and hitherto not synthesised SC, etc. A study has been devoted to the consideration of these questions.[23] In addition, its authors (see also Ref. 94) discuss questions associated with the application of the linear relations between E^0 and IP to the estimation of the reactivities of octahedral metal complexes in oxidation-reduction reactions and consider the factors which determine the slopes of these relations.

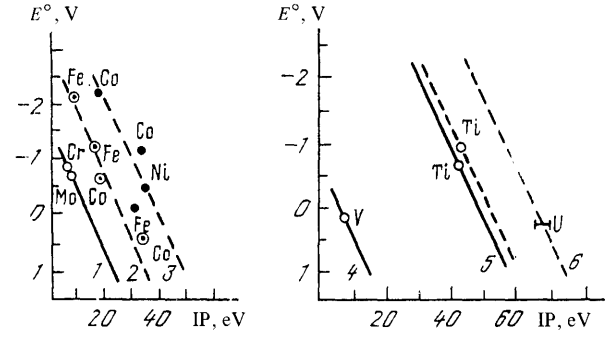


Figure 3. Dependence of E^0 on IP for the d^x/d^{x+1} redox transitions in the series of homo- and hetero-ligand sandwich complexes:[23] *1*, $(arene)_2M$; *2*, (arene)MCp; *3*, CpMCb; *4*, $CpM(C_7H_7)$; *5*, $(C_8H_8)MCb$; *6*, $(C_8H_8)_2M$. The dependences calculated from the values of a_i found previously are shown by dashed lines.

III. Electrochemical behaviour of bis(cyclopentadienyl) bent sandwich complexes

The enhanced interest in the mechanism of the electrochemical reduction of metallocene dichlorides is due to the fact that these compounds are components of catalytic systems used for the polymerisation, hydrogenation, and isomerisation of olefins,[96,97] while the products of their reduction activate small molecules such as molecular nitrogen,[98] and CO,[99–104] promote the reduction of the latter, etc. The catalytic activity of systems based on the complexes Cp_2MCl_2 is manifested as a rule for low oxidation states of the metal, so that the study of the mechanism of the reduction of these complexes is an important task.

Quantum-chemical analysis[12] shows that in both BC and SC the AO of the metal makes the main contribution to the HOMO and LUMO of the complexes, so that compounds of this type can also evidently undergo redox reactions with a change in the formal oxidation state of the metal, i.e. with a change in the electron density mainly on the metal atom.

Among the BC of Group IVB metals, titanocene dichloride has been most thoroughly investigated (as regards electrochemical properties). However, despite the fact that many studies have been carried out,[105–111] until recently there has been no unanimous view concerning the detailed mechanism of its reduction.

The reduction of Cp_2TiX_2 (X = Cl or Br) in THF has been investigated by polarography, cyclic voltammetry (Pt and carbon glass electrodes), preparative electrolysis, and EPR spectroscopy.[105] It has been suggested that the reduction takes place in three reversible one-electron stages:

$$Cp_2TiX_2 \overset{e}{\rightleftarrows} [Cp_2TiX_2]^- \overset{e}{\rightleftarrows} [Cp_2TiX_2]^{2-} \overset{e}{\rightleftarrows} [Cp_2TiX_2]^{3-}.$$

The $Cp_2TiX_2^-$ anion is stable in solution and can be obtained on a preparative scale, while the $Cp_2TiX_2^{2-}$ dianion is unstable and is converted under these conditions into Cp_2TiX^- with elimination of X^-. The paramagnetic $Cp_2TiX_2^-$ and $Cp_2TiX_2^{2-}$ complexes have been characterised by EPR spectra. The conclusion that the stage involving the transfer of the first electron is electrochemically and chemically reversible and that the $Cp_2TiX_2^-$ anion is stable in solution in the absence of moisture and oxygen has been confirmed also in subsequent studies.[106,107]

It has been found from cyclic voltammetric, preparative electrolysis, and EPR spectroscopic data[108–110] that, although Cp_2TiCl_2 does in fact undergo electrochemically reversible reduction to the $Cp_2TiCl_2^-$ anion in an aprotic medium, the anion is unstable and rapidly loses Cl^-, which is replaced by a molecule of the solvent or another suitable ligand (L) with formation of the complex $Cp_2Ti(L)Cl$. The complex $Cp_2Ti(L)Cl$ is in its turn capable of reversible one-electron oxidation to $Cp_2Ti(L)Cl^-$, which is converted into the initial Cp_2TiCl_2 in the presence of an excess of Cl^-.[109] As the electron-donating properties of L are enhanced in the sequence THF < Py < DMF, the rate of the forward reaction

$$Cp_2TiCl_2^- + L \rightleftarrows Cp_2Ti(L)Cl + Cl^- \qquad (3)$$

increases while that of the reverse reaction falls. The complex $Cp_2Ti(THF)Cl$ has been characterised by EPR spectroscopy.[108]

The electrochemical reduction of Cp_2TiCl_2 has also been investigated in the $AlCl_3$/1-butylpyridinium chloride melt.[37] It has been suggested that the product of the first reversible one-electron stage is the complex $Cp_2Ti[Al_2Cl_7]$ with two Ti–Cl–Al bridge bonds.

The replacement of Cl^- by the more electronegative ligand NCS^- greatly facilitates the reduction of Cp_2TiX_2.[111] The electro-chemically generated $Cp_2Ti(NCS)_2^-$ (characterised by EPR spectroscopy) is stable under these conditions in THF and CH_2Cl_2 at room temperature. The irreversibility of the first reduction stage in DMF has been attributed to the irreversible dimerisation of the anion, which forms a diamagnetic dimeric titanium(III) complex.

The data of Kukharenko et al.[112] in the main agree well with the results of other studies.[108–110] According to these data, the electro-chemically generated $Cp_2TiCl_2^-$ anion is unstable and is rapidly but reversibly dehalogenated in accordance with Eqn.(3) with formation of Cp_2TiCl_3.‡ The subsequent one-electron reduction of Cp_2TiCl leads to the formation of the unidentified "titanocene Cp_2Ti", which is capable according to the authors,[110–112] of undergoing one-electron reduction. However, it has been suggested[110] that the product of the reduction of Cp_2TiCl is a dimeric titanium(II) complex and not the "titanocene".

Among heavier analogues of Cp_2TiX_2, the dichlorides of zirconocene[105,112–115] and hafnocene[112,113,115] have been investigated in electrochemical reduction processes. In THF, these metallocene dichlorides undergo reversible one-electron reduction with formation especially at reduced temperatures (from –40° to –20 °C), of extremely stable $Cp_2MCl_2^-$ anions, which have been characterised by EPR spectroscopy.[113–115] The $Cp_2ZrCl_2^-$ and $Cp_2HfCl_2^-$ anions undergo further irreversible one-electron reduction in the region of extremely cathodic potentials (from –2.95 to –3.05 V) probably to the "corresponding metallocenes".[112] At room temperature the electrochemically generated $Cp_2MCl_2^-$ anions are apparently dehalogenated with formation of the more readily reduced mono-chlorides.[112] The rate of dehalogenation of $Cp_2MCl_2^-$ diminishes in the sequence Ti > Hf > Zr as a function of the nature of the metal, but the rate of the reverse reaction (3) increases in the sequence Hf $\lesssim$ Zr $\ll$ Ti.[112] Together with dehalogenation, there is also a possibility of the destruction of the zirconium- and hafnium-containing anions $Cp_2MCl_2^-$ via the reaction[113,115]

$$Cp_2MCl_2^- \rightleftarrows Cp^- + CpMCl_2.$$

The electrochemical behaviour of bridged titanocene dichlorides $(CH_2)_x(C_5H_4)_2TiCl_2$ (x = 1–3) and substituted titanocene dichlorides in THF has been investigated.[116,117] While the reduction mechanism is the same, the potentials $E_{1/2}$ for the reduction of the bridged monochloride complexes are displaced towards more cathodic values by 0.05–0.3 V compared with the non-bridged analogues. It has been suggested[116] that the influence of the bridging substituents on $E_{1/2}$ is due to their steric and not the inductive effect.

The reversible one-electron reduction of dialkyl derivatives of titanocene and zirconocene—Cp_2MR_2 (R = Me or $PhCH_2$)—in THF leads to the formation of corresponding unstable anions, which are destroyed with the elimination of R^- or Cp^-.[113,118–120] In THF, {2,3-bis(methylene)bicyclo[2.2.2]octane}zirconocene undergoes one-electron reduction to the corresponding radical-anion, which is relatively stable at 20 °C (characterised by its EPR spectrum), but decomposes with the dissociation of the zirconocene–diene bond on raising the temperature.[121] References to other studies on the electrochemical reduction of dialkylmetallocenes may be found in other reviews.[4,5]

The $Cp_2TiR_2^-$ anion, stable at –30 °C, has been obtained by the reversible one-electron reduction of Cp_2TiR_2 (R = C≡CPh) in THF. On heating to 25 °C, it slowly and reversibly splits off Cp^- with formation of $CpTiR_2$, which reacts in its turn with $Cp_2TiR_2^-$ to form $CpTiR_2^-$.[122]

Cp_2TiCl, generated electrochemically in THF, reacts with benzo[*c*]cinnoline (RN=NR) to form the dinuclear complex $Cp_2Ti(Cl)N(R)N(R)(Cl)TiCp_2$. This reaction has been considered[123] as a model for the activation of the N=N double bond.

The electrochemistry of Group VB metallocene dichlorides has been investigated in relation to vanadium and niobium compounds. However, there is no unanimous view in the literature concerning the detailed mechanism of the stability of the products of the electro-chemical reduction of these BC. Thus, the following mechanism for the reduction reaction has been proposed on the basis of data for the polarographic reduction of Cp_2VCl_2 in THF:[16]

$$Cp_2VCl_2 \overset{e}{\rightleftharpoons} [Cp_2VCl_2]^- \overset{e}{\rightleftarrows} [Cp_2VCl_2]^{2-} \xrightarrow{-2Cl^-} Cp_2V.$$

It has been claimed[16] that the $[Cp_2VCl_2]^-$ anion is stable and can be obtained by preparative electrochemical reduction. The agreement of the values of $E_{1/2}$ for the third wave on the Cp_2VCl_2 polarogram and the vanadocene reduction wave permitted the conclusion that vanadocene is the product of the two-electron reduction of Cp_2VCl_2.

In contrast to this, it has been concluded[18] that the transfer of the first electron to Cp_2VCl_2 is accompanied by the formation of the $Cp_2VCl_2^-$ anion, which, however, is extremely stable and rapidly but reversibly splits off Cl^- with formation of the monochloride Cp_2VCl, which is in fact reduced to vanadocene. Other data[124] confirm the validity of this conclusion.

‡Here and henceforth the coordinated solvent molecule is not shown for the sake of simplicity in the formulae of the monochloride complexes Cp_2MCl.

The study of the reduction of the biscyclopentadienylvanadium complexes with different types of chelating agents showed that the product of the two-electron multistage reduction of these complexes is vanadocene.[125]

A reversible one-electron wave, corresponding to the formation of the $Cp_2NbCl_2^-$ anion, has been observed in the electrochemical reduction of niobocene dichloride in THF.[126,127] On the basis of cyclic voltammetric and preparative electrochemical reduction data, it has been suggested[127] that the electrochemical reduction of Cp_2NbCl_2 proceeds via the *ECE*-mechanism and is completed by the formation of a dimeric μ-chloride complex, which is stable at −30 °C:

$$Cp_2NbCl_2 \overset{e}{\rightleftharpoons} Cp_2NbCl_2^- \xrightarrow{-Cl} Cp_2NbCl \xrightarrow{+Cp_2NbCl_2^-} [Cp_2NbClCl_2NbCp_2]^-.$$

At room temperature, the one-electron reduction of niobocene dichloride leads to the formation of $(Cp_2NbCl)_2$, while in the presence of L = Ph_3P or $(PhO)_3P$ it yields $Cp_2Nb(L)Cl$.[128] The subsequent one-electron reduction of $(Cp_2NbCl)_2$ is accompanied by the rapid dissociation of the anion generated to Cp_2NbCl and Cp_2NbCl^-; it has been suggested that the dehalogenation of Cp_2NbCl^- [128] results in the formation of metastable niobocene, which is destroyed in subsequent reactions. Previously the formation of niobocene as the primary metastable product of the amalgam reduction of Cp_2NbCl_2 was detected by EPR.[129]

The reversible one electron oxidation of niobocene dichloride in THF leads to the preparation of the unstable $Cp_2NbCl_2^+$ cation, which is converted into Cp_2NbCl^+ as a result of the reductive elimination of the chlorine atom.[130]

It has been established by cyclic voltammetry that the dithiolene complexes $(Cp_2NbS_2C_2R_2)^+$ (R = Me or Ph) are reduced in THF in two reversible one-electron stages to a neutral compound and a monoanion respectively. The complex $Cp_2NbS_2C_2R_2$ can be obtained by preparative electrolysis.[131]

The complex $[Cp_2TaL]^+$, where L = 1,2-bis(dimethylphosphino)-ethane, is oxidised in an aprotic medium (CH_2Cl_2, acetonitrile, or acetone) in two reversible one-electron stages to $[Cp_2TaL]^{2+}$ (characterised by its EPR spectrum) and $[Cp_2TaL]^{3+}$ respectively according to data obtained by cyclic voltammetry.[132]

In contrast to Group IVB and VB metallocene dichlorides, the complexes Cp_2MCl_2 (M = Mo or W) are reduced in an aprotic medium to the corresponding unstable metallocenes in one two-electron stage, [22,23] because the first electron in the Group IVB and VB complexes is transferred to a non-bonding orbital, while in the Group VIB metallocene dichloride the analogous transfer is to an antibonding MO. On the one hand, this entails a cathodic shift of the Cp_2MCl_2 (M = Mo or W) wave relative to the first reduction waves of the Group IVB and VB complexes, since the electron is transferred to an antibonding MO whose energy is significantly higher[12] and, on the other hand, it leads to marked destabilisation of the $Cp_2MCl_2^-$ form, which is rapidly and irreversibly dehalogenated with formation of an M(III) complex more readily reducible than the initial metallocene dichloride.[22] It has been shown[124] that Cp_2M^+ is a product of this kind. Thus the reduction of Group VIB metallocene dichlorides proceeds via the *ECE*-mechanism with $E^0 < E_2^0$.

The electrochemical oxidation of the complexes Cp_2MX_2 (M = Mo or W; X = Cl, Br, I, or SR, where R = alkyl) has been investigated.[133] In acetonitrile, these complexes undergo reversible one-electron oxidation to the metastable cations $Cp_2MX_2^+$, in which the ligand is substituted by a reductive elimination reaction with ejection of X$^{\cdot}$, which results in the formation of the complexes $[Cp_2M(MeCN)X]^+$. The potentials of the $Cp_2MX_2^0/Cp_2MX_2^+$ redox couples depend only on the nature of M and not X, which has led to the hypothesis that the oxidation involves a non-bonding MO of the complexes to which the main contribution comes from the AO of the metal. The electrochemically generated cations $[Cp_2MSR]^+$ can also dimerise with formation of $[Cp_2M(\mu\text{-}SR)_2MCp_2]^{2+}$. The redox properties of the trinuclear heterometallic complex $Cp_2Ti[(C_5H_4)FeCp]_2$ have also been investigated.[133]

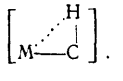
The electrochemical oxidation of the hydrides Cp_2WH_2 and $Cp_2W(Ph)H$ in acetonitrile has been investigated by cyclic voltammetry and preparative electrolysis.[134] The above compounds undergo reversible one-electron oxidation to the corresponding unstable radical-cations (lifetime from 10^{-3} to 20s; characterised by EPR spectroscopy), which are stabilised either via the reductive elimination reaction

$$Cp_2W(Ph)H^{+\cdot} \xrightarrow{-H^+} Cp_2WPh \rightarrow Cp_2W + Ph^{\cdot} \xrightarrow{MeCN} PhH,$$

or as a result of the additive dimerisation

$$Cp_2WH_2^{+\cdot} \xrightarrow{-H^+} Cp_2WH \xrightarrow{Cp_2WH_2} (Cp_2W)_2H_3 \xrightarrow{-e} (Cp_2W)_2H_3^+.$$

The oxidation of $Cp_2WR^1R^2$ (where R^1, R^2 = alkyl, aryl, or Cl) in acetonitrile has been studied.[134] It is suggested that the agostic interaction



takes place in the electrochemically generated cations $[Cp_2WR^1R^2]^+$.

Data on the electrochemical behaviour of lanthanide and actinide BC are extremely limited. It has been shown[136,137] that $(C_5Me_5)_2UCl_2$ undergoes reversible one-electron reduction to the anion in THF and acetonitrile, but the available data on the stability of this anion are contradictory. It has also been reported[138] that Cp_3UX (X = Cl or Me) undergo reversible one-electron reduction in THF with formation of the stable anion Cp_3UX^-. Finally it has been shown by cyclic voltammetry that the reversible one-electron reduction of $(C_5Me_5)_2NpCl_2$ to the anion takes place in acetonitrile.[139]

According to quantum-chemical calculations,[12] the structure of the frontier MO of the bent sandwich complexes Cp_2MCl_2 and Cp_2MCl is qualitatively virtually the same for different metals and the dominant contribution of the metal AO to the redox orbitals of the complexes is retained in all cases. One can therefore expect that the potentials $E_{1/2}$ for the Group IVB and VB biscyclodienylmetal chloride complexes, the characteristic reactions of which are one-electron reduction and oxidation, are also linearly related to the corresponding IP of the metals. This has been confirmed.[94,112] Thus it is seen from the relation between $E_{1/2}$ and IP presented in Fig. 4 that the values of $E_{1/2}$ for the metallocene dichloride complexes[112] fit satisfactorily on the straight line not only for the reversible $Cp_2MCl_2^0/Cp_2MCl_2^-$ redox couples but also for the irreversible $Cp_2MCl_2^-$ reduction reactions of the anions. This is due to the retention of the bent sandwich structure in the Cp_2MCl_2 and $Cp_2MCl_2^-$ complexes and the $Cp_2MCl_2^{2-}$ dianion formed as the primary reduction product of the latter. A specific linear relation exists also for the monochlorides Cp_2MCl, which differ somewhat in their structure (Fig. 4). The same figure shows by a dashed line the analogous relation for metallocenes. Evidently the slopes of all three relations are virtually the same ($\sim$0.1 V eV^{-1}), which is

probably associated with the retention of the dominant contribution of the AO of the metal to the SC and BC redox orbitals and with the similar changes in solvation energies in the redox transitions of the complexes of all three types. On the other hand, the discrepancy between the linear relations for complexes of different types is due to the energy differences between the corresponding redox orbitals of the complexes, which are associated with the differences in the angles of inclination between the cyclopentadienyl rings and with the presence of the electronegative Cl^- ligands.[94,112]

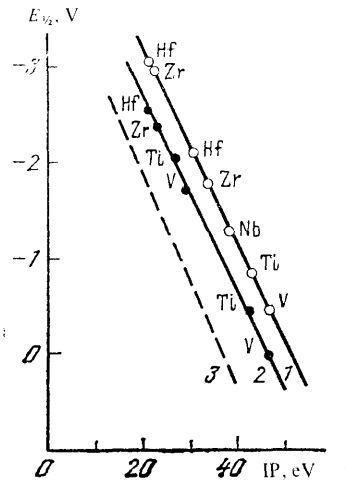
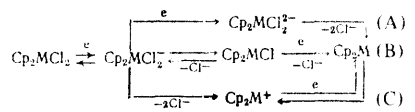


Figure 4. Linear dependences of the half-wave potentials of the complexes Cp_2MCl_2 (line *1*), Cp_2MCl (line *2*), and Cp_2M (line *4*) on the ionisation potentials of the corresponding metals in the gas phase according to Kukharenko et al.[112]

A single mechanism for the electrochemical reduction of the Group IVB–VIB metallocene dichlorides has been proposed on the basis of the linear relation between $E_{1/2}$ and IP established by Kukharenko et al.[112] and the consideration of the character of the redox MO of the complexes. It can be represented schematically as follows:



Pathway A obtains for M = Zr and Hf at a reduced temperature, pathway B for M = Ti and V and M = Zr and Hf at room temperature, and pathway C for M = Mo and W. When metallocenes whose lifetime is comparable to the time of the electrochemical measurement are formed (M = V, Mo, or W), their subsequent reduction to relatively unstable anions becomes possible.[22,24]

In conclusion of the consideration of the electrochemical reactions of the biscyclopentadienyl complexes, we shall deal briefly with the reactivities of the electrochemically generated species in relation to small molecules and certain other substrates. The products of the electrochemical reduction of metallocene dichlorides frequently activate inert molecules, especially CO,[99–103,140,141] CO_2,[140] and N_2,[98] in oxidation-reduction reactions, are inserted in the CH bond,[142] and participate in reactions involving the oxidative addition of olefins with formation of metallocycles,[143] i.e. play an important role in many synthetic reactions. So far there have been comparatively few studies of this kind, but the relative ease of the electrochemical generation of species in non-standard valence states, including unstable states, leads to considerable possibilities for the investigation of the reactivities of the low-valence products of the reduction of SC and BC in reactions with different substrates.

The products of the electrochemical reduction of titanocene dichloride react with CO to form $[Cp_2Ti(CO)Cl_2]^-$ and $Cp_2Ti(CO)_2$, the current yield of the latter amounting to approximately 100%.[107] However, it has been suggested[103] that the product of the one-electron reduction of Cp_2TiCl_2 in a CO atmosphere is the 17-electron complex $Cp_2Ti(CO)Cl$ and not the 19-electron anion $[Cp_2Ti(CO)Cl_2]^-$. This is confirmed by the fact that the significantly more stable $Cp_2MCl_2^-$ anions (M = Zr or Hf) do not react with CO.[103,112]

It is of interest to investigate the possibility of the electrochemically induced insertion of CO in the metal–carbon bond in the alkyl derivatives of metallocenes, because a reaction of this kind has been observed[144] in the electrochemical reduction of $CpFe(CO)_2Me$ in THF in the presence of Ph_3P and the acyl complex $CpFe(CO)(Ph_3P)(COMe)$ was formed as the product.

The interaction of the electrochemically generated "titanocene" with molecular nitrogen has been briefly mentioned.[110] A cathodic shift of the second reduction wave of bridged titanocene dichlorides, attributed to the electrochemical reduction of unidentified hydride and dinitrogen complexes of "titanocene", was observed in THF in the presence of N_2 and H_2. Finally, it has been claimed[145] that the products of the electrochemical reduction of Cp_2TiCl_2 in THF or methanol catalyse the electrochemical reduction of N_2 to NH_3 with a current yield of approximately 2%. However, the fixation of nitrogen was not confirmed by a blank experiment (Ar) and by experiments with $^{15}N_2$.

It has been shown by cyclic voltammetry and preparative electrolysis that the complexes Cp_2VL (L = CO or $C_6H_{11}NC$) undergo reversible one-electron reduction in THF to the corresponding anions, which rapidly decompose to the metal, L, and Cp^-, probably via the immediate formation of CpVL.[146,147]

In the presence of proton donors (phenols, diethylbarbituric acid) in non-aqueous media (THF, DMF, and DMSO, etc.), vanadocene catalyses the amalgam reduction of CO to C_1–C_4 hydrocarbons.[99–103] $Cp_2V(CO)$ behaves as a catalyst-substrate complex, which undergoes one-electron reduction during the catalytic cycle to the $Cp_2V(CO)^-$ anion, as a result of the subsequent protonation and reduction of which the methyl complex Cp_2VMe is formed. The protolysis of this intermediate leads to the formation of methane and chain growth takes place as a result of the insertion of CO in the V–Me bond. As a consequence of the rapid subsequent protonation of the $[Cp_2V(CO)]^-$ anion, the transfer of the first electron to the catalyst-substrate complex takes place against the standard potential gradient.[102] This reaction has been considered as a kind of electrochemical analogue of the Fischer–Tropsch reaction which takes place at room temperature and atmospheric CO pressure. It has been noted[103] that other metallocenes Cp_2M (M = Nb, Mo, or W) also form reducible carbonyl complexes, which can be observed polarographically, for example in the case of M = Mo and W.[22]

However, the deactivation of the unstable metallocenes during the catalytic process prevents their use as catalysts of the conversion of CO into hydrocarbons.

The electrochemical reactions of the complexes of bis(fulvalene)-divanadium with CO and acetonitrile, which take place with a change in the formal oxidation state, have been examined.[85]

IV. Electrochemical synthesis of sandwich and bent sandwich transition metal complexes and of metal complex catalysts based on them

The principal methods of synthesis of SC and BC involve the interaction of the cathodically generated carbanions with the transition metal cations formed on the dissolving anode.[8,148] Bis(cyclopentadienyl) derivatives of manganese, iron, and cobalt[148] and the dicarbaboryl complexes of iron, cobalt, and nickel[148,149] have been obtained recently by this method. The carbonyl complexes of the cyclopentadienyl derivatives of manganese, iron, cobalt, titanium and vanadium are formed when Cp^- is generated by the electrochemical reduction of cyclopentadiene in an aprotic medium and under a CO atmosphere under conditions where transition metal ions are generated anodically.[8,148]

A review[150] has been devoted to the synthesis of SC with cycloolefin ligands and to the reactions involving the introduction of functional groups into SC by the electrophilic addition of alkyl halides and CO_2 to the electrochemically generated metallocene anions with formation of monosubstituted metallocene compounds or via the anodic substitution of hydrogen atoms in ferrocene by alkyl or alkylcarboxy-groups, which are obtained by the anodic decarboxylation of the anions of monocarboxylic and dicarboxylic acids and the half esters of dicarboxylic acids. Individual examples of the introduction of functional groups into the ferrocene and other SC can be found in a number of communications.[4,5,151]

A review[152] has been devoted to the chemical synthesis from metallocenes of various complexes, including catalysts for the cyclooligomerisation and trimerisation of alkynes and nitriles and also for the hydrogenation of alkenes and arenes. The key stage in these reactions is the reduction of Cp_2M by an alkaline metal to the Cp_2M^- anion with subsequent substitution of one or both Cp ligands by an olefin, an arene, a phosphine, CO, N_2, etc. The reduction by an alkali metal can be fully replaced by electrochemical reduction, which makes it possible to expand significantly the scope of the electrochemical synthesis of metal complex catalysts.

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In conclusion one should note that the use of solvents which are stable in the regions of extremely anodic and cathodic potentials greatly expanded our ideas about the possible oxidation-reduction reactions of sandwich and bent sandwich complexes and the establishment of a linear relation between the standard potentials of the redox reaction of complexes of this class and the gas-phase ionisation potentials of the corresponding metals made it possible to find a convenient parameter for defining the reactivity of the SC and BC in oxidation-reduction reactions. The mechanisms of the electrode reactions involving SC and BC have been studied in fair detail. On the other hand, there exist a series of promising aspects of this field in which there are still many unsolved problems. These include the electrochemistry of the BC of the actinides and lanthanides, the reactivity of intermediates in the redox reactions of SC and BC in relation to reagents of different kinds (electrophiles, nucleophiles, small molecules, etc.), and the electrochemical synthesis of SC and BC and of the metal complex catalysts based on them. The study of the electrode reactions of SC and BC in the absence of supporting electrolytes by means of the technique using ultramicroelectrodes is also of interest.[153] This will permit an even more significant expansion of the working range of potentials (from −4 to +5 V) and will make it possible to generate and identify species with an unusual formal oxidation state of the metal and also to avoid the undesirable interaction of the species generated with the components of the supporting electrolyte. Finally, low-temperature studies (cryoelectrochemistry), which will probably make it possible to identify many metastable intermediates in the electrochemical reactions of SC and BC and to investigate their properties, are promising.

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During the preparation of the present review, there has been a sharp growth of the number of studies concerning the use of SC as promoting agents for reactions involving electron transfer from the electrode to different kinds of inorganic and organic substrates. The reduction reactions of oxygen, the nitrate ion, and carbonyl and other organic compounds catalysed by iron SC as well as ligand substitution, *cis–trans* isomerisation, chelation, and demetallation reactions and reactions involving the migration insertion of carbon monoxide in a carbon–metal bond in metal complex and organometallic compounds, induced by charge transfer in catalysis by SC, have been considered in a number of reviews.[154–156]

The oxidation-reduction reactions of the iron SC with polyaromatic hydrocarbons (L = biphenyl, naphthalene, phenanthrene, triphenylene, pyrene, perylene, and caronene), having the general formula $[(\eta^5\text{-}C_5R_5)Fe(\eta^6\text{-}L)]^+$ (R = H or Me) have been investigated.[157] It has been shown by cyclic voltammetry[158] that the reduction of the double decker dinuclear cations $\{[(\eta^5\text{-}C_5Me_5)Fe]_2(\eta^{12}, \mu^2\text{-}L\}^{2+}$ (L = biphenyl, 9,10-dihydrophenanthrene, or triphenylene) to the corresponding neutral complexes in non-aqueous solvents is a multistage process which proceeds via the intermediate formation of mixed valence [Fe(1+)Fe(2+)] complexes. The redox reactions of ferrocene-substituted phosphazenes and polyphosphazenes[159] and of the diferrocene complex containing germanium octaethylporphyrinate as the bridge linking the two ferrocene fragments have been investigated.[160] The oxidation-reduction reactions of polynuclear homo- and hetero-ligand SC of transition metals, especially bridged dimetallocenes, bis(fulvalene)-dimetal complexes, metallocenophanes, and multidecker SC have been examined in a review.[161]

On the basis of a comparative study of the electrochemical oxidation of $(C_5Me_2)_2M$ (M = Fe, Ru, or Os) to the corresponding cation in acetonitrile, it has been noted[162] that the variation of the potentials $E_{1/2}$ for the oxidation of the metallocenes investigated in the sequence Fe < Os < Ru parallels the variation of the ionisation potentials of the complexes and the atomic ionisation energies of the corresponding metals. It has been shown[163] by cyclic voltammetry in THF at temperatures in the range −90 to −70 °C that the cobaltocene and nickelocene anions are capable of subsequent one-electron reduction with formation of the unstable Cp_2M^{2-} dianions at potentials more cathodic than −3 V. Under analogous conditions, the formation of the corresponding substituted titanocene and

zirconocene derivatives has been detected in a study of the mechanism of the electrochemical reduction of pentamethyl- and t-butyl-substituted titanocene and zirconocene dichlorides.[164] Thus the cryoelectrochemical approach to the study of the oxidation-reduction reactions of SC and BC proposed by Kukharenko and co-workers[163,164] has made it possible to expand the redox series (1) for metallocenes by yet another member (Cp_2M^{2-}) and also to establish the fundamentally important fact of the existence of the previously unknown Group IVB metallocenes.

References

1. A Page, G Wilkinson *J. Am. Chem. Soc.*, 1952, **74** 6149
2. L I Denisovich, S P Gubin *Uspekhi Khim.*, 1977, **46** 50 [*Russ. Chem. Rev.*, 1977(1)]
3. S P Gubin, L I Denisovich *Elektrokhimiya* (Electrochemistry), Izd. VINITI, Moscow, 1978, Vol. 13 p. 94
4. C J Pickett *Electrochemistry*, The Chemical Society, London, 1983, **8** 81
5. C J Pickett *Electrochemistry*, The Chemical Society, London, 1984, **9** 162
6. S P Gubin, G B Shul'pin *Khimiya Kompleksov so Svyazyami Metall-Uglerod* (The Chemistry of Complexes with Metal–Carbon Bonds), Izd. Nauka, Novosibirsk 1984, 280 pp
7. Yu P Kitaev, T V Troepol'skaya, G K Budnikov *Promezhutochnye Produkty v Elektrokhimicheskikh Reaktsiyakh* (Intermediate Products in Electrochemical Reactions), Izd. Nauka, Moscow, 1982, 215 pp
8. A P Tomilov, I N Chernykh, Yu M Kargin *Elektrokhimiya Elementoorganicheskikh Soedinenii. Elementy I, II, III Grupp Periodicheskoi Sistemy i Perekhodnye Metally* (Electrochemistry of Organometallic Compounds. Group I, II, and III Elements and Transition Metals), Izd. Nauka, Moscow, 1985, 254 pp
9. R Bates *Electrochemistry of Metals in Non-aqueous Solutions* (Translated into Russian), Izd. Mir, Moscow, 1974, p. 305
10. G Grintzner, J Kuta *Pure Appl. Chem.*, 1982, **54** 1527
11. D R Armstrong, R Fortune, P G Perkins *J. Organometal. Chem.*, 1976, **111** 197
12. J W Lauher, R Hoffman *J. Am. Chem. Soc.*, 1978, **98** 1729
13. J C Green *Structure and Bonding*, Springer, Berlin, 1981, Vol. 43, p. 37
14. J E Bercaw, R H Marvich, L G Bell, H H Brintzinger *J. Am. Chem. Soc.*, 1972, **94** 1219
15. H Alt, M D Rausch *J. Am. Chem. Soc.*, 1974, **96** 5936
16. J D L Holloway, W E Geiger *J. Am. Chem. Soc.*, 1979, **101** 2038
17. J D L Holloway, W E Bowden, W E Geiger *J. Am. Chem. Soc.*, 1977, **99** 7089
18. Y Mugnier, C Moise, E Laviron *Nouv. J. Chim.*, 1982, **6** 197
19. A Lemenovskii, V P Fedin *J. Organometal. Chem.*, 1977, **132** 11
20. A Lemenovskii, V P Fedin *J. Organometal. Chem.*, 1977, **132** 14
21. J D L Holloway, F C Senftleber, W E Geiger *Anal. Chem.*, 1978, **50** 1010
22. V V Strelets, S V Kukharenko, G L Soloveichik, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 1484
23. V V Strelets, S V Kukharenko *Nouv. J. Chim.*, 1984, **12** 785
24. A N Nesmeyanov, K A Kocheshkov (Editors) *Metody Elementoorganicheskoi Khimii. Podgrupp Medi, Skandiya, Titana, Vanadiya, Khroma, Margantsa. Lantanoidy i Aktinoidy* (Methods of Organoelemental Chemistry. The Copper, Scandium, Titanium, Vanadium, Chromium, and Manganese Subgroup. Lanthanides and Actinides), Izd. Nauka, Moscow, 1974, Vols. 1 and 2, 971 pp
25. J C Smart, J L Robbins *J. Am. Chem. Soc.*, 1978, **100** 3936
26. P Grebenik, A J Downs, M L H Green, R N Perutz *J. Chem. Soc. Chem. Commun.*, 1979, 742
27. J Chetwynd-Talbot, P Grebenik, R N Perutz *Inorg. Chem.*, 1982, **21** 3647
28. J Chetwynd-Talbot, P Grebenik, R N Perutz, M H A Powell *Inorg. Chem.*, 1983, **22** 1675
29. S V Kukharenko, V M Ishchenko, G L Soloveichik, V V Strelets *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 483
30. R J Gale, P Singh, R Job *J. Organometal. Chem.*, 1980, **199** C44
31. P R Sharp, A J Bard *Inorg. Chem.*, 1983, **22** 2689
32. Y Mugnier, C Moise, J Tirouflet, E Laviron *J. Organometal. Chem.*, 1980, **186** C49
33. N Ito, T Saji, S Aoyagui *J. Organometal. Chem.*, 1983, **247** 301
34. N El Murr, A Chaloyard *J. Organometal. Chem.*, 1980, **193** 60
35. C A Koval, R L Austermann, J A Turner, B A Parkinson *J. Electrochem. Soc.*, 1985, **132** 613
36. U Koelle, A Salzer *J. Organometal. Chem.*, 1983, **243** C27
37. R J Gale, R Job *Inorg. Chem.*, 1981, **20** 42
38. W E Geiger, D E Smith *J. Electroanal. Chem.*, 1974, **50** 31
39. N El Murr *Transit. Metal Chem.*, 1981, **6** 321
40. W E Geiger *J. Am. Chem. Soc.*, 1974, **96** 2632
41. W E Geiger, W L Bowden, N El Murr *Inorg. Chem.*, 1979, **18** 2358
42. N El Murr, J E Sheats, W E Geiger, J D L Holloway *Inorg. Chem.*, 1979, **18** 1443
43. J D Payne, N El Murr *J. Chem. Soc. Chem. Commun.*, 1984, 1137
44. J R Gale, R Job *Inorg. Chem.*, 1981, **20** 4
45. R J Wilson, L F Warren, M F Hawthorne *J. Am. Chem. Soc.*, 1969, **91** 758
46. N O Connely, W E Geiger *Adv. Organometal. Chem.*, 1984, **23** 2
47. L P Yur'eva, L N Nekrasov, S M Peregudova *Dokl. Akad. Nauk SSSR*, 1982, **264** 876
48. L N Nekrasov, L P Yur'eva, S M Peregudova *J. Organometal. Chem.*, 1982, **238** 185
49. D M Braitsch, R Kumarapan *J. Organometal. Chem.*, 1975, **84** C37
50. R G Finke, R H Voegeli, E D Laganis, V Boekelheide *Organometallics*, 1983, **2** 347
51. V Koelle, B Fuss, M V Rajasekharan, et al. *J. Am. Chem. Soc.*, 1984, **106** 4152
52. T A Albright, J K Burdett, M H Whango *Orbital Interactions in Chemistry*, Wiley, New York, 1985, 362 p
53. R D Reike, J S Arney, W E Rich, et al. *J. Am. Chem. Soc.*, 1975, **97** 5951
54. S N Milligan, R D Reike *Organometallics*, 1983, **2** 171
55. W J Bowyer, W E Geiger *J. Am. Chem. Soc.*, 1985, **107** 5657
56. R R Gagne, C A Koval, G C Lisensky *Inorg. Chem.*, 1980, **19** 2854

57. B Keita, L Nadjo *J. Electroanal. Chem.*, 1987, **230** 267
58. U Mayer, A Kotočova, V Gutmann *J. Electroanal. Chem.*, 1979, **103** 409
59. V M Gerovich, M I Podgornaya, B B Damaskin *Elektrokhimiya*, 1985, **21** 1340
60. M F Hawthorne, D C Young, T D Andrews, et al. *J. Am. Chem. Soc.*, 1968, **90** 879
61. L I Zakharkin, V N Kalinin *Uspekhi Khim.*, 1974, **43** 1207 [*Russ. Chem. Rev.*, 1974(7)]
62. L F Warren, M F Hawthorne *J. Am. Chem. Soc.*, 1968, **90** 4823
63. N I Kirillova, A I Gusev, N V Alekseev, et al. *Dokl. Akad. Nauk SSSR*, 1985, **280** 1148
64. D F Dustin, G B Dunks, M F Hawthorne *J. Am. Chem. Soc.*, 1973, **95** 1109
65. C G Salestine, M F Hawthorne *Inorg. Chem.*, 1976, **15** 2872
66. J G M Linden, C A M van der Schrauwen, J E J Schitz, et al. *Inorg. Chim. Acta*, 1984, **81** 137
67. C A Butcher, R M Pagni, J Q Chambers *J. Organometal. Chem.*, 1980, **199** 223
68. N El Murr *J. Chem. Soc. Chem. Commun.*, 1981, 251
69. C Moinet, E Roman, D Astruc *J. Electroanal. Chem.*, 1981, **121** 241
70. E Samuel, D Guery, J Vedel *J. Organometal. Chem.*, 1984, **263** C43
71. W M Gulick, D H Geske *Inorg. Chem.*, 1967, **6** 1320
72. C Furlani, A Furlani, L Sestili *J. Electroanal. Chem.*, 1965, **9** 140
73. E L Muetterties, J R Bleeke *Account. Chem. Res.*, 1979, **12** 324
74. S R Weber, H H Brintzinger *J. Organometal. Chem.*, 1977, **127** 45
75. W Lamanna, M Brookhart *J. Am. Chem. Soc.*, 1980, **102** 3490
76. J Moraczewski, W E Geiger *Organometallics*, 1982, **1** 1385
77. A M McNair, D C Boyd, D A Bohling, et al. *Inorg. Chem.*, 1987, **26** 1182
78. P Lemoine, M Gross, P Braunstein, et al. *Organometallics*, 1984, **3** 1303
79. H L M van Gaal, J G M van der Linden *Coord. Chem. Revs.*, 1982, **47** 41
80. V V Strelets, S V Kukharenko *Dokl. Akad. Nauk SSSR*, 1984, **275** 894
81. M-H Desbois, D Astruc, J Guillin, et al. *J. Am. Chem. Soc.*, 1985, **107** 5280
82. E D Laganis, R H Voegeli, R T Swann, et al. *Organometallics*, 1982, **1** 1415
83. W J Bowyer, W E Geiger, V Boekelheide *Organometallics*, 1984, **3** 1079
84. A F Diaz, U T Mueller-Westerhoff, A Nazzal, M Tanner *J. Organometal. Chem.*, 1982, **236** C25
85. J C Smart, B L Pinsky *J. Am. Chem. Soc.*, 1980, **102** 1009
86. P Lemoine *Coord. Chem. Revs.*, 1982, **47** 55
87. D E Brennan, W E Geiger *J. Am. Chem. Soc.*, 1979, **101** 3399
88. J Moraczewski, W E Geiger *J. Am. Chem. Soc.*, 1978, **100** 7429
89. C Fabbrini, L Sacconi *Inorg. Chim. Acta*, 1979, **36** L407
90. J C Kotz *Topics in Organic Electrochemistry* (Edited by A J Fry and W B Britton), Plenum Press, New York, 1986, p. 83
91. I Omac *Coord. Chem. Rev.*, 1982, **42** 31
92. J K Kochi *Organometallic Mechanisms and Catalysis*, Acad. Press, New York, 1978, 432 p
93. A A Radtsig, B M Smirnov *Spravochnik po Atomnoi i Molekulyarnoi Fizike* (Handbook of Atomic and Molecular Physics), Atomizdat, Moscow, 1980, p. 68
94. V V Strelets, S V Kukharenko *Metalloorg. Khim.*, 1988, **1** 692 [English translation in *Organomet. Chem. USSR*, 1988(1)]
95. E L Muetterties, J R Bleeke, E J Wucherer, T A Albright *Chem. Rev.*, 1982, **82** 499
96. N M Chirkov, P E Matkovskii, F S D'yachkovskii *Polimerizatsiya na Kompleksnykh Metalloorganicheskikh Katalizatorakh* (Polymerisation in the Presence of Complex Organometallic Catalysts), Izd. Khimiya, Moscow, 1976, p. 415
97. G L Soloveichik, B M Bulychev *Uspekhi Khim.*, 1983, **52** 72 [*Russ. Chem. Rev.*, 1983(1)]
98. M E Vol'pin, V B Shur *Novoe v Khimicheskoi Fiksatsii Azota* (Advances in Chemical Nitrogen Fixation), Izd. Mir, Moscow, 1983, p. 77
99. V V Strelets, V N Tsarev, O N Efimov *Dokl. Akad. Nauk SSSR*, 1981, **259** 646
100. V V Strelets, V N Tsarev, *Kinet. Katal.*, 1983 **24** 73
101. V V Strelets, V N Tsarev, *Kinet. Katal.*, 1984, **25** 821
102. V V Strelets, V N Tsarev, *Kinet. Katal.*, 1985, **26** 1344
103. V V Strelets, S V Kukharenko, V N Tsarev *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 258
104. K Tatsumi, A Nakamura, P Hofmann, et al. *J. Am. Chem. Soc.*, 1985, **107** 4440
105. N El Murr, A Chaloyard, J Tirouflet *J. Chem. Soc. Chem. Commun.*, 1980, **446**
106. N El Murr, A Chaloyard *J. Organometal. Chem.*, 1981, **212** C39
107. N El Murr, A Chaloyard *J. Organometal. Chem.*, 1982, **231** 1
108. Y Mugnier, C Moise, E Laviron *J. Organometal. Chem.*, 1981, **204** 61
109. Y Mugnier, C Moise, E Laviron *J. Organometal. Chem.*, 1981, **210** 69
110. Y Mugnier, A Fakhr, M Fauconet, et al. *Acta Chim. Scand., B*, 1983, **37** 423
111. J Losada, M Moran *J. Organometal. Chem.*, 1984, **276** 13
112. S V Kukharenko, G L Soloveichik, V V Strelets *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 1020
113. E Samuel, D Guery, J Vedel, F Basile *Organometallics*, 1985, **4** 1073
114. A Fakhr, Y Mugnier, B Gautheron, E Laviron *J. Organometal. Chem.*, 1986, **302** C7
115. A Fakhr, Y Mugnier, B Gautheron, E Laviron *Nouv. J. Chim.*, 1986, **10** 601
116. V V Strelets, G L Soloveichik, A I Sizov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 2493
117. H Schwembin, W Trischler, H Kiesele, H H Brintzinger *J. Organometal. Chem.*, 1985, **293** 353
118. M Etienne, R Choukroun D Gervais *J. Chem. Soc. Dalton Trans.*, 1984, 915
119. M F Lappert, C J Pickett, P I Riley, P I W Yarrow *J. Chem. Soc. Dalton Trans.*, 1981, 805
120. A Chaloyard, A Darmond, J Tirouflet, N El Murr *J. Chem. Soc. Chem. Commun.*, 1980, 214
121. G Erker, K Engel, C Krüger, et al., *Z. Naturforsch. B*, 1985, **40** 150
122. L Koch, A Fakhr, Y Mugnier, et al. *J. Organometal. Chem.*, 1986, **314** C17

123. S Renaud, Y Mugnier, L Ronllier, E Laviron *J. Organometal. Chem.*, 1986, **309** C11
124. S V Kukharenko, V V Strelets *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 297
125. A M Bond, A T Gasey, J R Thackeray *Inorg. Chem.*, 1974, **13** 84
126. A Fakhr, Y Mugnier, R Broussier, et al. *J. Organometal. Chem.*, 1983, **255** C8
127. A Fakhr, Y Mugnier, R Broussier, B Gautheron *J. Organometal. Chem.*, 1984, **269** 53
128. A Fakhr, Y Mugnier, R Broussier, et al. *J. Organometal. Chem.*, 1986, **317** 201
129. A A Lemenovskii, V P Fedin *J. Organometal. Chem.*, 1977, **132** C14
130. A Fakhr, Y Mugnier, R Broussier, B Gautheron *J. Organometal. Chem.*, 1985, *279* C15
131. B Viard, J Amaudrut, J Sala-Pala, et al. *J. Organometal. Chem.*, 1985, **292** 403
132. A M Bond, J W Bixler, E Mocellin, et al. *Inorg. Chem.*, 1980, **19** 1760
133. J C Kotz, W Vining, W Coco, et al. *Organometallics*, 1983, **2** 68
134. R J Klinger, J C Huffman, J K Kochi *J. Am. Chem. Soc.*, 1980, **102** 208
135. M F Asaro, S R Cooper, N J Cooper *J. Am. Chem. Soc.*, 1986, **108** 5187
136. R Finke, G Gaughan, R Voegeli *J. Organometal. Chem.*, 1982, **229** 179
137. R Reeb, Y Mugnier, A Dormond, E Laviron *J. Organometal. Chem.*, 1982, **239** C1
138. Y Mugnier, A Dormond, E Laviron *J. Chem. Soc. Chem. Commun.*, 1982, 257
139. D C Sonnenberger, J Gaudiello *Less Common Metals*, 1986, **126** 411
140. M E Silver, O Eisenstein, R C Fay *Inorg. Chem.*, 1983, **22** 759
141. P T Wolczanski, J E Bercaw *Acc. Chem. Res.*, 1980, **13** 121
142. K L Tang Wong, J L Thomas, H H Brintziner *J. Am. Chem. Soc.*, 1974, **96** 3694
143. M Moran, J J Santos-Garcia, J R Masanger, V Fernandez *J. Organometal. Chem.*, 1985, **295** 327
144. D Miholova, A A Vlček *J. Organometal. Chem.*, 1982, **240** 413
145. J Y Becker, S Avraham, B Posin *J. Electroanal. Chem.*, 1987, **230** 143
146. C Moise, N El Murr, M Riveccie, J Tirouflet *C.R. Seances Acad. Sci. (Paris)*, 1978, **287** 329
147. N El Murr, C Moise, M Riveccie, J Tirouflet *Inorg. Chim. Acta*, 1979, **32** 189
148. V L Shirokii *XI Vsesoyuznoe Soveshchanie po Elektrokhimii Organicheskikh Soedinenii: Tezisy Dokladov. L'vov* (The XIth All-Union Conference on the Chemistry of Organic Compounds: Abstracts of Reports, Lvov), 1986, p. 19
149. A A Erdman, Z P Zubreichuk, V L Shirokii, et al. *XI Vsesoyuznoe Soveshchanie po Elektrokhimii Organicheskikh Soedinenii: Tezisy Dokladov. L'vov* (The XIth All-Union Conference on the Chemistry of Organic Compounds: Abstracts of Reports, Lvov), 1986, p. 259
150. L I Denisovich, I N Chernykh *Ion-Radikaly v Elektrodnykh Protsessakh* (Radical-Ions in Electrode Processes), Izd. Nauka, Moscow, 1983, p. 147
151. I Pavlik, J Klikorka *Chem. Listy*, 1987, **81** 907
152. K Jonas *Pure Appl. Chem.*, 1984, **56** 63
153. A Bard, M Fleischmann, J Rolinson *J. Electroanal. Chem.*, 1984, **168** 299
154. D Astruc *Acc. Chem. Res.*, 1986, **19** 377
155. D Astruc *Comments Inorg. Chem.*, 1987, **6** 61
156. D Astruc *Angew. Chem. Inter. Ed.*, 1988, **27** 643
157. M Lacoste, D Astruc *J. Chem. Soc. Chem. Commun.*, 1987, 667
158. M Lacoste, F Varret, L Toupet, D Astruc *J. Am. Chem. Soc.*, 1987, **109** 6504
159. R A Saraceno, A G Ewing *Abstr. Pap. Pittsburg Conf. and Expo. Anal. Chem. and Appl. Spectrosc., Atlantic City, New Jersey, March 9–13, 1987*, Pittsburg, Pennsylvania, 1987, p. 54
160. K M Kadish, Q Y Xu, J -M Barbe *Inorg. Chem.*, 1987, **26** 2665
161. W E Geiger, N G Connelly *Adv. Organometal. Chem.*, 1985, **24** 87
162. L I Denisovich, M G Peterleitner, D N Kravtsov, et al. *Metalloorg. Khim.*, 1988, **1** 301 [English translation in *Organomet. Chem. USSR*, 1988(1)]
163. S V Kukharenko, E M Koldasheva, V V Strelets *Dokl. Akad. Nauk SSSR*, 1988, **303** 112
164. S V Kukharenko, G L Soloveichik, V V Strelets *Metalloorg. Khim.*, 1989, **2** 395 [English translation in *Organomet. Chem. USSR*, 1989(2)]

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The formation, structure, and properties of network polyurethanes

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ABSTRACT. Questions concerning the influence of the density and chemical nature of the cross-links on the properties of cross-linked polyurethanes are examined. The existing ideas about the mechanism of the formation of the network structure in polyurethanes are analysed and the causes of the inhomogeneity of the three-dimensional network in cross-linked polyurethanes are discussed. The principal advances in the study of the influence of the chemical microstructure of the macrochains of polyurethanes on the microphase separation process in thermoelastoplastics are described.
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I. Introduction

Probably none of the classes of industrial polymers existing at the present time and produced on a large scale, with the exception of polyurethanes (PU), permits the variation of their properties, from those of elastomers, thermoelastoplastics, and foams to plastics and fibres by a slight alteration of the chemical structure of the macromolecules. A combination of increased hardness, a high modulus of elasticity, and a high elasticity is characteristic of polyurethane elastomers alone, while as regards resistance to wear they have no equal. It is not fortuitous that the industrial output of PU in the countries of Western Europe, the USA, and Japan has been doubling in each decade[1] and has reached about four million tonnes in 1986. In the USSR, the output of PU is approximately 100 000 tonnes per year and a growth of the manufacture of network polyurethanes (NPU) by a factor of four relative to 1985 is planned for 1990. The aim of the present review is to consider the principal results of research into the formation, structure, and properties of network polyurethanes.

II. Network formation in polyurethanes and its influence on the properties of network polyurethane

Processes involving the branching and subsequent cross-linking of linear macromolecules of a polymer have a decisive influence on its properties.[2] At the present time, one may claim that the formation of a network suppresses the microphase separation characteristic of certain polyesterurethanes to a greater extent the denser the network formed.[3,4] On the other hand, when a more flexible polydiene block has been introduced into the PU macromolecule instead of the ester block, then the microheterogeneity is retained regardless of the density of the network.[5]

Numerous studies have been devoted to the influence of the frequency of the cross-linking on the crystallisation and glass point (T_g) of network polyurethanes (NPU). Whereas the available data on the crystallisation of NPU are unambiguous,[6,7] namely the degree of crystallisation diminishes down to zero with increasing degree of cross-linking, the results for T_g differ greatly. It has been established for the NPU based on polyoxy(ethylene glycol) and 4,4′-diphenylmethane diisocyanate (MDI) [8] that T_g increases linearly with the density of cross-linking. On the other hand, when hexamethylene diisocyanate (HMDI) is used, the above relation passes through a maximum. On these grounds, it has been concluded that the aromatic nuclei and urethane groups in the macrochains exert a decisive influence and that T_g depends only slightly on the chemical cross-linking. A similar conclusion that the interaction of the polar groups in NPU has a strong influence has been reached in another study.[9] Nevertheless, some investigators believe that the T_g for NPU tends to increase with increasing degree of cross-linking.[10] Using the principle that individual structural elements influence independently the T_g for the polymer, Becker and Neumann[11] obtained formulae for the theoretical calculation of T_g taking into account the degree of cross-linking. An experimental test was performed on 59 linear and 27 cross-linked amorphous PU and demonstrated a satisfactory agreement between the calculated and experimental data.

The influence of the chemical nature of the cross-links on T_g is characteristic of NPU. It has been observed by broad band NMR [12] that T_g for PU based on poly(ethylene glycol adipates) (PEGA) and MDI with allophanate cross-links is −20 °C, while that for the PU with biuret cross-links is −15 °C. On the other hand, when ionic cross-links are introduced into the same PU, the mobility of the segment diminishes and T_g is in the range between −13° and −8° C. With increase in the concentration of interchain carbon–carbon bonds, T_g increases from −50 °C for a weight fraction of dicumenyl peroxide of 1.4 to 0 °C for a weight fraction of 2.5 relative to the non-cross-linked PU. Cross-linking by chemical bonds by employing trifunctional polyesters (PE) with a molecular weight (MW) in excess of 5000 g mol^{-1} does not alter the degree of self-association compared with linear PU.[13]

The nature of the cross-links influences not only T_g and the degree of self-association but also many other properties of the NPU. Thus the interaction of 2,4-tolylene diisocyanate (2,4-TDI) with the ions of 3*d* elements[14,15] in certain solvents can yield in the

final stage polynuclear complex forms of the diisocyanate whose functionality with respect to the NCO group is greater than two. Subsequent reaction with polyesters results in the formation of an NPU whose specific conductance is 5–6 orders of magnitude greater[16] than that of the usual NPU.[17] The strengths and thermal parameters of such NPU are close to those of the industrially manufactured PU, while their elasticity and resistance to wear are actually greater. The thermal stability of NPU can be significantly increased by using Mannich bases as catalysts of the urethane formation reaction.[18] This entails not only an increase in the length of the macromolecules as a result of the interaction of the macrodiisocyanate with polyesters but also the formation of a network as a result of the cyclotrimerisation of the terminal NCO groups.

The degree of homogeneity of the reactions occurring in the reaction system has become one of the first controversial problems as regards the formation of NPU. Two points of view have arisen in this connection. According to the studies by Lipatova and co-workers,[19–21] the formation reaction of the three-dimensional structure consists of two stages which differ sharply in their rates. The reaction is described by a second-order kinetic equation only up to 45–50% conversion owing to a change in the physical process conditions.[19] Beyond the gel point, the formation of the polyurethane network is described satisfactorily by the Avrami-Erofeev equation. It has been suggested that, after the attainment of a certain degree of conversion, the system undergoes microphase separation and the urethane formation kinetics begin to be determined by physical and no longer by chemical processes. Indeed, studies on the formation of NPU by the turbidity spectrum methods[20] have shown that, in the two-stage method of synthesis of NPU, particles of sizes of the order of 650 Å appear by the time of attainment of 70% conversion. Measurements of the angular dependence of the scattered light intensity indicate the presence of cross-linked microparticles and not aggregates of macromolecules. A single network is produced by the chemical cross-linking of network microblocks.[21] On the other hand, it is now difficult to regard the conclusion that physical factors have a decisive influence on the urethane formation kinetics beyond the gel point as rigorously demonstrated, because the power exponent in the Avrami-Erofeev equation is almost unity.

The study of the urethane formation kinetics before the attainment of the gel point and beyond it revealed[22] that in the temperature range 20–60 °C the reaction rate constants are virtually identical and the activation energies are 40.8 and 45.6 kJ mol^{-1} respectively, from which it is concluded that the rate of reaction is not diffusion controlled after gel formation. This conflicts with the view expressed by Lipatova and Ivashchenko[23] and Rumyantsev et al.[24] Data obtained[25] by the repeatedly distorted total internal reflection method led to the analogous conclusion that the kinetics of the formation of PU both in the liquid phase and beyond the gel point are the same. These results conflict with the conclusions reached by Lipatova and co-workers. It is notable that experimental data similar to the observations by the Kiev group of investigators have been obtained in a number of foreign studies. Hager et al.[26] and Huang et al.[27] arrived at the conclusion that phase separation takes place during the urethane formation process. A dependence of the urethane formation rate constant on the degree of conversion starting from 30 – 40% conversion has also been reported.[28]

In our view, the conflict between the conclusions reached by these research groups is only apparent. As will be seen from further exposition, the chemical processes leading to gel formation are extremely sensitive to many factors: the chemical nature of the reaction system, the presence and nature of a solvent, the concentration and stoichiometry of the reactants, the temperature, etc. For this reason, in each case a specific situation can arise. Under certain conditions, microregions with an increased content of the cross-linking agent or an increased concentration of NCO groups can appear in the reaction system even at the beginning of the reaction. This can occur either as a result of self-association,[29] or as a result of the poor compatibility of the components,[30,31] or because of the physical influence of the urethane groups which have appeared in the reaction system.[32,33] Clearly cross-linking in these regions occurs already in the early stages, which results in the appearance of the microgel. Further consumption of the NCO groups can take place in regions with different ratios of the functional groups, which is the reason for the observed change in kinetics. On the other hand, when the gel formation conditions are such that the concentration of the reactants is constant throughout the reaction volume, the microgel is not formed up to the gel point. The kinetics of the consumption of the NCO group beyond the gel point remain the same as before, because their reactions occur mainly in the sol fraction. The results of the studies considered above and our own data[34,35] lead to these conclusions. Thus the study of the influence of the number of stages in the formation of NPU on their strength parameters revealed that the bimodality of the distribution on the probability curve for the appearance of a particular tensile strength is more pronounced for the single-stage NPU preparation conditions. On the other hand, when the network polyurethane was obtained via a stage involving the synthesis of the macrodiisocyanate, the bimodality was much less marked, which can be explained by the lower concentration inhomogeneity of the terminal NCO group and hence by the lower inhomogeneity of the three-dimensional network of the PU. When rolled PU was vulcanised, the distribution curve was unimodal.

The change in the urethane formation mechanism is frequently inferred from the deviation of the kinetics of the consumption of NCO group from a second-order irreversible reaction. Apparently this can be done legitimately only for non-catalytic urethane formation processes. In the case of catalysed reactions, the consumption of NCO groups is described by more complex relations. Indeed, in a study of the urethane formation reaction between the macrodiisocyanate based on PEGA and 2,4-TDI and butane-1,4-diol (BD) in the presence of iron acetylacetonate,[36] the order of the reaction varied from three at the beginning to two at the end. The analytical expression describing the rate of consumption of NCO groups assumes the following form:

$$R = (AX^3 + BX^2)/(CX + K_1^-),$$

where A, B, and C are algebraic combinations of the rate constants for the individual urethane formation stages and the catalyst concentration, X is the current concentration of NCO groups, and K_1^- the rate constant for the decomposition of the binary intermediate complex into the initial reactants. At the beginning of the reaction, $AX^2 < BX^3$ and $CX < K_1^-$, so that the order of the reaction is three. As the reaction proceeds, the term BX^3 diminishes faster than AX^2 and the order tends to two. For other reaction systems, where this mechanism operates, a situation may be encountered where $AX^2 > BX^3$ and $CX \gg K_1^-$. The order of the reaction should then be unity throughout the kinetic curve. Thus the observed change in the rate of urethane formation is presumably in many cases associated with purely kinetic factors and not with a change in mechanism.

A complex gel formation process depends on many factors. In a study of the formation of NPU from PE, 1,1,1-tri(hydroxymethyl)-propane (THMP) and 2,4-TDI, it was shown[37] that, depending on the type of medium and the degree of dilution, the relative reactivities of the reactant as well as the tendency of the system towards ineffective macrocyclisation or three-dimensional polycondensation change significantly. The changes in the relative reactivities of the hydroxylated components in the reaction with diisocyanate can be achieved also by introducing a catalyst. The addition of tin dibutyl dilaurate [bis(butyl laurate)tin?] to the reaction system described above leads to the formation of a NPU with good physicomechanical properties,[38] while in its absence gel formation does not occur at all. The presence of hydroxylated compounds with different reactivities can entail a non-equilibrium distribution of cross-links in the polymer network and can reduce the modulus of elasticity compared with the calculated value.[39] The self-association of THMP can actually result in the appearance of polyfunctional branching units.[29]

Network formation in PU is frequently complicated by cyclisation especially near the gel point.[40,41] The fraction of cyclised molecules in the synthesis of PU in bulk can attain 2–3% for a degree of conversion of 0.9 and an initial ratio of the NCO and OH groups of unity. In the 0.1% solution, the fraction of cyclised molecules for the same conversion in the synthesis of PU increases to 85%.[42] The study of the cyclisation process is also essential because the pre-gel formation of loops and not entanglement make the main contribution to the defects.[43] Furthermore, there is a close relation between the intramolecular reactions before the gel formation point and the network defects. Such reactions result in the formation of elastically ineffective rings whose influence on the physical parameters of the network is opposite to that exerted by molecular entanglement.[44] The elastically ineffective rings at a concentration of 3% diminish the concentration of elastically active chains and the equilibrium modulus by ~30%.[45] With increase in the degree of cyclisation, the molecular weight of the region between neighbouring nodes of the network increases.[46] The degree of cyclisation depends not only on the ratio of the NCO and OH groups in the system, the degree of its conversion, and its dilution, but also on the MW of the polyester[47] as well as on the presence or absence of the catalyst in the system.[48] The higher the MW of the polyester, the greater the tendency towards cyclisation.[47,49] The tendency towards cyclisation is greater in the case of a two-stage cross-linking process than for a single-stage process, which is associated, according to the authors, with the possibility of the formation of MDI–THMP clusters when the reactivities of the OH groups are not the same.

It is of interest to note that macrocyclisation is observed even in those cases where the possibility of the formation of NPU is ruled out[50,51]—for example, the degree of cyclisation increases with increasing MW of the chain.

The influence of the flexibility of the polyester chain on the effective density of the three-dimensional network of the PU and on their structure has been traced in the study of Eremeeva et al.[52] It was then found that a denser and more stable effective three-dimensional network is formed in NPU based on flexible-chain oligoesters compared with PU having rigid macromolecules.

There exist interesting data concerning the influence of the nature of the PE on the gel formation process.[53] In the synthesis of linear oligoesters based on diethylene glycol and various dicarboxylic aliphatic and aromatic acids and the study of their reactions with the adduct 2,4-TDI–THMP in cyclohexanone, it was found that the rate of formation of MPU up to a degree of conversion of 60–70% is described by a second-order equation, while for higher conversions the process is complicated by gel formation and takes place under microheterogeneous conditions. The degree of reaction at the gel point and the critical degree of branching depend on the nature of the acid residue of the PE and particularly the greater the flexibility and the smaller the steric hindrance characterising the PE chain.

Complex PE [polyethylene(diethylene glycol adipates)], characterised by different degrees of molecular and topological inhomogeneity have been synthesised.[54] The degree of inhomogeneity of the chemical three-dimensional network of the NPU obtained on their basis depended directly on the degree of inhomogeneity of the initial PE. On the other hand, the inhomogeneity of the physical three-dimensional network, observed for small degrees of monoaxial equilibrium stretching deformation (<2%), was proportional to the concentration of the urethane groups in the macrochain. A transition from linear to viscoelastic behaviour, occurring in the region of low deformations of ~0.5–3.0%, has been reported.[55] The authors believe that the phenomenon is due to the thixotropic breakdown of the aggregate formed via intramolecular interaction.

The influence of a solid surface on the characteristics of gel formation in PU has been traced.[56,57] The data obtained have been interpreted from the standpoint of the heterogeneity in the reaction mixture, which is manifested at a specific stage of the PU formation process.[56] The nature of the PE does not alter the character of the influence of the filler (aerosil) on the structure formation in the hardening system. The filler prevented the formation of a gel in the system comprising a polyether, THMP, and MTI. On the other hand, when 2,4-TDI was used instead of MDI,[57] then the aerosil actually created more favourable conditions for gel formation. The strong influence of fillers on the structure of the three-dimensional network has been indicated.[58,59] A strong chemical interaction of the PU macromolecules based on a polyester with technical carbon particles has been observed.[60] The activation energy for the formation of the chemical bond was 123 kJ mol^{-1} and the limiting surface area of the technical carbon per bond of this kind was 11 $Å^2$. Under conditions where physical as well as chemical interaction between the technical carbon and PU is possible, this area is 7 $Å^2$, which indicates an appreciable fraction of physical cross-links.

The presence of a well developed physical network, whose appearance is due to a broad spectrum of intermolecular interactions, is characteristic of PU. This is no longer disputed at the present time but quite a few studies have been devoted to the determination of the quantitative relation between the densities of the chemical and physical networks in the NPU and also to the elucidation of factors influencing this relation. Such studies have been stimulated primarily by the strong influence of the nodes of the three-dimensional physical network on a series of physicochemical and operational characteristics of the PU. Thus sorption, thermo-mechanical, and spectroscopic studies have been carried out[61,62] on the network in the PU based on tri(hydroxymethyl)propane phthalate and aliphatic polyisocyanate. It has been shown that a fairly open chemical network is formed with M_n = 2500 g mol^{-1}. The physical nodes are extremely varied with respect to density (M_n of the order of 200 and 500 g mol^{-1}) and greatly increase the effective density of the network. The appearance of three-dimensional structures with network nodes, formed as a result of specific physical interactions, has been noted[63] already in the initial stages. Deformation tests on an NPU with a controllable network topology led Allen et al.[64] to the conclusion that the influence of physical entanglements in unswollen specimens on the modulus of the network is comparable

in magnitude to the influence of chemical cross-linking. Admittedly, the nature of the physical entanglement was not specified and one cannot therefore rule out the possibility that the increase in the modulus is associated with the occurrence of intermolecular interactions. Indeed, Dusek and Ilavsky[65] found in the determination of the equilibrium moduli of urethane networks that the structural front-factor A may be greater than unity, i. e. greater than the value expected for phantom networks, for which $A \leqslant 1$. This confirms the hypothesis that the interchain contacts may contribute to the equilibrium moduli. It has been stated[66] that the networks obtained are affine rather than phantom. This shows that polyurethane networks are more perfect than fully random networks.

As a rule, the dependence of the conventional strain in the NPU (σ) on the degree of its deformation (λ) is described satisfactorily by the Mooney–Rivlin equation.[67,68] However, it has been observed[69] that the classical relation $\sigma = f(\lambda - \lambda^{-2})$ for the PU investigated is represented by straight lines as far as $\lambda - \lambda^{-2} \simeq 0.1$, which subsequently become bent as the origin of coordinates is approached. In terms of the variables of the Mooney–Rivlin equation, the experimental data did not fit on the straight line and the constant C_2 did not really remain constant. It decreased with increasing degree of deformation and became a maximum at $\lambda = 1$; analogous data have been described elsewhere.[70]

Walsh et al.[71] concluded that polyurethane networks containing short polyol chains differ significantly in their deformation behaviour from ideal networks. They explain the results in terms of phase separation occurring in such PU. In a study of the deformation of diamine-hardened PU,[72] the constant C_2 of the Mooney–Rivlin equation actually proved to be negative.

All these facts definitely indicate that, with rare exceptions, the polyurethane networks are not ideal. This is apparently associated with the occurrence of strong intermolecular interactions in the NPU. These physical interactions are responsible for the large contribution by the energy component of the highly elastic deformation of NPU.[73,74]

The great influence of the chemical and topological structures of polyurethane networks on the properties of NPU has already been noted frequently above and in certain cases the effect of the network topology is comparable or even superior to the effects of the remaining factors. It is therefore extremely important to investigate the homogeneity of the polyurethane networks. The ideas of various authors on this question agree[75–79] and reduce to the fact that the network structure of the PU formed is inhomogeneous. The studies[80,81] in which it was concluded that the networks are highly homogeneous after investigating the mechanical, dielectric, rheopectic, and optical properties of model polyurethane networks constitute an exception. Admittedly, the same workers[82] reported the observation of an inhomogeneous network, but they explained its appearance by the microsyneresis occurring when the temperature of the synthesis is altered abruptly.

Lipatova et al.[77] also explained the increase in the heterogeneity of the NPU with increasing degree of cross-linking or the MW of the oligomer by the increase in the number of associated rigid chain fragments. The possibility of regulating the microheterogeneity of NPU by varying the intermolecular interactions in this system has been discussed.[74] It has been suggested in 1973 [32] that intermolecular interactions, leading to the fluctuation of the structural network in the oligomer even before the formation of a continuous chemical network, may play a major role in gel formation in oligomeric systems. Under such conditions, a preliminary order, leading to the microheterogeneity of the system, is established beforehand. X-Ray diffraction and other studies on swollen polyurethane networks[78,83] have also led to the development of an approach to the NPU as heterogeneous systems, their microregions being characterised by different parameters of interaction with the solvent.

It has likewise been demonstrated[84] that polyurethane networks are inhomogeneous, but the kinetic aspect of urethane formation, in particular the presence of monofunctional molecules in the system, is used as the mainstay of the explanation of the causes of this phenomenon. The observation of additional maxima in the thermostimulated depolarisation current is attributed to the accumulation of charge at the boundaries of regions with different degrees of cross linking.[85] The existence of a relation between the kinetics of the main chemical reaction (the formation of the urethane linkage), the gel formation process, and the structural characteristics of the hardened NPU has been reported also in another study by the same workers.[49]

The inhomogeneity of polyurethane networks as regards the cross-linking density results in a variable rather than a constant (as in an ideal network model) MW of the regions between the cross-linking nodes. In the treatment of the experimental data obtained, this must be taken into account, since a change in the conditions governing the synthesis of the polyurethane network can entail a significant alteration of the properties of the finished material.[86] An increase in the temperature of the synthesis led to an increase in the density of the three-dimensional chemical network as a result of a change in the ratio of the rate constants for the reactions of bi- and tri-functional alcohols with diisocyanate. Since the concentration of THMP was unaltered in all the experiments, the results obtained can be accounted for by a change in the distribution of M_n with respect to length.

Theoretical analysis of the MWD of the macrochain fragments between neighbouring cross-links carried out in a number of studies[87–89] makes it possible to approach the control of the molecular structure of network polymers with the aid of purely kinetic methods. Thus it has been shown theoretically[88] that, if the MWD in the initial oligomer is narrow, then the network chain distribution curve has a polymodal character. If the MWD becomes wider, the polymodality of the network chain distribution can ultimately vanish. An interesting outcome of the application of Zabrodin's theory[88,89] is the demonstration of the theoretical possibility of obtaining a narrower network chain distribution under certain kinetic conditions than the initial distribution. This conclusion has been criticised by Irzhak as erroneous.[2]

The kinetic approach to the study of the influence of the MWD and of the distribution with respect to different types of functionality (DTF) of the initial oligomers on the MWD and the DTF of linear molecules and network fragments has been developed.[90–92] It is notable that systems of differential equations are obtained with difficulty for the most realistic conditions in the synthesis of NPU, the equations often being simply insoluble, and the statistical approach to the solution of problems of this kind therefore appears more promising.[2]

When the mathematical theory of graphs was used in the study of the topology of a network polymer, it was demonstrated from the standpoint of conformational statistics[93] that the topological factors influencing the entropy of the system are responsible for the inhomogeneity of the networks, the inhomogeneity being greater the higher the network density.

Technological factors exert an enormous influence on the properties of the NPU and in the first place comes the number of stages in the urethane formation process.[94] In the single-stage

process, all the components of the reaction mixture are charged into the reactor simultaneously. In the two-stage version, the macrodiisocyanate pre-polymer is obtained initially by the reaction of the oligomer having terminal OH groups with an excess of the diisocyanate to which a chain lengthening cross-linking agent is added in the second stage. In the single-stage method of synthesis, the melting range of the PU crystallising is wider[95] than in the case where the pre-polymer with terminal NCO groups is formed in the preliminary step. According to the results of a number of workers, the set of physicomechanical properties is found to be best with the single-stage synthesis regime,[95,96] but the results of one study[97] permit the conclusion that the method of synthesis of PU based on polyethers is not appreciably reflected in the mechanical properties. For PU based on polyesters, the two-stage method has led to more effective mechanical parameters. The content of the sol fraction is reduced,[13,98] while the modulus of elasticity increases in the two-stage method of synthesis. Admittedly, Cherkasova et al.[99] arrived at the opposite conclusion that the less regular disposition of the units in the chain, observed in the single-stage method, ensures a higher value of the modulus.

A detailed comparison of the gel formation processes established[100] that the gel formation in NPU obtained in a single stage begins earlier. The networks formed in the single-stage process exhibit broader transitions at the glass point,[98] in agreement with data[95] indicating a broadening of the melting temperature range.

The facts presented show that the topological structure of the three-dimensional PU network depends greatly on the method by which it is produced and the results of different workers concerning the dependence of the mechanical properties on the regime used in the synthesis of the NPU do not agree. This is apparently due to the dependence of these properties on many factors and not only on the synthesis regime.

It has been shown in relation to the preparation of the network structure in rolled and cast PU [101] that the macromolecules of the oligomer obtained in the first stage are highly branched even in the presence of a small excess of the diisocyanate relative to the polyester. Since the kinetic characteristics of the linear growth of the oligomer macromolecules and of their branching are various, the possibility arises of regulating the temperature of the first stage to alter specifically the degree of branching of the prepolymer and hence the topology of the network obtained in the second stage of the synthesis of the NPU. By carrying out the first stage of the synthesis in accordance with the temperature regime ensuring a low probability of the branching of the prepolymer macromolecules, a significant increase in the tensile strength and in the relative elongation of the NPU was achieved compared with specimens obtained in accordance with the traditional isothermal regime.[102] Furthermore, there was a sharp growth of the viability of the cast composition and the densities of the effective and chemical three-dimensional networks diminished somewhat. In view of the demonstration of the strong influence of the degree of branching of the macromolecules being cross-linked on the properties of the NPU, an accelerated method for its estimation, based on a combination of intrinsic and maximum Newtonian viscosity data, was developed.[103] It has already been mentioned earlier[86] that the density of the nodes of the three-dimensional network formed varies as a function of the urethane-formation temperature. Later the same workers[104] studied in detail the influence of the polycondensation temperature on the gel formation kinetics and the properties of cross-linked polyester urethanes based on the copolymer of tetrahydrofuran with epoxypropane, THMP, and 2,2-bis(4-isocyanatophenyl)hexafluoropropane. It was then found that the amount of the gel fraction and the effective concentration of the chains between the branching nodes are maximum at 27 °C, diminishing with increase in the hardening temperature. The glass point of the NPU obtained depends only slightly on the hardening temperature. The conventional tensile stress is a maximum for a hardening temperature of 50 °C and the relative tensile deformation at rupture increases with increasing gel formation temperature. Somewhat different results have been obtained for another reaction system using a copolymer of tetrahydrofuran with epoxypropane, THMP, BD, and 2,4-TDI. With increase in the synthesis temperature from 30° to 60 °C, the limiting content of the gel fraction rose and the gel point appeared for a lower degree of conversion of the isocyanate groups and tended to the theoretically calculated value. An increase in the density of cross linking, the conventional tensile stress, and the modulus of elasticity accompanied by a decrease in the tensile deformation were also observed. The authors see an explanation of these findings in a decrease in the fraction of the unreacted THMP cross-linking agent with increase in the temperature of the synthesis as a result of the equalisation of its reactivity to that of the tetrahydrofuran–epoxypropane copolymer.

At the same time, the changes in the growth of the macromolecules with increase in the reaction temperature from 70° to 125 °C have also been attributed[105] to the decrease under these conditions in the molecular interaction, which leads to a greater mobility of the macromolecules. There has been a tendency to explain the influence of the synthesis temperature on the structure and relaxation properties of elastic polyurethane networks in terms of purely physical factors.[96,106] The observed anomaly in the elastic properties and in the effective density of the network, consisting in a decrease in these characteristics with decrease in the hardening temperature when the latter is below 80 °C has been attributed to a corresponding increase in the amount of globular formations—the main type of supermolecular structures in the majority of NPU.[96] The size of the globules depends both on the MW of the PE and on the hardening temperature.

Globular formations in NPU have been observed also in other investigations.[12,107,108] The specimens synthesised by the single-stage method sometimes do not exhibit any signs of a globular structure and have better mechanical properties.

The possibility of regulating the dimensions and morphology of the supermolecular PU structures with the aid of the temperature regime has been reported.[109] A low-temperature regime ensured the formation of PU with a monodisperse granular structure.

The conditions in the synthesis of the NPU have a definite effect also on their resistance to thermal degradation.[110] Whereas the NPU synthesised at 40–90 °C decompose with an effective activation energy of 159–169 kJ mol^{-1}, the kinetic parameters of the thermal degradation of the specimens obtained at 30 °C depend on the rate of hardening of the polymer: the higher the rate of urethane formation, the lower the activation energy for thermal degradation. It has been suggested that the decrease in the activation energy for the cross-linked polyesterurethanes can be due to the formation of stressed chemical bonds.

The thermal stability of NPU is determined to a large extent by the chemical nature of the diisocyanate (DI). The NPU based on aromatic dinuclear DI exhibit the greatest thermal stability, while that of the NPU based on aliphatic DI is smallest.[111]

The hardening temperature can influence significantly the mechanical behaviour of NPU on extension. It has been observed[112] that a specimen of cast NPU, hardened at 80 °C, has a higher initial modulus and relative deformation on monoaxial extension compared with the specimen obtained at 140 °C (Fig. 1), which indicates the existence in it of a structure divided into separate regions.

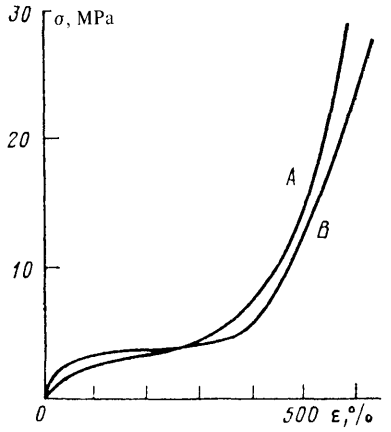


Figure 1. Dependence of the conventional stress σ on the relative elongation ε on monoaxial extension of the NPU: *A*, NPU specimen hardened at 140 °C; *B*, NPU specimen hardened at 80 °C.[112]

The influence of the ratio of the isocyanate and hydroxy-groups and also of the nature of the chain elongating agent on the chemical and physical nodes of the NPU network has been examined.[113] It was found that an increase in the NCO/OH molar ratio from 2.75 to 5.0 in the macrodiisocyanate formation stage leads to an increase in the densities of both the chemical and physical networks, the effective network density being much higher when the chain elongating agent is an aromatic diamine and not a low-molecular-weight diol. The study of the IR absorption spectra of the NPU obtained led the authors to the conclusion that hydrogen bonds exist up to 200 °C. The same view was arrived at also in other studies[114,115] where it was discovered that urethane–urethane hydrogen bonds exist even at 200 °C. On the other hand, Hagawa et al.[116] assume that hydrogen bonds begin to dissociate at ~70 °C. The differences between the results are apparently due to the presence in the NPU of hydrogen bonds of different nature and hence to their different thermal stabilities.

III. Urethane thermoelastoplastics

One of the most interesting types of network polyurethanes is that of thermoelastoplastics (UTEP), sometimes referred to as segmented PU. Their distinctive feature compared with the usual NPU consists in the fact that the three-dimensional network of the UTEP is capable of reversible decomposition on heating. Depending on the nature of the three-dimensional network of the UTEP, it is possible to classify them in the following way. The first type of UTEP is characterised by a linear structure of the macromolecules and the presence of domains, whose appearance is due to microphase separation as a result of the presence in the macrochains of sections differing sharply in flexibility and in the strength of intermolecular interaction. The domains play the role of multifunctional physical cross-links between the macromolecules, which decompose reversibly at an elevated temperature. The presence of a chemical three-dimensional network with allophanate or biuret nodes is characteristic of the second variety of UTEP. The density of the chemical three-dimensional network is such that there is no microphase separation or it is extremely weak. At temperatures of the order of 110–150 °C the allophanate (or biuret) nodes decompose reversibly and the UTEP macromolecules acquire the ability to move relative to one another when a load is applied. The third variety of UTEP is intermediate between the first and second.

The greatest number of structural studies have been devoted to the microphase UTEP. The development of the ideas of Cooper and Tobolsky[117] about the morphology of PU using wide and small angle X-ray diffraction and light scattering methods as well as differential thermal analysis (DTA) has led to the demonstration that the rigid units of the macromolecules, formed when the diisocyanate interacts with a low-molecular-weight diol (and/or diamines), aggregate into individual microphases.[118–121] A microscope study of the segmented PU established[122,123] that the domains have a lamellar structure, whose extent can reach in certain cases 3000–8000 Å but is usually in the range 30–200 Å.[124–127] The rigid units in the domain are extented into a rod-like tactoid form,[128] the length of the rigid block being identical with the width of the domain.[129]

It has been recently observed[130] that flexible polyesterurethane segments of UTEP based on polyoxy(tetramethylene glycol) (POTMG) with a MW of 2000 g mol^{-1}, MDI, and BD are also capable of becoming ordered. They form lamellae ~300 Å high and 2000 Å wide.

Treatment of UTEP with polar solvents leads to the formation of domains with a more ordered structure, which affects the physicomechanical parameters.[131]

Two types of fine structure have been discovered by IR spectroscopy in UTEP based on di(hydroxyethyl)terephthalamide, MDI, and POTMG.[132] A difference in the orientational behaviour of different sections of the rigid segment in the more ordered structure has been established and its inhomogeneity has been postulated.

The conclusion that the structure of the domains is inhomogeneous has been reached also by Vatulev et al.[133] from calculations of the orientation factor for the probable conformation of the diphenylmethaneurethane fragment. The calculated data do not make it possible to reduce the difference in the dichroism of the corresponding bands solely to a difference in the mutual orientation of the urethane and amide carbonyls.

Interpretation of literature data showed[134] that the kinetics of phase separation in segmented PU based on polyethers and polyesters can be represented as the segregation of two types of rigid segments with relaxation times τ_1 and τ_2.

Various physical and chemical processes, influencing greatly the formation of domains, may occur in the reaction system where the complex urethane formation process takes place. The chemical cross-linking of macromolecules lowers their mobility, inhibiting the ordering processes,[132] and thereby prevents microphase separation. The physical three-dimensional network restricts the process involving the segregation of the flexible and rigid blocks in the

NPU to a greater extent than does the chemical network.[135] The cross-linking resulting from the introduction of low-molecular-weight agents diminishes the degree of self-association to a greater extent than the network with the same density formed by a trifunctional polyester with MW $\geqslant$ 5000 g mol^{-1}.[136] The degree of phase separation increases with increasing MW of the PE [137] and, in the case where oligodienediols are used in the reaction instead of PE,[138] is independent of the density of the network.

The question of the influence of hydrogen bonds on the microphase separation process in PU is extremely interesting. Bonart and Morbitger[139] believe that the degree of microphase separation depends on the affinity of the rigid segments for one another and also for the flexible segments. Owing to the affinity of the ester groups of the flexible segments for the urethane groups of the rigid segments, the degree of separation in UTEP of the ester type is systematically lower than in elastomers based on polyethers. Indeed, IR spectroscopic studies[140] have shown that mainly hydrogen bonds of the urethane–flexible segment type with inclusions of small self-associated species (dimers and trimers) exist at the beginning of the microphase separation. Subsequently the microphase separation is accompanied by the redistribution of the hydrogen bonds towards the occurrence of urethane–urethane interactions in the domains. As a consequence of kinetic and viscosity effects, this process is prolonged and it has been shown[141] that the time of attainment of equilibrium in the segregation process depends on the nature of the soft phase and is determined by molecular mobility and not thermodynamic parameters. Thus one must conclude that the greater the degree of hydrogen bonding in the system the less effective is the domain formation in it.[142,143] However, it has been shown[144,145] that the hydrogen bonds between the C=O group and the NH groups of the urea linkage intensify the phase separation effect in PU. All these facts show that the domain formation process is very complex and the ratio of the hydrogen bonds between rigid segments and also between rigid and flexible segments is not the least important factor on which it depends. The conclusion[146] that the flexible segments play the role of a diluent should be regarded not as a rule but rather as an exception to it. The hydrogen bonds between rigid and flexible units are responsible for the appearance of a transitional layer at the interface even in highly dilute systems.

Presumably the hydrogen bonds between rigid segments promote microphase separation, especially since the energy of the hydrogen bonds in polyesterurethaneureas can reach 50–100 kJ mol^{-1},[147] i. e. may be comparable to the energy of the covalent bonds and is the decisive factor in the free energy gain on microphase separation in PU.

In segmented PU with a rigid segment of the glycol diisocyanate type, the energy of the hydrogen bond is appreciably lower and microphase separation can also be caused by the thermodynamic incompatibility between the rigid and flexible segments and not only by the hydrogen bonds. This is supported by the occurrence of microphase separation on passing from PU with the –NHCOO– group to polymers without hydrogen bonds and containing >NCOO– or –COO-groups.[148]

The glass point T_g of UTEP is closely related to the question of microphase separation. A linear dependence of T_g on the concentration of urethane groups in the chain is characteristic of non-thermoplastic PU,[149] whereas for segmented PU containing an appreciable number of polar and primarily urethane or urea groups such a dependence becomes more complex. This is due to the dominant influence on T_g of the overall concentration of urethane groups and the character of their distribution along the macrochain. When all the rigid segments have been segregated into domains and there is no interaction between the rigid and flexible segments, two glass points should be observed theoretically: the glass point of the soft block in the low-temperature region, which is identical with the T_g of the initial polydiol, and the glass point of the rigid segment in the high-temperature region, equal to the T_g of the polymer obtained from the low-molecular-weight diol (and/or diamine) and the diisocyanate. However, the glass point in the low-temperature region is usually higher than for the initial PE, which indicates an increase in the rigidity of the PE macromolecules as a result of the interaction with the rigid segments.[150,151] A formula has been proposed[151] for the calculation of the mole fraction of the hydrogen bonds formed by the rigid and flexible blocks (X_b):

$$(T_{g,pe} - T_{g,pu})/T_{g,pu} = k \cdot X_b(1 - X_b),$$

where $T_{g,pe}$ and $T_{g,pu}$ are the glass points of PE and the soft PU segments and k = 1.2–1.5.

The mobility in the transitional regions formed by the flexible and rigid blocks as a consequence of their limited compatibility can be sometimes observed by the calorimetric method[152] from the heat change in the intermediate temperature range. This intermediate phase is observed especially clearly on the thermomechanical curves.[153] With increase in the MW of the PE, the individual sections of the flexible block emerge from the sphere of action of the domains, which lowers the T_g of the UTEP matrix.[154] An analogous picture is also observed when poly(isobutylene glycol) is used as the flexible block instead of the PE,[155,156] although the influence of the MW of the flexible block on the T_g is not so great.

The theoretical prediction of the temperature T_d of the reversible decomposition of the domain structure is extremely important for the practical utilisation of the UTEP of the first kind. A thermodynamic theory of UTEP with a domain structure has been proposed.[157] The equation for the calculation of the temperature T_d has the following form:

$$1/T_d = -(R/\Delta H_A) \ln [e^{\nu/Z}(\nu - 1)/N_A], \quad (1)$$

where ΔH_A is the enthalpy of the ordering of 1 mol of rigid units (the enthalpy of the phase transition), N_A the mole fraction of the rigid units (the enthalpy of the phase transition), N_A the mole fraction of the rigid units, ν the coordination number of the lattice, and Z the number of rigid and soft units of the macrochain forming the $A-B$ block.

The change in the disordering temperature on passing from the PU whose macrochains consist solely of rigid units (T_d^0) to the PU containing flexible segments is described by the formula

$$1/T_d - 1/T_d^0 = (R/\Delta H_A) \ln N_A. \quad (2)$$

Eqn. (2) is analogous in form to Flory's formula for the equilibrium crystallisation of polymers.

Analysis of Eqn. (1) shows that the decomposition temperature of the domain structure depends to a considerable extent on the chemical microstructure of the UTEP. Thermodynamic theory makes it possible to calculate the minimum number of rigid units Z_A^{min} in the block for which microphase separation is observed. It was found that Z_A^{min} should increase with increase in the MW of the flexible block (Fig. 2).

For the same MW of the flexible block, the increase in the continuous sequence of rigid units should lead to an increase in T_d.

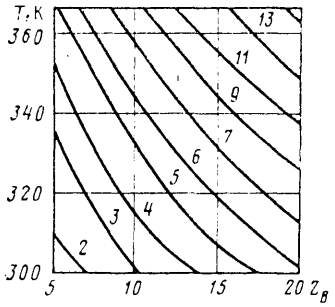


Figure 2. Dependence of Z_A^{min} on the number of units Z_B forming the flexible block and on the ambient temperature; ΔH_A = -9.8 kJ mol^{-1}; ν = 12.[157]

The conclusions of the theory have been confirmed by a series of experimental data. Thus UTEP with a specified chemical microstructure have been synthesised, the number of rigid units in the block varying from unity to three.[158] X-Ray diffraction study of the specimens showed that microphase separation is manifested following the attainment of a definite length of the rigid block. This conclusion agrees with other data,[159,160] which also reveal a 'critical' length of the rigid block, beyond which microphase separation is observed. The study of the dependence of T_d on the MW of POTMG of a urethane thermoelastoplastic based on MDI and BD showed[154] that the decomposition temperature of the domain structure shifts towards higher values with increase in the MW of the polyester. Analogous data have been obtained also in another investigation.[161] An increase in the length of the rigid block for the same MW of the PE entailed an increase in T_d.[162]

The marked dependence of the T_d for UTEP of the first kind on the chemical microstructure of the macrochains requires the development of quantitative methods for its calculation. We have suggested[163] that the theory of Markov chains be used for this purpose. It has been found that the chemical microstructure of the UTEP of both the first and second kinds can be defined fully with the aid of simple expressions involving the mole fractions of units of different types. It was found that the chemical microstructure of the UTEP of the first kind for a degree of conversion close to unity is almost independent of the relative reactivity of the hydroxylated monomers in the reaction with the diisocyanate and is determined by their initial molar ratio (Fig. 3). The microstructure of UTEP with allophanate or biuret branching and network nodes depends to a large extent on the rate constants for the branching process K_b. For a low value of K_b, the UTEP obtained contain virtually no cross-linking nodes and belong to the first type. On the other hand, for K_b comparable to the urethane formation rate constants the PU microstructure belongs to the UTEP of the second kind.

The chemical nature of the diisocyanates has a considerable influence on the properties of the UTEP. The asymmetry of the disposition of the isocyanate groups in 2,4-TDI leads to an amorphous structure of the domains, while symmetrical 2,6-TDI produces a crystalline rigid block.[7] It has been noted that the UTEP with the highest moduli of elasticity and tensile strengths are formed from symmetrical aromatic diisocyanates (MDI, 2,6-TDI, etc.). The symmetry of the structure of the diisocyanate influences also the degree of microphase separation. Koberstein[164] established by the small angle X-ray diffraction and small angle polarised light scattering methods that the PU specimens based on 2,4-TDI exhibit a smaller phase separation than the specimens obtained from MDI. However, the interface itself is more diffuse in the PU based on MDI.

Like the methyl substituent in the ring of the aromatic diisocyanate, the methyl side group in the diol also produces steric hindrance to the aggregation of the rigid segments into domains, which increases the T_g of the polymer.[165] On the other hand, apart from the increase in the fluidity temperature as a consequence of the decomposition of microregions with rigid blocks, the introduction of a polar substituent into the rigid blocks of polyurethanoureylenes

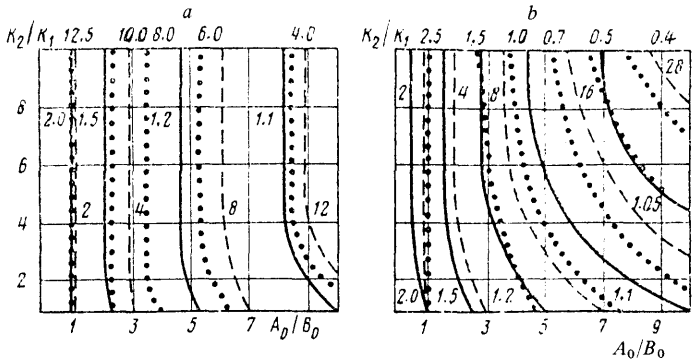


Figure 3. Dependence of the chemical microstructure of the UTEP macromolecules of the first kind $(A_mB_n)_c$ on the degree of conversion of the reaction system [*a*, α = 0.98; *b*, α = 0.90], on the initial molar ratio of the diol (A_0) and the polyester (B_0), and on the ratio of the rate constants for the interaction of the diol (K_2) and the polyester (K_1) with the diisocyanate; dashed line—*m*; continuous line—*n*; circles—*c*.

leads to an anomalous decrease in T_g owing to the manifestation of segmental mobility by the flexible oligoester blocks.[166]

During the past 10–15 years, many relations established previously as regards the influence of the molecular and chemical structures of the urethane formation process components and of the domain formation conditions on various properties of the UTEP have hardly changed significantly. They have all been described superbly in Kercha's monograph[7] and will not be considered in this review.

A series of novel investigations[30,31] devoted to the elucidation of the influence of the incompatibility of certain urethane formation process components with one another and of the rigid segments of different lengths on the structure and morphology of segmented polyurethanes have been published recently.

An interesting idea has been put forward by Teitel'baum et al.[167] According to their view, based on X-ray diffraction and thermomechanical investigations, the "kinetic limitation of the structure formation processes" can occur at a certain stage in the urethane formation process. The degree of perfection of the domain structure depends on the temperature of its formation. It has been shown that the ordering of the domain structure of amorphous polyesterurethanourea may be prolonged when it is heated above the hardening temperature. Analogous results have been obtained in the annealing or limited swelling of segmented polyesterurethanoureas in a series of low-molecular-rate solvents, which leads to further improvement of the microheterogeneous structure,[168] caused, according to the authors, by the orientational ordering of the rigid blocks.

A novel study of the influence of kinetic factors on the formation of the domain structure has been carried out.[169] By keeping PU based on POTMG, MDI, and PD at 190 °C, a specimen with microphase separation was obtained. This was followed by annealing at 120°, 90°, 80°, 60°, and 22 °C. With increase in annealing time, the glass point of the domain structure produced fell linearly with time in terms of semilogarithmic variables to a constant value and to a greater extent the lower the annealing temperature. The authors suggest that at low temperatures short and long sequences of rigid segments are rapidly segregated from the elastic phase, while at high annealing temperatures only the long sequences are segregated.

The significant influence of the number of stages in the synthesis of NPU on their parameters was already noted above. The two-stage synthesis of UTEP from POTMG, MDI, and ethylenediamine in solution with the reactants added in markedly different orders leads to the formation of sharply differing morphological structures.[170] UTEP with 50–80 Å crystalline domains has been obtained by adding ethylenediamine to the POTMG prepolymer and MDI. On the other hand, if ethylenediamine was added initially and then the product of its interaction with MDI was treated with POTMG, then the segmented PU formed had amorphous domains whose size reached 1000–2000 Å. The degree of phase separation was greater when POTMG was added gradually to MDI than for the converse addition.[171]

Studies by small angle X-ray scattering have shown[172] that the two-stage method of synthesis of UTEP from poly(tetramethylene glycol adipate) (PTMGA), MDI, and BD leads to a greater scattering intensity and width of the transition zone in the specimen than under conditions where it is synthesised by the single-stage method. When PTMGA is replaced by POTMG, the differences in the scattering intensity as a function of the methods of synthesis are significantly smaller. The observed behaviour can be explained by the greater degree of interaction of the flexible and rigid segments in the case of the polyester and the broadening of the distribution of the lengths of the rigid segments for the two-stage methods of synthesis of UTEP.

It has been suggested[173] that the UTEP based on POTMG, MDI, and BD, obtained in several stages, contains rigid blocks consisting predominantly of a single rigid diolurethane unit. In the segmented PU synthesised in one stage, the number of units forming the rigid block is greater than unity, which is the reason for the observed differences on deformation.

The physicomechanical properties of UTEP are greatly influenced by the MW and the MWD of the polyesters.[70] Segmented PU have been obtained by the reaction of poly(ethylene butylene glycol adipate) and BD with MDI. Two oligoesters with $\overline{M}_p$ = 1200 and 3000 were chosen for the investigation, a set of oligoesters with degrees of polydispersity ranging from 1.8 to 3.2 corresponding to each number-average molecular weight. The conventional tensile strength σ_t of PU-3000 proved to be greater and its relative elongation smaller than for PU-1200. In a series of PU-1200 specimens, σ_t fell with increase in polydispersity from 49.3 to 33.5 MPa. In contrast to PU-1200, σ_t for PU-3000 remained almost constant when the polydispersity was raised from 1.94 to 2.99. Deformation test calculations for the UTEP obtained using the model proposed by Kazama et al.[174] have led to the conclusion that the effective number of domains diminishes with increase in the polydispersity of the oligoester, which can be explained by the incompatibility of the rigid segment with the low-molecular-weight part of the polyester whose fraction is greater in specimens with a greater dispersity. With increase in dispersity, the boundary layer becomes more diffuse. It has been observed that phase separation takes place most effectively in PU-3000 specimens and improves as the polydispersity of the PU is reduced. Evidently this is the reason why the residual elongation and hysteresis losses are smaller by a factor of 2–3 for PU-3000 compared with PU-1200.

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The present review has shown that in most cases it is possible to obtain network polyurethanes with the required set of properties by the specific regulation of the chemical, physical, and technological factors. The greatest advances in the control of the properties of network polyurethanes have been made as regards thermoelastoplastics, which makes this type of polyurethanes most promising in view of the relative ease of their synthesis and their capacity for being worked repeatedly.

References

1. *Eur. Plast. News*, 1979, **6**(8) 10
2. V I Irzhak, B A Rozenberg, N S Enikolopyan *Setchatye Polimery* (Network Polymers), Izd. Nauka, Moscow, 1979, 248 pp
3. Z H Ophir, G L Wilkes *Multiphase Polymer Symposium*, 175th Meeting of the American Chemical Society, Washington, 1979, p. 53
4. I I Nazarova, Yu A Ol'khov, V E Nazarov, S M Baturin *Vysokomol. Soedin., Ser. A*, 1975, **17**(1) 78
5. L I Dashevskii, S M Kavun, A S Lykin *II Vsesoyuznaya Konferentsiya po Khimii i Fiziko-khimii Oligomerov, Alma-Ata, 1979* (The IInd All-Union Conference on the Chemistry and Physical Chemistry of Oligomers, Alma-Ata, 1979), Chernogolovka, 1979, p. 46

6. I Slowikowska, I Danilewska *J. Polym. Sci., Polym. Symp.*, 1975, (53) 187
7. Yu Yu Kercha *Fizicheskaya Khimiya Poliuretanov* (The Physical Chemistry of Polyurethanes), Izd. Naukova Dumka, Kiev, 1979, 224 pp
8. N Sasaki, T Yokoyma, T Tanaka *J. Polym. Sci., Polym. Chem. Ed.*, 1973, **11**(8) 1765
9. V S Kulakov, K G Misyuk, M G Fal'kovskii, M A Lagutin *Sintez i Fizikokhimiya Polimerov* (The Synthesis and Physical Chemistry of Polymers), Izd. Naukova Dumka, Kiev, 1975, No. 16, p. 51
10. E Schlosser *Plaste Kautsch.*, 1985, **32**(1) 20
11. R Becker, G Neumann *Plaste Kautsch.*, 1973, **20**(11) 809
12. M Rutkowska, P Tekely *Polym. Bull.*, 1982, **7**(9–10) 481
13. T V Kozlova, M P Letunovskii, V V Zharkov *Vysokomol. Soedin., Ser. A*, 1983, **25**(9) 1929
14. V P Dorozhkin, I M Davletbaeva *Tezisy Dokladov XXII Vsesoyuznoi Konferentsii po Vysokomolekulyarnym Soedineniyam* (Abstracts of Reports at the XXIInd All-Union Conference on Macromolecular Compounds), Chernogolovka, 1985, p. 71
15. I M Davletbaeva, V P Dorozhkin, A N Glebov, et al., USSR P. 1 071 627; *Byull. Izobret.*, 1984, (5) 17
16. P A Kirpichnikov, I M Davletbaeva, V P Dorozhkin, V V Parfenov *Dokl. Akad. Nauk SSSR*, 1984, **277**(6) 1430
17. O V Volkova, V S Domkin, V V Strakhov, O A Ol'khovikov *Vysokomol. Soedin., Ser. B*, 1982, **24**(3) 226
18. Yu O Averko-Antonovich, L A Averko-Antonovich, I N Bakirova, et al. *XII Mendeleevskii S'ezd po Obshchei i Prikladnoi Khimii. Baku, 1981* (The XIIth Mendeleev Congress on General and Applied Chemistry. Baku, 1981), Moscow, 1981, p. 206
19. T E Lipatova, S A Zubko *Vysokomol. Soedin., Ser. A*, 1970, **12**(7) 1555
20. A E Nesterov, T E Lipatova, S A Zubko, Yu S Lipatov *Vysokomol. Soedin., Ser. B*, 1971, **13**(5) 346
21. A E Nesterov, T E Lipatova, V K Ivashchenko, Yu S Lipatov *Vysokomol. Soedin., Ser. H*, 1970, **12**(2) 150
22. A I Ivanov, Yu A Ol'khov, S M Baturin, S G Entelis *Vysokomol. Soedin., Ser. B*, 1969, **11**(9) 659
23. T E Lipatova, V K Ivashchenko *Sintez i Fizikokhimiya Polimerov* (The Synthesis and Physical Chemistry of Polymers), Izd. Naukova Dumka, Kiev, 1970, No. 6, p. 73
24. L Yu Rumyantsev, L I Golovko, G P Kovernik *Tezisy Dokladov III Vsesoyuznoi Konferentsii po Khimii Oligomerov. Odessa, 1986* (Abstracts of Reports at the IIIrd All-Union Conference on the Chemistry of Oligomers, Odessa, 1986), Chernogolovka, 1986, p. 205
25. M S Vilenskii, N P Spasskova, L V Lisnevskaya, et al. *Vysokomol. Soedin., Ser. A*, 1972, **14**(8) 1685
26. S L Hager, T B MacRury, R M Gerkin, F E Critchfield *Am. Chem. Soc., Polym. Prepr.*, 1980, **21**(2) 253
27. Y J Huang, T J Hsu, L J Lee *Polymer*, 1985, **26**(8) 1247
28. G Menges, H Schwesing *Kautsch. Gummi Kunstst.*, 1979, **32**(9) 643
29. Yu A Ol'khov, S M Baturin, S G Entelis *Vysokomol. Soedin., Ser. A*, 1976, **18**(1) 150
30. M Xu, W S Macknight, C H Chen, E L Yimas *Polymer*, 1983, **24**(10) 1327
31. C H Chen, R M Briber, E L Tomas, et al. *Polymer*, 1983, **24**(10) 1333
32. T E Lipatova *Vysokomol. Soedin., Ser. A*, 1973, **15**(2) 327
33. D P Kochetov *Tezisy Dokladov III Vsesoyuznoi Konferentsii po Khimii Oligomerov. Odessa, 1986* (Abstracts of Reports at the IIIrd All-Union Conference on the Chemistry of Oligomers. Odessa, 1986), Chernogolovka, 1986, p. 106
34. V P Dorozhkin *Polymer*, 1985, **26**(6) 918
35. P A Kirpichnikov, V P Dorozhkin, L A Zenitova, Y O Averko-Antonvich *Polymer Mater. Sci. Eng.*, 1983, **49** 269
36. V P Dorozhkin, V I Kimelblat *J. Polym. Sci., Polym. Chem. Ed.*, 1982, **20** 2863
37. L T Kasumova, Yu A Ol'khov, S M Baturin *Vysokomol. Soedin., Ser. A*, 1980, **22**(12) 2780
38. Yu A Ol'khov, S M Baturin, S G Entelis *Vysokomol. Soedin., Ser. A*, 1973, **15**(9) 2058
39. S M Baturin, Yu A Ol'khov, V B Lugovoi, S G Entelis *Sintez i Fizikokhimiya Polimerov* (The Synthesis and Physical Chemistry of Polymers), Izd. Naukova Dumka, Kiev, 1973, No. 12, p. 58
40. R F T Stepto *Faraday Discuss. Chem. Soc.*, 1974, (57) 69
41. W Hopkins, R H Peters, R F T Stepto *Polymer*, 1974, **15** 315
42. J L Stanford, R F T Stepto *Br. Polym. J.*, 1977, **9**(2) 124
43. N G Hunt, R F T Stepto, R H Still *XXVI International Symposium on Macromolecules, Mainz, 1979*, Prepr. Short. Comm., Mainz, Vol. 1, p. 697
44. J L Stanford, R F T Stepto *Am. Chem. Soc., Polymer Prepr.*, 1981, **22**(2) 165
45. K Dusek *Rubber Chem. Technol.*, 1982, **55**(1) 1
46. J L Stanford, R F T Stepto, R H Still *International Rubber Conference, Kyoto, 1985*, p. 359
47. L Matejka, K Dusek *Polym. Bull.*, 1980, **3**(8–9) 489
48. Yu A Ol'khov, V P Lodygina *Tezisy Dokladov III Vsesoyuznoi Konferentsii po Khimii Oligomerov. Odessa, 1986* (Abstracts of Reports at the IIIrd All-Union Conference on the Chemistry of Oligomers. Odessa, 1986), Chernogolovka, 1986, p. 60
49. G A Gorbushina, Yu A Ol'khov, S M Baturin *Vysokomol. Soedin., Ser. A*, 1986, **28**(11) 2419
50. V V Komratova, I I Nazarova, V A Grigor'eva, et al. *Tezisy Dokladov II Vsesoyuznoi Konferentsii po Khimii i Fiziko-khimii Oligomerov. Alma-Ata, 1979* (Abstracts of Reports at the IInd All-Union Conference on the Chemistry and Physical Chemistry of Oligomers. Alma-Ata, 1979), Chernogolovka, 1979, p. 62
51. V A Grigor'eva, V V Komratova, A I Kuzaev, S M Baturin *Tezisy Dokladov III Vsesoyuznoi Konferentsii po Khimii Oligomerov. Odessa, 1986* (Abstracts of Reports at the IIIrd All-Union Conference on the Chemistry of Oligomers, Odessa, 1986), Chernogolovka, 1986, p. 214
52. T V Eremeeva, E V Davydova, M I Karyakina, Yu S Lipatov *Vysokomol. Soedin., Ser. A*, 1977, **19**(12) 2701
53. T I Kadurina, S I Omel'chenko *Sintez i Fizikokhimiya Polimerov* (The Synthesis and Physical Chemistry of Polymers), Izd. Naukova Dumka, Kiev, 1976, No. 16, p. 31
54. P P Sukhanov, V S Minkin, V I Kimel'blat, et al. *Vysokomol. Soedin., Ser. A*, 1983, **25**(7) 1370
55. M P Letunovskii, F A Kryuchkov, Yu V Zelenev, et al. *Vysokomol. Soedin., Ser. A*, 1985, **27**(11) 2397
56. L S Sheinina and T E Lipatova *Fiziko-khimicheskie Svoistva i Struktura Polimerov* (The Physicochemical Properties and Structure of Polymers), Kiev, 1977, p. 62
57. L S Sheinina, T E Lipatova, T I Vladimirova, M G Vengerovskaya *Vysokomol. Soedin., Ser. A*, 1981, **23**(3) 559

58. Yu S Lipatov, N A Chesnokova, L M Sergeeva, L V Karabanova *Vysokomol. Soedin., Ser. A*, 1978, **20**(2) 355
59. Yu Yu Kercha *Tezisy Dokladov V Respublikanskoi Konferentsii po Vysokomolekulyarnym Soedineniyam. Donetsk, 1984* (Abstracts of Reports at the Vth All-Republic Conference on Macromolecular Compounds. Donetsk, 1984), Kiev, 1984, p. 32
60. V P Dorozhkin, V I Kimel'blat, Yu O Averko-Antonovich *Vysokomol. Soedin., Ser. A*, 1974, **16**(9) 2024
61. E V Davydova, T V Eremeeva, M I Karyakina, Yu S Lipatov *Vysokomol. Soedin., Ser. A*, 1976, **18**(9) 1951
62. T V Eremeeva, E V Davydova, M I Karyakina *Dokl. Akad. Nauk Ukrain. SSR. Ser. B*, 1976, (2) 152
63. A Ya Malkin, V P Begishev, S G Kulichikhin, V A Kochnina *Vysokomol. Soedin., Ser. A*, 1983, **25**(9) 1948
64. G Allen, P L Egerton, D J Walsh *Polymer*, 1976, **17**(1) 65
65. K Dusek, M Ilavsky *Am. Chem. Soc., Polym. Prepr.*, 1981, **22**(2) 167
66. R F T Stepto *IX European Conference on Macromolecular Physics. Jablonna, 1979*, Warsaw, Papers, p. 55
67. W Dzierna, J Janacek *J. Polym. Sci., Polym. Symp.*, 1975, (53) 313
68. P-H Sung, J E Mark *J. Polym. Sci., Polym. Symp.*, 1981, **19**(3) 507
69. A B Fasina *Rubber Chem. Technol.*, 1977, **50**(4) 780
70. G Lunardon, Y Sumida, O Vogl *Angew. Macromol. Chem.*, 1980, **89** 1
71. D J Walsh, J S Higgins, H H Hall *Polymer*, 1979, **20**(8) 951
72. T Yokoyama *Adv. Urethane Sci. Technol.*, 1979, **6** 30
73. Yu S Lipatov, V V Gorichko, L M Sergeeva *Sintez i Fizikokhimiya Polimerov* (The Synthesis and Physical Chemistry of Polymers), Izd. Naukova Dumka, Kiev, 1977, No. 21, p. 79
74. W J Dzierza *J. Polym. Sci., Chem. Ed.*, 1979, **17**(3) 693
75. T E Lipatova *Tezisy Dokladov I Vsesoyuznoi Konferentsii po Khimii i Fiziko-khimii Oligomerov* (Abstracts of Reports of the Ist All-Union Conference on the Chemistry and Physical Chemistry of Oligomers), Chernogolovka, 1977, Vol. 1, p. 230
76. Yu V Brestkin, L S Andrianov, G P Belonovskaya, et al. *Vysokomol. Soedin., Ser. A*, 1980, **22**(12) 2682
77. T E Lipatova, V V Shilov, N M Minenko *Angew. Makromol. Chem.*, 1981, **100** 99
78. Yu S Lipatov, V V Shilov, V A Bogdanovich, L M Sergeeva *Dokl. Akad. Nauk Ukrain. SSR, Ser B*, 1982, (3) 31
79. S A Patlazhan, G I Kachina, Yu A Ol'khov *Tezisy Dokladov III Vsesoyuznoi Konferentsii po Khimii Oligomerov. Odessa, 1986* (Abstracts of Reports at the IIIrd All-Union Conference on the Chemistry of Oligomers. Odessa, 1986, Chernogolovka, p. 84
80. A Havranek, J Nedbal, C Bercik, M Ilavsky *Polym. Bull.*, 1980, 3(8–9), 497
81. M Ilavsky, K Dusek *Macromolecules*, 1986, **19**(8) 2139
82. M Ilavsky, J. Hrouz, K Dusek *J. Macromol. Sci.*, 1981, **19**(2) 227
83. V V Shilov, V A Bogdanovich, Yu S Lipatov *Protsessy Studneobrazovaniya v Polimernykh Sistemakh* (Gel Formation Processes in Polymer Systems), Saratov, 1985, Part 2, p. 60
84. Yu A Ol'khov, V B Lugovoi, S M Baturin, S G Entelis *Vysokomol. Soedin., Ser. A*, 1972, **14**(12) 2662
85. S M Baturin, G B Manelis, A G Melent'ev, et al. *Vysokomol. Soedin., Ser. A*, 1976, **18**(11) 2461
86. Yu A Ol'khov, S M Baturin, S G Entelis *Sintez i Fizikokhimiya Polimerov* (The Synthesis and Physical Chemistry of Polymers), Izd. Naukova Dumka, Kiev, 1973, No. 12, p. 61
87. V I Irzhak, Doctoral Thesis in Chemical Sciences, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1977
88. V B Zabrodin, V I Zykov, G N Chui *Sintez i Fizikokhimiya Polimerov* (The Synthesis and Physical Chemistry of Polymers), Izd. Naukova Dumka, Kiev, 1973, No. 12, p. 69
89. V B Zabrodin, V I Zykov, G N Chui *Vysokomol. Soedin., Ser. B*, 1974, **16**(3) 224
90. S G Entelis, V V Evreinov, A K Romanov, L T Sarynina *J. Prakt. Chem.*, 1971, **313**(3) 484
91. V V Evreinov, Yu G Tkach, S G Entelis *Vysokomol. Soedin., Ser. A*, 1973, **15**(4) 936
92. V B Zabromin, V I Zykov, G N Chui *Vysokomol. Soedin., Ser. A*, 1974, **16**(7) 1551
93. B G Ozol'-Kalnin, Ya A Gravitis *Vysokomol. Soedin., Ser. B*, 1982, **24**(5) 329
94. P Wright, A Cummings *Polyurethane Elastomers* (Translated into Russian), Izd. Khimiya, Leningrad, 1973, 304 pp
95. N V Panova, B E Myuller, N P Apukhtina *Vysokomol. Soedin., Ser. B*, 1971, **13**(2) 129
96. T E Lipatova, V K Ivashchenko, L I Bezruk *Vysokomol. Soedin., Ser. B*, 1971, **13**(8) 1701
97. S Abouzahr, G L Wilkes *Am. Chem. Soc.*, Polym. Prepr., 1980, **21**(2) 193
98. K Dusek, M Ilavsky, A Nesterov, L Matejka *IUPAC Symp. Macromol. Chem., Tashkent, 1978*
99. L A Cherkasova, E A Sidorovich, N P Apukhtina *Vysokomol. Soedin., Ser. A*, 1972, **14**(4) 735
100. A E Nesterov, T E Lipatova, S A Zubko, Yu S Lipatov *Vysokomol. Soedin., Ser. B*, 1971, **13**(5) 346
101. V P Dorozhkin, T V Aleksandrova *Vysokomol. Soedin., Ser. A*, 1977, **19**(4) 853
102. V P Dorozhkin, V I Kimel'blat, P A Kirpichnikov *Vysokomol. Soedin., Ser. A*, 1981, **23**(11) 2525
103. M G Karp, V P Dorozhkin, S I Vol'fson, P A Kirpichnikov *Vysokomol. Soedin., Ser. A*, 1981, **23**(3) 712
104. Yu A Ol'khov, S M Baturin, S G Entelis *Vysokomol. Soedin., Ser. A*, 1979, **21**(4) 861
105. T E Lipatova, A E Nesterov, V K Ivashchenko, Yu S Lipatov *Vysokomol. Soedin., Ser. A*, 1970, **12**(5) 1039
106. V I Pavlov, T E Lipatova, S A Zubko, et al. *Vysokomol. Soedin., Ser. A*, 1971, **13**(3) 682
107. T E Lipatova, V F Babich, L S Sheinina, M G Vengerovskaya *Vysokomol. Soedin., Ser. A*, 1978, **20**(9) 2051
108. J M Sivergin, S M Kirejeva, A V Gracev *Plaste. Kautsch.*, 1984, **31**(9) 321
109. J Foks, H Janik *XII European Conference on Macromolecular Physics, Leipzig, 1981*, Oberlungwitz, 1981, p. 285
110. N N Volkova, Yu A Ol'khov, S M Baturin, L P Smirnov *Sintez Polyuretanov* (The Synthesis of Polyurethanes), Izd. Naukova, Dumka, Kiev, 1981, p. 90
111. L A Zanitova, N P Apukhtina, P A Kirpichnikov, L V Mozzhukhina *Sintez i Fizikokhimiya Polimerov* (The Synthesis and Physical Chemistry of Polymers), Izd. Naukova Dumka, Kiev, 1977, No. 20, p. 51
112. M E Kimball, G S Fielding-Russell *Polymer*, 1977, **18** 777
113. M Rutkowska, A Balces *J. Appl. Polym. Sci.*, 1980, **25**(11) 2531
114. M F Froix, J M Pochan *J. Polym. Sci., Polym. Phys. Ed.*, 1974, **14**(6) 1040

115. M M Coleman, K H Lee, D J Skrovanek, P C Painter *Macromolecules*, 1986, **19**(8) 2149
116. H Hagawa, K Kurita, E Wada *Makromol. Chem.*, 1984, **185**(10) 2233
117. S L Cooper, A V Tobolsky *J Appl. Polym. Sci.*, 1966, **10**(12) 1837
118. S B Clough, N S Shneidet *J. Macromol. Sci.*, 1968, **2**(4) 553
119. R Bonart *J. Macromol. Sci.*, 1968, **2**(1) 115
120. C S Paik Sung, C B Hu, C S Wu *Macromolecules*, 1980, **13**(1) 111
121. Yu Yu Kercha, Yu S Lipatov *Usp. Khim.*, 1977, **46**(2) 320 [English translation in *Russ. Chem. Rev.*, 1977(2)]
122. C E Wilkes, C E Yusek *Macromol. Sci.*, 1973, **7**(1) 157
123. C H V Chen-Tsai, E L Thomas, W J Macknight, N S Schneider *Polymer*, 1986, **27**(5) 659
124. J A Koutsky, N V Nein, S L Cooper *J. Polym. Sci.*, 1978, **138**(5) 2489
125. R R Lagasse *J. Appl. Polym. Sci.*, 1977, **21**(9) 2489
126. A R Korigodskii, T M Babchintser, Ya V Genin *Tezisy Dokladov III Vsesoyuznoi Konferentsii po Khimii Oligomerov. Odessa, 1986* (Abstracts of Reports at the IIIrd All-Union Conference on the Chemistry of Oligomers. Odessa, 1986), Chernogolovka, 1986, p. 107
127. K W Chau, P H Geil *Polymer*, 1985, **26**(4) 490
128. K S Hwang, G Wu, S B Lin, S L Cooper *J. Polym. Sci., Polym. Chem. Ed.*, 1984, **22**(7) 1677
129. C H V Chen-Tsai, E L Thomas, W J Macknight *Am. Chem. Soc., Polym. Prepr.*, 1985, **26**(2) 64
130. K W Chan, P H Geil *Polym. Commun.*, 1983, **24**(2) 50
131. S V Laptii, Yu Yu Kercha, Yu S Lipatov *Vysokomol. Soedin., Ser. A*, 1986, **28**(10) 2177
132. C R Desper, N S Schneider *Am. Chem. Soc., Polym. Prepr.*, 1983, **24**(1) 180
133. V N Vatulev, R L Gaiduk, Yu Yu Kercha, et al. *Kompozitsionnye Polimernye Materialy* (Composite Polymeric Materials), Izd. Naukova Dumka, Kiev, 1983, No. 16, p. 55
134. K K Chee, R J Farris *J. Appl. Polym. Sci.*, 1984, **29**(8) 2529
135. L A Shelkovnikova, Yu Yu Kercha, V F Rosovitskii, et al. *Kompozitsionnye Polimernye Materialy* (Composite Polymeric Materials), Izd. Naukova Dumka, Kiev, 1986, No. 29, p. 7
136. T V Kozlova, M P Letunovskii, V V Zharkov *Vysokomol. Soedin., Ser. A*, 1983, **25**(9) 1929
137. H Nishimura, H Kojima, T Yarita, M Noshiro *Polym. Eng. Sci.*, 1986, **26**(9) 585
138. A S Lykin, I M Tunkel', L Ya Dashevskii *Tezisy Dokladov III Vsesoyuznoi Konferentsii po Khimii Oligomerov. Odessa, 1986* (Abstracts of Reports at the IIIrd All-Union Conference on the Chemistry of Oligomers. Odessa, 1986), Chernogolovka, 1986, p. 318
139. R Bonart, L Morbitger *Kolloid. Z. Z. Polym.*, 1970, **241**(1) 909
140. R L Gaiduk, S V Laptii, Yu Yu Kercha *Vysokomol. Soedin., Ser. B*, 1985, **27**(2) 154
141. Y Camberlin, J Pascault *J. Polym. Sci., Polym. Phys. Ed.*, 1984, **22**(10), 1835
142. A E Allegrezza, R W Seymour, H N Hg, S L Cooper *Polymer*, 1974, **15**(7) 433
143. A E Allegrezza, R W Seymour, S L Cooper *Am. Chem. Soc., Polym. Prepr.*, 1974, **15**(1) 76
144. C S Paik Sung, C B Hu, C S Wu, T Smith *Am. Chem. Soc., Polym. Prepr.*, 1978, **19**(2) 692
145. C S Paik Sung, T W Smith, N H Sung *Macromolecules*, 1980, **13**(1) 117
146. L L Harrell *Am. Chem. Soc.*, Polym. Prepr., 1969, **10**(2) 869
147. V V Zharkov *Sintez i Fizikokhimiya Polimerov* (The Synthesis and Physical Chemistry of Polymers), Izd. Naukova Dumka, Kiev, 1977, No. 21, p. 71
148. K J Cell *J. Polym. Sci.*, 1973, **C42** 727
149. N P Apukhtina, B E Myuller, E A Sidorovich *Vysokomol. Soedin., Ser. A*, 1969, **10**(7) 1600
150. P Sung, S Chang, N Schneider *Macromolecules*, 1975, **8**(1) 68
151. C Seefried, J Koleske, F Crichfield *J. Appl. Polym. Sci.*, 1975, **19**(12) 3185
152. Yu Yu Kercha, Yu S Lipatov, A P Grekov, R L Shapoval *Vysokomol. Soedin., Ser. A*, 1972, **14**(5) 1187
153. G Pohl, H Goering, B Gert, S Engelschalt *Plaste. Kautsch.*, 1982, **29**(12) 695
154. M A Vallance, S L Castles, S L Cooper *Polymer*, 1984, **25**(12) 1734
155. T A Speckhard, K S Hwang, S L Cooper, et al. *Polymer*, 1985, **26**(1) 70
156. T A Speckhard, P E Gibson, S L Cooper, et al. *Polymer*, 1985, **26**(1) 55
157. V P Dorozhkin, V I Kimel'blat *Vysokomol. Soedin., Ser. A*, 1975, **17**(5) 1027
158. Yu S Lipatov, V V Shilov, V V Vorona, et al. *Dokl. Akad. Nauk SSSR*, 1983, **279**(3) 634
159. T M Gricenko, Yu S Lipatov *Faserforsch. Textiltech.*, 1977, **28**(11/12) 575
160. Yu S Lipatov, T M Gritsenko, F G Fabulyak, V V Anokhin *Vysokomol. Soedin., Ser. A*, 1977, **19**(8) 1707
161. V F Matyushev, A V Shevchuk *Tezisy Dokladov III Vsesoyuznoi Konferentsii po Khimii Oligomerov. Odessa, 1986* (Abstracts of Reports at the IIIrd All-Union Conference on the Chemistry of Oligomers. Odessa, 1986), Chernogolovka, 1986, p. 92
162. A V Shevchuk, V F Matyushev, Yu S Lipatov *Plast Massy*, 1986, (9) 22
163. V P Dorozhkin, P A Kirpichnikov *Dokl. Akad. Nauk SSSR*, 1986, **287**(3) 658
164. J T Koberstein *Am. Chem. Soc., Polym. Prepr.*, 1983, **24**(11) 180
165. L A Cherkasova, E A Sidorovich, N P Apukhtina, A I Marei *Sintez i Fizikokhimiya Polimerov* (The Synthesis and Physical Chemistry of Polymers), Izd. Naukova Dumka, Kiev, 1974, No. 13, p. 108
166. Yu Yu Kercha, Yu S Lipatov, S S Krafchik, et al. *Dokl. Akad. Nauk Ukrain. SSR, Ser. B*, 1974, (8) 714
167. B Ya Teitel'baum, E T Magdalev, T A Yagfarova, et al. *Vysokomol. Soedin., Ser. A*, 1983, **25**(9) 1823
168. M P Letunovskii, G S Kitukhina, V V Zharkov, F A Kryuchkov *Tezisy Dokladov I Vsesoyuznoi Konferentsii po Smesyam Polimerov* (Abstracts of Reports at the Ist All-Union Conference on Polymer Blends), Ivanovo, 1986, p. 88
169. T K Kwei *J. Appl. Polym. Sci.*, 1982, **27**(8) 2891
170. F Yang, F Feng, X Feng *Polym. Commun.*, 1982, (4) 302
171. N Tian, Z Qi, X Feng *Polym. Commun.*, 1985, (1) 6
172. S Abourhr, G Wilkes *J. Appl. Polym. Sci.*, 1984, **29**(9) 2695
173. S B Lin, K S Hwang, S X Tsay, S L Cooper *Colloid Polym. Sci.*, 1985, **263**(2) 128
174. Y Kazama, Y Sumida, H Ogawa, S Okai *Preprints of the International Rubber Conference, Tokyo, 1975*, p. 205

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The separation of stable isotopes of carbon

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ABSTRACT. The present state of work on the separation of carbon isotopes by diffusion, fractional distillation, chemical isotopic exchange, and the selective excitation and dissociation of molecules in electrical discharges or in the field of laser radiation has been examined. The characteristics of new laboratory and industrial assemblies for separating carbon isotopes have been described. Promising directions of study aimed at developing effective technological processes for separating carbon isotopes have been noted.

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I. Introduction

Natural carbon consists of two stable isotopes: ^{13}C (1.11%) and ^{12}C (98.89%). The ^{13}C isotope is now widely used in various branches of science and technology.

The stable isotopes of carbon are used in physics to study nuclear reactions, to determine nuclear constants, to study the inelastic scattering of polarised protons, etc.[1–5] The heavy carbon isotope ^{13}C is particularly important for investigating the mechanisms of processes taking place in living organisms.

The development of NMR spectrometers and methods for determining the position of a ^{13}C tracer in complex organic compounds and even in biological materials without decomposing them has provided a powerful stimulus for devising effective methods for separating the stable isotopes of carbon and synthesising a wide range of isotopically substituted compounds, and for the development of different forms of ^{13}C NMR spectroscopy. It has made it possible to obtain rapidly valuable information on the structure and dynamics of the structural components and on the nature of the intracellular medium, the primary and secondary exchange paths in a culture medium, etc.[6]

A promising sphere of application of stable isotopes of carbon is in the identification of various types of functional breakdown in the organism: liver deficiency, breakdown of exchange processes in the liver, diabetes, oxygen starvation of the heart muscle, lung deficiency, etc. A large number of papers have been published on the diagnosis of metabolic breakdown due to the dysfunction of the endocrine and other organs, using compounds labelled with ^{13}C.[7–12] In the USA, 2.5 kg of the ^{13}C isotope are used annually for medical research and diagnosis alone.[6]

The wide interest in the use of stable isotopes to study processes in living organisms is indicated by the large number of published papers on this topic (see for example the bibliography in Ref. 13 and the published proceedings of special symposia and conferences).[6,14–17]

The extensive use of carbon isotopes in turn is stimulating the further development of methods and technology for their separation. Extensive material has accumulated on the separation of carbon isotopes by traditional methods such as the chemical exchange, fractional distillation, and diffusion of gaseous compounds of carbon, etc. In the last ten years, studies of the possible separation of carbon isotopes using lasers have shown that this method is highly effective for large-scale production.

II. Separation by diffusion

Methods for separating carbon isotopes by diffusion include diffusion through a porous membrane and diffusion in a stream of vapour.

The separation of isotopes using porous partitions results from the fact that the relative frequency with which the molecules of the components being separated enter the small openings is inversely proportional to the square root of their molecular weight. Since the separation effect of a single diffusion step is small, gas-diffusion cascades are usually employed, as illustrated schematically in Fig. 1. Part of the stream being separated, entering the gas-diffusion stage, passes through the partition, while the other part (the heavy fraction) does not. The heavy gas fraction, with the higher molecular weight, is taken to the next stage in the direction of the tail of the cascade. The light fraction, after moving through the partition into the higher-pressure region, is passed by the compressor to the next stage in the direction of the head of the cascade.[18]

Carbon-13 enrichment by a factor of 6.6 has been achieved by diffusion through a porous membrane in a cascade of 35 single stages.[19] The material used in the diffusion cascade was methane, whose molecules, containing different carbon isotopes, have a greater relative difference in mass than any other gaseous compound of carbon. Later,[20] a heavy methane fraction containing about 16% $^{13}CH_4$† was obtained in the assembly after operation for 12 h.

The porous partition can be replaced by a stream of mercury vapour, through which diffusion takes place.[21–23] The separate stages of this cascade are mercury diffusion pumps, which move the lighter component slightly faster than the heavy component. An advantage of this cascade is the use of the diffusion pump simultaneously as the generator of the original mixture, the assembly

† Here and subsequently the concentrations of the isotopes are given in at. %.

for the fractionation, and the pump for moving the richer and depleted fractions from one stage to another.

Separating pumps with an output of 1 cm^3 per day at a pressure of 266.6 Pa gave an enrichment in $^{13}CH_4$ of up to 12.4% relative to the natural concentration.[23] An experimental assembly consisting of 51 pumps has also been described.[24-26] The starting material was methane with the natural concentration of ^{13}C. At a pressure of 213–266 Pa after operation for 30 h at a rate of 300 cm^3 per day, a heavy methane fraction containing 30–32% $^{13}CH_4$ was obtained.

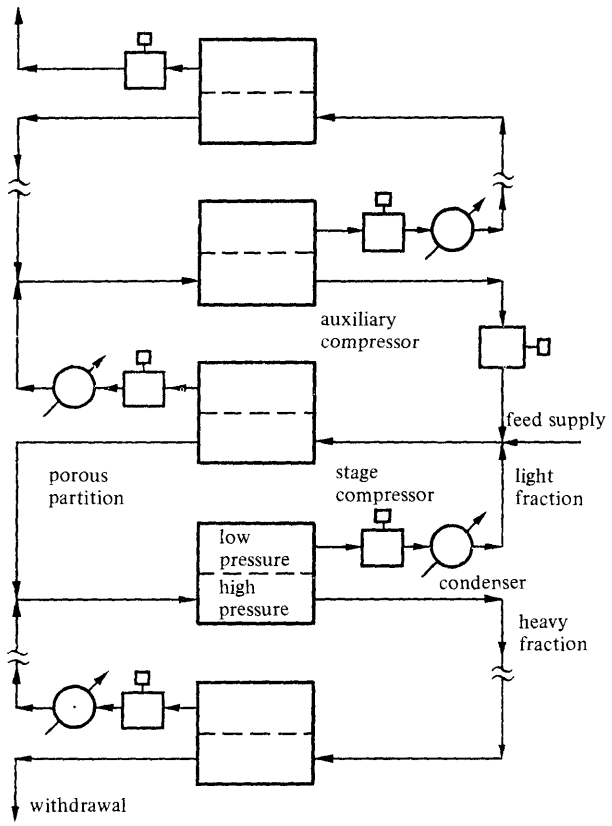


Figure 1. Schematic diagram of a gas-diffusion cascade.

The main disadvantage of the first diffusion cascade assemblies was their low output, which made it possible to obtain only tracer quantities of highly-enriched isotope fractions.

The problem of developing highly efficient assemblies with a high specific productivity was solved by using high pressures (1333 Pa).[26,27] ^{13}C concentrations of 88% and 70.2% were obtained at take-off rates of 30 cm^3 per day and 200 cm^3 per day respectively in a cascade consisting of 70 separating pumps. The starting material was methane with a ^{13}C concentration of 2.7%. The average separation coefficient in one stage was 1.086, that is it was slightly lower than that of analogous assemblies operating at pressures of 133–266 Pa (usually 1.1).

A separating column using xylene vapour as auxiliary gas has been described.[28] On this column the enrichment in ^{13}C reached 2%. Subsequently, the combination of 10 diffusion columns of this type in a cascade gave an enrichment in $^{13}CH_4$ of up to 12% with an output of 500 cm^3 per day.[29]

Since the development of the first thermal diffusion column,[30] this method has been used fairly frequently to enrich natural methane for preparative purposes. The start of systematic studies in this field was probably made in Ref. 31, which gave the theoretical principles of the thermal diffusion method for the separation of a $^{12}CH_4-^{13}CH_4$ mixture. The essential feature of the thermal diffusion phenomenon is that when a temperature gradient is created in a mixture of several components, a concentration gradient is also produced.

The Clusius–Dickel thermal diffusion column consists of two vertically arranged surfaces, the space between which contains the mixture being separated. The temperatures of each surface are constant but different.[31] The temperature difference produces a concentration gradient in the horizontal direction. Simultaneously, as a result of the density difference in the mixture being separated, convective movement is produced close to the cold and hot surfaces; the less extensively heated stream of liquid or gas moves downwards, and the more extensively heated stream moves upwards, as shown schematically in Fig. 2. As a result, a counter-flow movement is established in the column, leading to repeated multiplication of the separation effect and to a change in the concentrations of the components of the mixture along the height of the column.

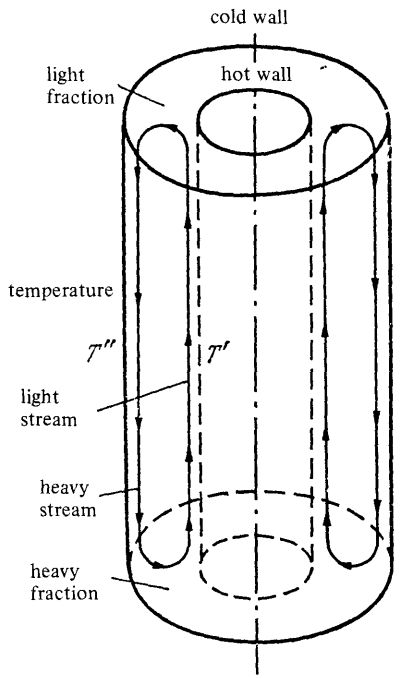


Figure 2. Diagram of a Clusius–Dickel thermal-diffusion column.

The principal gaseous compounds of carbon used to concentrate the ^{13}C isotope by thermal diffusion are methane and carbon monoxide (mainly the former).[32-42] The separation is carried out in thermal-diffusion columns with different dimensions at pressures from several Pa to atmospheric, and a temperature difference between the central tube (filament) and the outer wall of 573–673 K.

Table 1. Enrichment coefficients in the separation of carbon under liquid–vapour phase equilibrium conditions for different compounds.

System	Temperature, K	ε	Method of determination	Temperature dependence of the separation	Refs.
$^{12}CH_4 - {}^{13}CH_4$	90.5 111.8	0.0049 0.0010	differential	$\varepsilon = 2.3\,(4.1986/T^2 + 0.0775T - 0.1959)$	[53]
$^{12}CH_4 - {}^{13}CH_4$	90.5 97.5 111.8	0.0114 0.0108 0.0029	Rayleigh distillation	$P_{^{12}CH_4}/P_{^{13}CH_4} = 0.0040 + 0.6689/T$	[54]
$^{12}CH_4 - {}^{13}CH_4$	90.5	0.0125	ditto	$P_{^{12}CH_4}/P_{^{13}CH_4} = 2.7526/T - 0.0180$	[55]
$^{12}CH_4 - {}^{13}CH_4$	90.5 96.0 111.8	0.0055 0.0046 0.0029	differential	$\varepsilon = 85.0/T^2 - 0.442/T$	[56]
$^{12}CH_4 - {}^{14}CH_4$	90.5 111.8	0.0123 0.0085	Rayleigh distillation	$\varepsilon = 1.1275/T - 0.0019$	[57]
$^{12}C^{16}O - {}^{13}C^{16}O$	68.1 81.0	0.0125 0.0104	ditto	$\varepsilon = P_{^{12}CO}/P_{^{13}CO} = 0.889/T - 0.0006$	[58]
$^{12}C^{16}O - {}^{13}C^{16}O$	69.0 81.6 101.2	0.0131 0.0093 0.0062	"	$P_{^{12}CO}/P_{^{13}CO} = 0.9954 \exp(1.447/T)$	[59]
$^{12}C^{16}O - {}^{13}C^{16}O$	68.3 75.0 81.0	0.0109 0.0086 0.0070	differential	$\varepsilon = 78.2/T^2 - 0.384/T$	[56]
$^{12}C^{16}O - {}^{13}C^{16}O$	68.1 81.1	0.0120 0.0104	ditto		[56]
$^{12}C_2H_6 - {}^{13}C_2H_6$	130 147	0.0022 0.0012	Rayleigh distillation	$P_{^{12}C_2H_6}/P_{^{13}C_2H_6} = 0.3985/T - 0.0021$	[55]
$^{12}C_2H_4 - {}^{13}C_2H_4$	120 149	0.0014 0.0016	ditto		[55] [60]
$^{12}CH_3OH - {}^{13}CH_3OH$	307.4	0.0002	»		[60]
$^{12}C_6H_6 - {}^{13}C_6H_6$	307.4	0.00025	»		[60]
$^{12}CH_3Cl - {}^{13}CH_3Cl$	307.4	0.0008	»		[60]

A high concentration of ^{13}C in methane (99.8%) was achieved[34] in 2 weeks using a cascade consisting of nine columns with a total length of 24 m. The starting material was methane previously enriched in ^{13}C to 55–73%.

In thermal diffusion processes, the purity of the working material is particularly important. In the design of a ten-stage cascade in Ref. 42, therefore, provision was made for the continuous removal of impurities from the last stage; the concentration of impurities was determined from the thermal conductivity. After operation for 300 d, the cascade gave methane with a ^{13}C concentration of 96%.

In Ref.42 it was proposed that carbon monoxide be enriched in the ^{13}C isotope and then hydrogenated with electrolytic hydrogen with a deuterium concentration lower than 5×10^{-5} % to eliminate the accumulation with the $^{13}CH_4$ molecules of the CH_3D impurity present at a concentration of 0.06% in natural methane.[43] An assembly consisting of eight glass columns with internal diameter 12.1 mm and length 2.85 m, connected in series, has been described.[44] The starting material was $^{13}CH_4$ containing 55–70% ^{13}C, obtained from enriched carbon monoxide. The process was carried out at a pressure of 94.5 kPa and a temperature of 673 K, and gave several litres of methane containing 99–99.8% $^{13}CH_4$. This complex separation scheme uses a large amount of energy, however, and is not justified economically.

In thermal diffusion, the separation factor depends on three main features: the temperature difference between the hot and cold walls, the molecular masses of the components of the gas being separated, and the properties of the molecules themselves. Methane has the highest relative differences in the masses of the isotopic molecules of all known gaseous compounds of carbon, but it is less thermally stable than carbon monoxide, and decomposes appreciably even at 700 °C. Thus the replacement of methane by carbon monoxide and hence an increase in the temperature difference should increase the efficiency of the thermal-diffusion column. Carbon monoxide was apparently first used instead of methane in thermal diffusion in Ref. 45. A column of length 5 mm and diameter 12 mm gave a separation factor of 5.85 at an optimum CO pressure of 71 581 Pa. Carbon monoxide was also used as the starting material in Refs. 46 and 47.

Comparison of the results obtained by the thermal diffusion of methane and carbon monoxide showed that the use of CO as the working gas makes it possible to decrease the volume of the assembly, but the consumption of electrical energy is appreciably higher.[47] Because of this the toxicity of CO, methane has definite advantages over carbon monoxide as the working gas. This probably explains why methane is used in the great majority of cases. Thermal diffusion has also been used to concentrate the ^{14}C isotope.[48–50]

Calculations of the cost of production[51,52] by thermal diffusion and the diffusion of methane through a porous partition showed that these methods are economically profitable only at a level of production of 100–200 g $^{13}CH_4$ with a concentration up to 60%.

Disadvantages of all methods for separating isotopes by diffusion are their low efficiency, which is related to the need to work at a low gas pressure, and the large amount of energy required by the process. According to Ref. 31, the power required to produce CH_4 enriched to 20% in the ^{13}C isotope by thermal diffusion is 6700 kW. h g^{-1} ^{13}C. It is therefore appropriate to use diffusion methods only in combined separation processes in the final stages of the concentration to obtain ^{13}C with an enrichment > 99%.

III. Fractional distillation

The separation of isotopes by fractional distillation is based on the isotopic effects appearing as a difference in the saturated vapour pressures of the components when the liquid–vapour equilibrium is

reached. The magnitude of the elementary separation factor α in fractional distillation (α is the ratio of the quantities of the isotopes present in the two phases in equilibrium) is determined chiefly by the properties of the isotopic molecules and by the nature of their interaction in the condensed phase. The lack of a well developed theory of the liquid state creates certain difficulties, however, in the selection of compounds suitable for separating isotopes by this method. Analysis of published data shows that the selection of carbon compounds giving acceptable values of α is restricted to the first members of the homologous series of saturated aliphatic hydrocarbons and carbon monoxide.[53-59] Table 1 gives the enrichment factors ($\varepsilon = \alpha - 1$) for carbon isotopes at the vapour pressure equilibrium. These data show that of the compounds studied, only methane and carbon monoxide are promising for separating carbon isotopes by fractional distillation. The factors α have been determined by Rayleigh distillation with equilibrium evaporation of the compounds C_2H_6, C_2H_4, CH_3OH, C_3H_8O, CH_3Cl, CCl_4, and C_6H_6.[60-65] The separation factors for methane, found by Rayleigh distillation, agree with one another, but their absolute values are greater than the values of α obtained by the differential method. These discrepancies may be due to the insufficient purity of the specimens used to determine α in Refs. 53 and 56.

The separation of carbon isotopes by the fractional distillation of carbon monoxide on a glass laboratory column with internal diameter 17 mm and height of the packed layer 134 cm at a pressure of 66 650 Pa and a reflux density of 7 $cm^3(cm.\ min)^{-1}$ has been studied.[58] The packing consisted of stainless steel spirals with dimensions 1.5 × 2 mm, prepared from wire with a diameter of 0.2 mm. A steady state was established in about 5 h. The lowest value of the height equivalent to a theoretical plate (HETP) was 4 cm. The HETP on a metal column with internal diameter 17 mm and height 370 cm with the same packing as in the experiments on the glass column was 2.7 cm. In the opinion of the authors cited,[58] the reason for this difference in the HETP values is that the process in the glass column was insufficiently adiabatic.

The results of the experiments on the metal column[56] agree with experimental data[66] on the separation of carbon isotopes on a column with the same geometric dimensions and the same packing. In Ref. 66 the steady state was established in 50 h, and the maximum separation factor (overall separation factor) was 3.67. The height equivalent to a theoretical plate, calculated from this value and $\alpha = 1.01$, is 2.82 cm. Experiments were also carried out on a 12-metre column consisting of an exhaustion section with length 2 m and diameter 25 mm and a lower concentration section. The concentration section consisted of two parts: a lower part with length 5 m and internal diameter 17 mm, and an upper part with length 5 m and diameter 25 mm. All the sections of the column were made of stainless steel, and the packing consisted of triangular spirals with dimensions 1.5 × 2 mm, prepared from wire with diameter 0.2 mm. For a separation factor of 67.8, achieved in 52 days, an approximate estimation of the HETP gave the value 2.2 cm. About 82 g of product with a ^{13}C concentration of 10–20% was obtained.

A three-column cascade with a total length of 36 m, with an output of 0.13 mol per day, for obtaining carbon monoxide with a ^{13}C concentration of 60% has been described.[67-69] Prolonged use of the experimental assembly revealed a number of unsatisfactory features, mainly in the system used to purify the original carbon monoxide. After purification, the concentration of CO_2 in the CO supply stream was only 0.003%, but even this amount gradually led to contamination of the packed part of the assembly. Experiments showed that for this assembly the optimum pressure was 86.6 kPa.

The parameters of a pilot plant for obtaining ^{13}C were also given in Ref. 69. The separation part consisted of a three-section cascade with a total length of 74 m and an output of 8.3 g ^{13}C per day. This cascade gave a ^{13}C enrichment of 90–92%. A period of use confirmed the high productivity and reliability of the assembly, resulting from the use of small-diameter columns connected in parallel in the first section and the positioning of the column of the third section among the columns of the first section (Fig. 3).

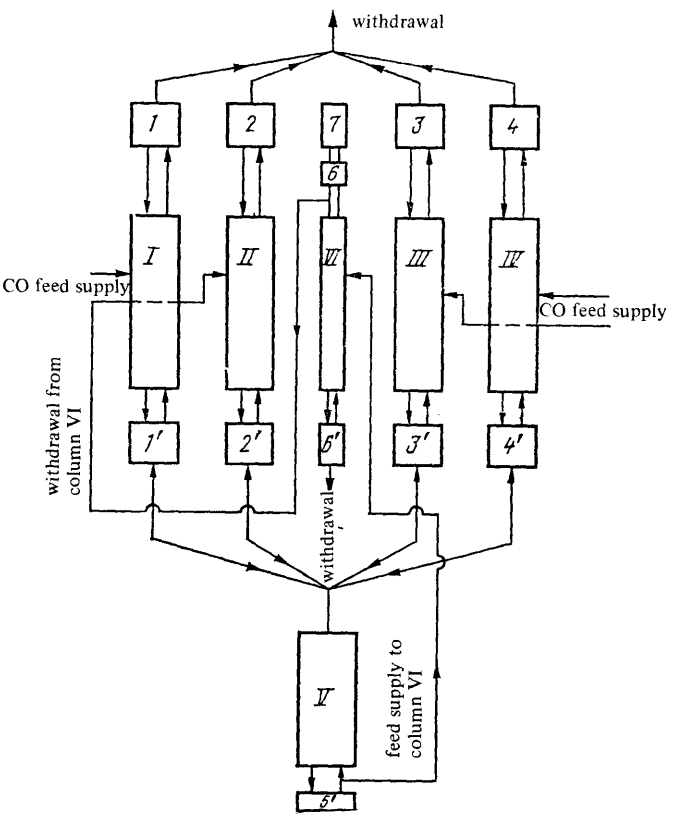


Figure 3. Schematic diagram of a pilot-plant assembly for obtaining the ^{13}C isotope by the fractional distillation of carbon monoxide: *I, II, III, IV*, columns of the first section; *1, 2, 3, 4*, condensers of the columns of the first section; *1', 2', 3', 4'*, evaporators of the columns of the first section; *V*, column of the second section; *5'*, evaporator of the column of the second section; *VI*, column of the third section; *6*, main condenser of the third section; *6'*, evaporator of the third section; *7*, intermediate condenser of the third section.

It is difficult to obtain high concentrations of ^{13}C by the fractional distillation of CO, because of the presence of the heavy oxygen isotope ^{18}O in the carbon monoxide.[67-69] Natural carbon monoxide is a $^{12}C^{16}O + {}^{13}C^{16}O + {}^{12}C^{18}O$ mixture. According to Ref. 56, the difference between the partial vapour pressures of

$^{12}C^{18}O$ and $^{13}C^{18}O$ is so small (α = 1.002 at 74.4 K) that fractional distillation in a column leads to the practical separation of only $^{12}C^{16}O$ from the binary $^{12}C^{18}O$ + $^{13}C^{16}O$ mixture. It can readily be shown that if it is assumed that the pressures of $^{12}C^{18}O$ and $^{13}C^{16}O$ are equal, the maximum enrichment in ^{13}C cannot exceed 95%. The further concentration of ^{13}C by this method requires an additional column. Thus on an industrial assembly with an annual output of 1.5 kg ^{13}C, further enrichment of the product from 95% to 97.7% was achieved by the fractional distillation of the enriched $^{12}C^{18}O$ + $^{13}C^{16}O$ mixture in an additional column.[70] It is possible to carry out the catalytic exchange reaction[56,71]

$$^{13}C^{16}O + {}^{12}C^{18}O \rightleftarrows {}^{13}C^{18}O + {}^{12}C^{16}O. \quad (1)$$

Up to the present, however, low-temperature catalysts for effective homomolecular exchange according to reaction (1) have not been found, so that on existing assemblies the ^{13}C concentration does not exceed 95%. Of these assemblies, mention must be made of a cascade operating in the Los Alamos research laboratory (USA), consisting of twelve parallel columns with diameter 2.54 cm and length 12 m (first stage), four parallel columns with diameter 2.54 cm and height 6.1 m (second stage), and one column with diameter 2.54 cm and length 24.4 m (third stage). The HETP for an input of 0.09 mol min^{-1} is 2.5 cm. The assembly produces 10.2 g of 92.4% ^{13}C per day.[51]

In Ref. 58, methane was used to separate carbon isotopes by fractional distillation. The experiments were carried out on the same column as the fractional distillation of CO, at a working pressure of 34 658 Pa. The steady state was reached in 7.5 h, and the HETP, calculated from α = 1.0108 and the maximum separation factor of 1.34, was 4.9 cm.

A comparative estimation of the efficiency of the fractional distillation of methane and carbon monoxide, carried out in Ref. 58 using the data from Ref. 46, showed that the use of methane to obtain ^{13}C with a concentration of 60–70% is economically less favourable. The applicability of this conclusion to the range of higher ^{13}C concentrations apparently requires special study. It may be noted that the use of methane requires the use of condensers of more complicated design, since the normal boiling point of liquid nitrogen is much lower than the freezing point of methane.

IV. Chemical isotopic exchange

Chemical isotopic exchange, proposed in the mid-nineteen-thirties,[72] is an effective method for separating the isotopes of light elements. It occupies a unique position, on the one hand because of the wide variety of reactions and compounds which can be used to separate isotopes and on the other hand because it is comparatively inexpensive. The production of isotopes by chemical exchange is based on the use of thermodynamically reversible separation processes in two-phase systems. In these systems there are deviations from the equally-probable distribution of the isotopes between the phases present in thermodynamic equilibrium. The isotopic effect is characterised quantitatively by the elementary separation factor α.

1. The bicarbonate method

One of the first reactions used to separate carbon isotopes was the exchange reaction between carbon dioxide and aqueous solutions of alkali metal bicarbonates:[73]

$$^{13}CO_2(\text{gas}) + H^{12}CO_3^-(\text{liquid}) \rightleftarrows {}^{12}CO_2(\text{gas}) + H^{13}CO_3^-(\text{liquid}). \quad (2)$$

At equilibrium, however, aqueous solutions of bicarbonates contain not only HCO_3^- ions but also carbonate ions and molecules of dissolved CO_2, so that the main exchange reaction (2) is accompanied by exchange reactions between the CO_2 in the gas phase and the CO_2 dissolved in the liquid phase, and also between CO_2 and carbonate ions.[74,75] At 298 K the separation factors for the carbon isotopes in these reactions are 1.013, 1.0008, and 1.0077 respectively.[75] The overall effective separation factor under different specific conditions depends on the mole fraction of each compound in the solution, and according to Ref. 73 is 1.012 at 298 K and a pressure P_{CO_2} = 101 308 Pa. With increase in temperature to 313 K, α decreases to 1.008.[75]

Despite the comparatively high separation factor and the simplicity of stream reversal, which is brought about by decomposing the bicarbonate with sulphuric acid, the bicarbonate method suffers from a serious disadvantage, namely the low rate of isotopic exchange.[73,76,77]

The influence of the material and geometric form of the packing on the efficiency of a column using the bicarbonate method has been studied.[78] At 293 K and a rate of supply of 20% potassium bicarbonate solution of 4 ml min^{-1}, in a two-metre column with diameter 16 mm filled with an aluminosilicate catalyst, the HETP was 53 cm. This agrees with the value obtained in another study[47] using a similar catalyst.

The addition to the aqueous potassium bicarbonate solution of acetone, in which the solubility of carbon dioxide is 7 times that in water, increases the separation of the carbon isotopes.[75,79,80] The optimum concentration of acetone in water is 5 vol.%.

The bicarbonate method uses large quantities of reagents for stream reversal. A method of separation using the bicarbonate of 2-aminoethanol instead of alkali metal bicarbonates does not suffer from this disadvantage.[81] Stream reversal in this case is achieved by simple thermal decomposition of the bicarbonate of 2-aminoethanol to the original CO_2 and 2-aminoethanol, and the 2-aminoethanol solution, saturated with CO_2 in an absorber, is returned to the cycle. This eliminates almost completely the irreversible consumption of reagents, and the expenditure on stream reversal reduces mainly to the cost of electrical energy. The effective carbon isotope separation factor when the bicarbonate of 2-aminoethanol is used is approximately the same as for isotopic exchange between CO_2 and alkali metal carbonates.[82]

The influence of temperature and the concentrations of the bicarbonate of 2-aminoethanol and the added catalyst carbonic anhydrase on the efficiency of the column was studied.[83] The experiments were carried out on a column with length 6 m and internal diameter 15 mm. The packing consisted of activated carbon and ShCM grade silica gel with a particle size of 2.5–3.5 mm. Neither silica gel nor activated carbon catalyses isotopic exchange between the bicarbonate of 2-aminoethanol and CO_2. With increase in temperature from 5 °C to 50 °C, the degree of separation passes through a maximum at 20 °C. The optimum 2-aminoethanol concentration is 0.9–1.0 M. The HETP decreases by a factor of 1.3–1.5 when an alcohol–chloroform specimen of carbonic anhydrase (1–10%) is added, and is 65–80 cm, depending on the catalyst concentration.

The bicarbonate method for separating carbon isotopes can compete with the fractional distillation of CO only when catalysts capable of giving comparable HETP are found.

2. The carbamate method

In the early nineteen-sixties it was established[84] that the salt-like carbamates formed by the reaction of secondary amines with CO_2 in anhydrous organic solvents may be promising for separating carbon isotopes by the isotopic exchange reaction:

$$^{13}CO_2(gas) + R_2N^{12}CO_2^-(liquid) \rightleftarrows R_2N^{13}CO_2^-(liquid) + {}^{12}CO_2(gas). \quad (3)$$

The product of the reaction of the amine with CO_2 is thermally unstable, so that stream reversal in the carbamate system is achieved by simple heating, and the separation can be carried out using the simple scheme shown in Fig. 4.

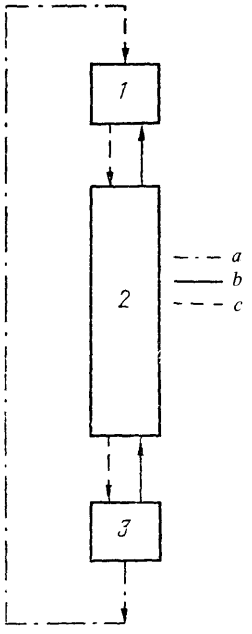


Figure 4. Schematic diagram of the separation of carbon isotopes by the carbamate method: *1*, absorber, *2*, exchange column, *3*, desorber, *a*, stream of complex former (amine + solvent), *b*, stream of gas (CO_2), *c*, stream of complex (amine + solvent + CO_2).

The presence of moisture in the solvent can produce a radical change in the nature of the product obtained by the reaction of CO_2 with a secondary amine. The reactions taking place in this case are probably accompanied by the reaction of water to give carbonates.

A column with length 196 cm and internal diameter 10 mm, containing stainless steel Helipak packing, was used to determine the degree of separation of carbon isotopes under identical conditions (reflux density, amine concentration, temperature) using fifteen different amine solutions in methanol.[85] The degree of separation of ^{13}C decreased in the order isobutylamine > 2-aminoethanol > n-butylamine. The optimum concentration of the solution of n-butylamine in methanol is 1–1.2 M, and the optimum temperature 298 K. Further increase in the n-butylamine concentration is inappropriate, because of the appreciable deterioration in mass transfer as a result of the increase in the viscosity of the solution.

The hydrodynamic characteristics of the system were improved using a whole series of non-aqueous solvents[86,87] having a lower viscosity and greater solvent power for carbamate, compared with methanol. The best of these was triethylamine (TEA). Of the amines, di-n-butylamine (n-DBA) has the most favourable characteristics. In the Mound Laboratories (USA), data obtained for solutions of n-DBA in TEA were used to construct and operate a five-stage cascade in which CO_2, previously enriched to 20% in ^{13}C, gave 4 g ^{13}C per day with 90% enrichment.[88] The incomplete stream reversal when TEA is used as solvent lowers considerably the efficiency of the separation of the isotopes in the carbamate system.[51]

Pyridine and triethylamine have been used as solvents, and dibutylamine as the amine.[89] Experiments showed that solutions of dibutylamine in triethylamine with a water concentration $\geqslant 0.1\%$ are unsuitable for the separation, because of the formation of an insoluble precipitate in the desorber and in the column. On a column with diameter 2.5 cm and length 100 cm, the greatest separation factor (1.77) was achieved using a 1 M solution of n-DBA in TEA. With increase in the molarity of the solution, the separation deteriorated, due to the increase in the viscosity of the liquid phase. Triethylamine has a number of disadvantages as solvent: 1) the high saturated vapour pressure of TEA under the working conditions in a prolonged separation process leads to extensive loss of solvent and requires the use of special assemblies to keep the composition of the liquid phase constant; 2) preliminary drying of the solvent is essential; and 3) quantitative stream reversal in the desorber cannot be achieved when TEA is used.

A search has therefore been carried out for a more effective solvent which would satisfy the following requirements: low viscosity and boiling point; good solvent power for carbamate; low surface tension; chemical inertness and thermal stability; comparatively low vapour pressure; low physical solvent power for CO_2 and low solvent power for water; low cost; and availability. From these properties, octane was selected as solvent for di-n-butylamine.[89] On a column with length 100 cm and diameter 2.5 cm, using a 1 M solution of n-DBA in octane, the separation factor was 1.93, which is slightly greater than that for triethylamine, for which the separation factor was 1.77. Moreover, when octane was used, the time taken for the assembly to reach the steady state was reduced by 30%. The dependence of the degree of separation on the reflux density for the 2 M n-DBA–octane–CO_2 system was studied on a large-scale metallic laboratory assembly (length of packed column 250 cm, diameter 56 mm). The highest separation factor, 2.4, was achieved at a reflux density of 1 ml cm^{-2} min^{-1}.

Table 2. Influence of temperature on the value of α and the degree of separation of carbon isotopes in the system formed by CO_2 and a solution of n-DBA in octane.[90]

Temperature, K	α	Reflux density ml cm^{-2} min^{-1}	Degree of ^{13}C separation	Time to reach steady state, h	HETP, cm
298	1.0100±0.0003	0.840	1.67	48	1.94
318	1.0075±0.0004	1.070	1.60	30	1.62
333	1.0060±0.0003	1.170	1.46	25	1.61

When the separation was carried out for 60 d using the same working mixture, the concentration of moisture in the liquid phase did not increase, and remained at 0.03%. Thermal phase reversal at

the lower end of the assembly was achieved by boiling the liquid phase at 131 °C. The loss of CO_2 did not exceed 5 μg ml^{-1}.

The influence of temperature on the separation of carbon isotopes using the system formed by CO_2 with a solution of n-DBA in octane was studied on a column with diameter 2.5 cm and length 100 cm at different reflux densities calculated to give the same carbon dioxide flux at all temperatures.[90] Table 2 shows that α decreases regularly with increase in temperature. Increase in temperature above 318 K is not appropriate. Because of the appreciable dependence of the HETP on temperature in the range 298–318 K, the decrease in α is compensated by the decrease in the HETP and by the decrease in the accumulation time of the isotopic product.

The results of published studies[89,90] were used to calculate versions of a cascade assembly for obtaining highly concentrated ^{13}C. To obtain a ^{13}C concentration of 99% with α = 1.01, approximately 1400 theoretical separation stages are required. It was found most suitable to use a four-column cascade, with minimum total volume and minimum time to reach the steady state (about 53 d). It was shown that for a calculated assembly operation time of 300 days per year, half of the expenditure is for the starting materials (amine and solvent).

3. The cyanide method

The exchange between hydrogen cyanide and alkali metal cyanide solutions is one of the most effective methods for separating carbon isotopes. The concentration of ^{13}C by the reaction

$$H^{12}CN(gas) + Na^{13}CN(liquid) \rightleftarrows H^{13}CN(gas) + Na^{12}CN(liquid) \quad (4)$$

takes place in the gas phase, and the calculated separation factor α is 1.026–1.030 at 298 K.[91–93] A slightly higher value of α (1.035) is obtained for the separation of ^{12}C and ^{14}C.[94] The effective separation factor is lowered to 1.013[91] as a result of exchange between gaseous HCN and hydrogen cyanide absorbed by the NaCN solution. For this last reaction, α = 0.995.

A two-stage cascade with a total length of 19.5 m gave 20 g of carbon containing 25% ^{13}C.[93] The column diameter was 22 mm in stage I, and 10 mm in stage II. The working pressure in the lower part of the column was 166 652 Pa. The column of stage I was supplied with sodium cyanide formed by neutralising the ascending stream of HCN with NaOH solution in the absorber.

A cascade consisting of two columns was used to study the influence of pressure and the NaCN concentration on the efficiency of the separation.[95] The diameters of the columns of stages I and II were 24.8 mm and 14.4 mm respectively, and the height of each column was 2.5 m. The optimum concentration of the solution was 4.5 M, and the optimum pressure 166 625 Pa. Later,[96] the data from Ref. 95 were used to construct a four-stage cascade with a total length of 13 m, with packing consisting of Fenske glass spirals with diameter 4 mm. The output of the cascade was 0.16 mol ^{13}C per day.

The exchange reactions taking place in a liquid–liquid system between cyanohydrins in the organic phase and aqueous potassium cyanide solutions have also been studied:[97]

$$R_2C(OH)^{12}CN + K^{13}CN \rightleftarrows R_2C(OH)^{13}CN + K^{12}CN. \quad (5)$$

The high lability of the cyanide groups of the cyanohydrins leads not only to high separation factors (1.035–1.040) but also to a fairly high rate of isotopic exchange.

In addition to its advantages (a high separation factor and medium HETP), the cyanide method also has a number of significant disadvantages, primarily the extreme toxicity and the high cost of cyanides, and their tendency to polymerise with blockage of the packing. Moreover, the need to work at a reduced pressure reduces the carrying power of the column and hence its productivity. Changing to columns with a large diameter leads to a sharp increase in the HETP. These disadvantages make the process unsuitable for obtaining ^{13}C on the industrial scale.

4. Ion exchange and other methods of separation

The first publications on the separation of isotopes on ion exchange resins appeared in the mid-nineteen-fifties,[98] when a carbon isotopic effect was detected in the separation of ^{14}C-labelled amino-acids on cation exchange resins. The effect depended significantly on the position of the tracer in the aminoacid molecule. The presence of the ^{14}C isotope in a position at a distance from the ionogenic groups had no influence on the ion exchange properties of the acid.

In the separation of carbon isotopes using hydrogen cyanide, a separation factor close to 1.01 was obtained.[99] The process was carried out by depositing a band of cyanide ions on Dowex-2 anion exchange resin and displacing the band with dilute solutions of hydrochloric and acetic acids. No further studies were carried out, however, because of the high volatility and toxicity of hydrogen cyanide.

Subsequently, carbon isotopes were separated using formate ions,[100,101] deposited on the strongly basic Dowex-2 resin in the acetate form. When the band was displaced with hydrochloric acid solution, its leading edge was enriched in the heavy isotope. With increase in temperature from 279 K to 308 K, α decreased from 1.0062 to 1.0032.

Analysis of the experimental data showed that the use of ion exchange resins with a very high degree of cross-linking does not always lead to an increase in the efficiency of the separation, since there is a simultaneous increase in the dehydrating action of the resin on the ions. Moreover, increase in the degree of cross-linking (the concentration of divinylbenzene in the resin) may lead to a deterioration in mass transfer. In the separation of sulphur isotopes in a band of bisulphite ions in a column of Dowex-2 × 10 anion exchange resin in the acetate form, carbon isotopes were also separated at the boundary between the bisulphite and acetate ions.[102] The heavy ^{13}C isotope was concentrated in the solution. The separation factor α was approximately 1.0016.

A combined method for the simultaneous separation of sulphur and carbon isotopes on Wofatit-150 [?Ambeslite IR-20 (Ed. of Translation)] ion exchange resins with displacement of CN^- and HSO_3^- with sulphuric acid solution has been described .[103,104]

The use of ion exchange processes to separate carbon isotopes has not yet gone beyond laboratory studies. Nevertheless, in a number of cases, ion exchange can probably compete with traditional methods, particularly for isotopes of elements of medium mass, whose separation by chemical exchange or fractional distillation is difficult. The most promising methods involve ion exchange using counter-current movement of the phases analogous to that in the two-phase separation processes of fractional distillation and chemical isotopic exchange.

Of other chemical exchange systems used to separate carbon isotopes, mention may be made of systems based on carbonyl complexes. The complexes of CO with Ag_2SO_4 (in concentrated H_2SO_4), CuCl (in concentrated HCl), $CuSO_4$ (in concentrated H_2SO_4), di-n-propylamine, $Cu_2Cl_2.8NH_4Cl$, etc. have been tested.[105] The most suitable for the exchange reaction was found to be the $Cu_2(CO)Cl_2.8NH_4Cl-CO$ system, for which at 20 °C α = 1.016 and the half-exchange time is ~5 s. The stream reversal in the desorber

at 140 °C was quantitative (>99.99%).[105] A characteristic feature of the liquid phase of this system is the formation, on contact with atmospheric oxygen, of a sparingly soluble precipitate which blocks the packing in the column and disrupts its operating conditions. Technological difficulties probably represent the main obstacle to the industrial application of this system.

The simultaneous separation of carbon and sulphur isotopes by chemical exchange between carbon disulphide and potassium xanthate ($S=C<^{OR}_{SK}$) [106,107] has not found practical application, probably because of its high cost.

V. Isotopic effects in electrical discharges

In many countries in recent years, considerable attention has been paid to methods for separating stable isotopes based on the selective excitation of atoms and molecules in electrical discharges.[108,109]

Isotopic effects in the synthesis and dissociation of molecules in gas discharges had been observed even earlier, but they were slight. Thus it was shown[110–112] that in the dissociation of carbon dioxide in a silent discharge, the heavy ^{13}C isotopes of carbon accumulate in the undissociated CO_2 molecules. The degree of separation is independent of the power of the discharge and the rate of flow and pressure of the gas in the discharge tube, and its average value is 1.028 ± 0.008. A study of the redistribution of the isotopes in the dissociation of carbon dioxide in a glow discharge showed that, as in the silent discharge, the carbon monoxide formed has a lower concentration of the heavy ^{13}C isotope, and the undissociated carbon dioxide fraction is enriched in ^{13}C by an average factor of 1.020 ± 0.008.[113] Analysis of the mechanisms of the dissociation of carbon dioxide in glow[114] and silent[115–118] electrical discharges indicates that the dissociation passes through a number of stages with the formation as intermediate products of oxygen and ozone, which also accumulate in appreciable quantities in the final products.

A method has been proposed for separating isotopes by chemical reactions taking place under thermodynamically non-equilibrium conditions,[109,119] when the difference in the rate constants of the reactions involving different isotopic forms of the molecules may be considerable.[119]

The possibility of separating carbon isotopes in the reaction CO + CO taking place in an electrical discharge under different conditions (pulse, direct, alternating) has also been studied.[120,121] The chosen duration of the discharge pulse was much shorter than the vibrational-relaxational relaxation time. The pulse repeat frequency was 0.3 Hz, and its duration 5 μs. The experiments were carried out in a stream of gaseous CO at 298 K and 77 K in a reaction vessel consisting of a discharge tube with diameter 20 mm, length 300 mm, with molybdenum electrodes. The gas pressure in the reactor was varied from 133 Pa to 1330 Pa, and the flow rate from 10^{-2} litre s^{-1} to 1 litre s^{-1}. The composition of the mixture before and after the reaction was determined mass-spectrometrically. The measurements showed that in the pulse discharge with the walls of the reactor cooled to liquid-nitrogen temperature, the average concentration of ^{13}C in the C_2O formed reached 3.5%. No significant enrichment in ^{13}C was observed in the alternating and direct current discharges.

The presence of C_2O in the reaction products apparently indicates that the mechanism of the reaction CO + CO in the pulse electrical discharge is analogous to that of the photolysis of CO using an iodine lamp (wavelength 2064 Å):[122]

$$CO^* + CO \rightarrow CO_2 + C, \quad (6)$$

$$C + CO \rightarrow C_2O, \quad (7)$$

$$C_2O + CO \rightarrow C_3O_2 \quad (8)$$

(CO^* represents an excited CO molecule). Reaction (6) can take place in two directions:

$$^{13}CO + {}^{12}CO \rightarrow {}^{12}CO_2 + {}^{13}C \quad (9)$$

and

$$^{13}CO + {}^{12}CO \rightarrow {}^{13}CO_2 + {}^{12}C. \quad (10)$$

Since the experiments showed ^{13}C enrichment in the compound C_2O, which is formed with the participation of C, and not CO_2, reaction (9) apparently predominates.

The degree of separation of ^{12}C and ^{13}C in an electrical discharge is much greater than that in other single-stage processes. Because of the complexity of the accumulation of the products of the separation in the reactions in electrical discharges, and the large quantities of energy required for these processes, however, they still remain at the stage of laboratory studies.

VI. Separation of isotopes using lasers

In the last ten years, the laser separation of isotopes (LSI) has been intensively studied in the Soviet Union and other countries. This is related to a number of potential advantages of the LSI method over traditional methods, namely the high selectivity of the elementary act of separation ($\alpha \gg 1$) resulting from the monochromatic nature of the laser radiation and the possibility of its preferential action on one isotopic form; the fairly low expenditure of energy per atom of the isotope separated (energy is required practically only to isolate the required isotope); the rapid attainment of the steady state of the process; and its universal character.

Of the forms of the LSI method known at present, the most suitable for practical application is the isotopically selective multiphoton dissociation (MPD) of molecules, based on the phenomenon of the selective decomposition of molecules under the influence of resonance infrared radiation. Experiments on isotopically selective MPD have been carried out for many isotopes, from the light (hydrogen) to the heavy (osmium) elements.[123]

The selectivity coefficient of the dissociation, which corresponds to the separation factor, is usually defined as the ratio of the effective rate constants of the dissociation of the molecules with different isotopic compositions in a single irradiation. This definition is close to that adopted in traditional methods for separating isotopes;[124] in both cases the value of α is a measure of the selectivity of the elementary act of the separation.

Although the processes of multiphoton excitation and dissociation of molecules under the influence of infrared radiation have potentially a high isotopic selectivity, there are a number of factors which may lower the separation factor considerably. One of the main factors is vibrational relaxation, as a result of which high selectivity is achieved at low pressures (not higher than 133 Pa).

The study of the isotopically selective dissociation of the CF_3I [125] and CF_3Br [126] molecules shows that carbon LSI has promising possibilities. These molecules are of interest since the dissociation energies of the weak C–I and C–Br bonds are only 2.3 eV and

2.8 eV respectively. The high isotopic selectivity is preserved at a comparatively high gas pressure (up to 670 Pa).[127] Since it is desirable to carry out the process at increased gas pressures to increase the productivity, the dependence of the selectivity of the MPD on pressure was studied for CF_3I,[125,128,129] CF_3Br,[130] CF_2Cl_2,[131] and C_6H_5F.[132] In all cases the selectivity of the dissociation decreased regularly with increase in the pressure of the gas used.

Experiments have shown that it is better to use molecules which are not too complex for separation by the LSI method, since the MPD of polyatomic molecules gives numerous fragments, and the isotopic selectivity is decreased. At the same time, complex molecules dissociate more readily under the influence of laser radiation, and higher energy densities are required for molecules containing few atoms.[123] In molecules containing few atoms, the density of the levels up to the dissociation energies is small. This, firstly, restricts the possibility of attaining an energy sufficient for decomposition of the molecule, and, secondly, decreases the rate of the intramolecular redistribution of the excitation energy. Collisions with the buffer gas, however, may change the rotational state of a molecule in the ground or excited state. Since simple molecules (HFCO, CHF_3, CF_3I, CF_3Br) may be promising for carbon LSI, the MPD of these compounds in the presence of large quantities of buffer gases (Ar, He, NO, N_2) has been studied.[133–135] The dependence of the effective rate constant of the dissociation on the pressure of the buffer gas has been studied. An appreciable decrease (by an order of magnitude or more) in the rate of the MPD of these molecules was observed with increase in the pressure of the buffer gases from 1.33×10^3 Pa to 26.6×10^3 Pa.

Even with the fairly high selectivity coefficients of the MPD of molecules, one enrichment cycle is insufficient to achieve a high concentration of the required isotope, and a multistage process is necessary.[129,133,134,136–138] In the field of a pulse CO_2 laser, CF_3X molecules decompose by the reaction

$$CF_3X \rightarrow CF_3 + X \quad (X = I, Br, Cl)$$

to give molecules of C_2F_6 and halogen as final products. Since the C_2F_6 molecule does not absorb in the range of the radiation of the CO_2 laser, and its chemical transformation into CF_3X is fairly complicated, the dissociation of CF_3X may be carried out in the presence of, for example, acceptors of CF_3 radicals such as HBr and NO.[136] This gives CF_3H and CF_3NO molecules, which are then easily reconverted into the original compound CF_3X. When CF_3NO is heated with an excess of Br to 200 °C, CF_3Br is formed quantitatively in several minutes, so that one or several additional enrichment stages can be carried out.

Another method for cascading the laser separation process involves the use of I_2 and Br_2 molecules as acceptors. Thus the MPD of CF_3I mixed with Br_2 led to the complete conversion of the original molecules to CF_3Br, and, on the other hand, the dissociation of CF_3Br in the presence of I_2 led to the complete conversion of CF_3Br into CF_3I.[133,134,137,138] The experiments showed that in the presence of acceptors the yield of the dissociation and the selectivity of the MPD may be not only preserved but in many cases increased. The dependence of the yield of the MPD of CF_3I (CF_3Br) on the pressure of the acceptor is not monotonic, and has a clearly defined maximum, close to which the yield of the dissociation is higher than in the absence of the acceptor.

In principle, a high enrichment in the required isotope can be achieved by using laser radiation to 'burn off' from the starting material the molecules containing the isotope which is not required. In this separation scheme, the required isotope is concentrated in the residual products. For carbon, this method can effectively concentrate only the ^{12}C isotope, by 'burning off' from the mixture the small quantity of molecules containing the ^{13}C isotope. Gram quantities of CF_3I with a ^{12}C concentration of 99.99% have been obtained in this way.[139]

To obtain a highly enriched ^{13}C fraction, a two-stage scheme is best. In the first stage, the $^{13}CF_3I$ molecule is dissociated, and in the presence of an acceptor a new compound CF_3X is formed (X = Br, NO) with 20–30-fold enrichment in ^{13}C. The CF_3X is then transformed either into the original compound[137] or into a compound which undergoes isotopically selective dissociation under the influence of a CO_2 laser (for example CF_3Br).[133] The second stage involves the dissociation of the $^{12}CF_3X$ molecules. In this way it is possible to obtain a product with a ^{13}C enrichment of 90–99%.

The above results were obtained under single-pulse conditions. They were later reproduced[140,141] on a specially constructed assembly consisting of a pulse-periodic CO_2 laser with a kilowatt power level and a laser separating cell with transverse pumping of the working gas. The results obtained make it possible to proceed to the development of an industrial assembly for carbon LSI by isotopically selective MPD using CF_3I or CF_3Br molecules as the starting material.[140]

Analysis of the experimental data shows, however, that in addition to their advantages (the low dissociation energy of the carbon–halogen bond, and the high isotopic selectivity at a comparatively high gas pressure up to 600 Pa), halogen-substituted methane molecules have certain disadvantages: they decompose by a radical mechanism, and the primary act of dissociation of the CF_3X molecules (X = I, Br) to a CF_3 radical and halogen is followed immediately by the start of secondary chemical reactions which lower the selectivity and the yield of the required isotope. Moreover, the isotopically enriched halogen-substituted hydrocarbons obtained as final products in these processes may find only limited application. The conversion of CF_3X molecules into simple molecules (CO, CO_2) convenient for subsequent application involves technological difficulties and additional expense. A search has therefore been carried out for molecules whose isotopically selective dissociation will give products widely used in the synthesis of labelled compounds, and also in traditional methods of separation by low-temperature fractional distillation and exchange.[142] In particular, for carbon LSI it has been suggested that carbonyl-containing compounds, many of which give CO and CO_2 on decomposition, may be used. Moreover, in carbonyl-containing compounds, the C=O bond stretching vibrations (1700–1800 cm^{-1}) show large isotopic shifts (40–50 cm^{-1}),[143] and this is important for achieving a high isotopic selectivity in the MPD process.

It should be emphasised that the frequency of the C=O stretching vibration lies in the range of the generation of the CO_2 laser, which has not yet been used to separate isotopes, although its specific energy characteristics and the broad spectral composition of the radiation makes this a realistic possibility.[144–146] Carbonyl chloride $COCl_2$ enriched in ^{13}C and ^{18}O has been used to study MPD under the influence of pulse CO_2 laser radiation and to determine the yield of products and the selectivity with respect to carbon and oxygen simultaneously. The isotopic analysis of the dissociation product (CO) and the residual product ($COCl_2$) was carried out by mass spectrometry. The energy of the lasing pulse was ~0.5 J, and its duration ~5 μs. The irradiation of carbonyl chloride at a pressure of 66 Pa gave a selectivity of 4 with respect to carbon and oxygen.[147,148]

VII. Summary

At the present time, the principal industrial method for obtaining the ^{13}C isotope is the low-temperature fractional distillation of carbon monoxide. Extensive studies of the fractional distillation of CO in counter-current laboratory, pilot-plant, and industrial packed columns with different diameters have given the optimum parameters of the technological separation process, providing a reliable basis for increasing their productive capacity and making it possible to arrange cascades of columns to reduce the time taken to achieve a given ^{13}C concentration. At the same time, the method involving low-temperature fractional distillation of CO has a number of disadvantages, of which the most significant are the comparatively low separation fator α and the high energy consumption associated with the large quantities of coolant used, the complexity of the technological equipment for the process, and the rigorous requirements for pure CO. These disadvantages, particularly the first, become important when the scale of ^{13}C production is increased.

Promising technical and economic characteristics are shown by processes for obtaining carbon isotopes by chemical isotopic exchange between carbon monoxide or dioxide and their molecular compounds with organic ligands. The main advantages of these systems, in addition to the comparatively high values of the factor α, are the possibility of thermal enrichment of the streams and the fact that the separation can be carried out at room temperature. The carbamate system appears promising. The efficiency of the carbamate method of separation can be increased by using aliphatic hydrocarbons as solvents for the amines. The disadvantages of this method are, firstly, the need to use a large quantity of inert solvent, which requires an increase in the cross-section of the mass-exchange assembly and the processing of large streams. The main volume of the assembly and most of the material expenditure are associated with the first two stages of the cascade, where the ^{13}C concentration is increased to only 10%.

Another promising direction for the large-scale production of carbon isotopes is the laser method. The laser separation of carbon isotopes may in the near future compete with traditional methods such as fractional distillation and chemical isotopic exchange. An important task in the development of a technological LSI process is to find effective starting materials. To obtain a highly enriched required isotopic product, several cycles of the laser separation are usually required. After each separation stage it is necessary to convert the enriched product into the starting material or into compounds which absorb the energy of the CO_2 laser; this is often difficult and always requires the expenditure of energy and materials.

A method of separation using only lasers is probably not always the optimum method. It may be technologically appropriate to combine carbon LSI with traditional methods of separation, in particular chemical exchange and fractional distillation. In this combination, simple carbon-containing molecules (CO, CO_2, etc.) with a low degree of enrichment (up to 10–15 at.%), obtained in a single laser-separation cycle, can be subjected to further enrichment by traditional methods. This would make it possible to eliminate from cascade separating assemblies the first two stages, in which, as noted above, the greatest quantities of energy and materials are used, and this should lead finally to a significant decrease in the cost of carbon isotopes.

Important directions in the separation of carbon isotopes are still the development of rational technological schemes for combining separation processes and the search for less expensive starting materials, taking account of the possibility of using industrial waste products to give ecologically clean processes.

References

1. K Fox, G W Halsey, S J L Daunt, W E Blass, D E Jennings *J. Chem. Phys.*, 1980, **72** 4657
2. H O Meyer, P Schwandt, G L Moake, P P Singh *Phys. Rev.*, 1981, **23** 616
3. H Goeringer, B Schoch *Phys. Rev. Lett.*, 1980, **97** 41
4. P Lezoch, H J Trost, M A Rahman *Phys. Rev. Lett.*, 1981, **98** 158
5. A C Shotter, A N Bice, J M Wouters, et al. *Phys. Rev. Lett.*, 1981, **46** 12
6. N A Matwiyoff *Proc. IV Intern. Conf. on Stable Isotopes, Jülich*, 1981, 573
7. A D Newcomer, P J Thomas, A F Hofmann *Gastroenterology*, 1976, **70** 923
8. B H Lauterburg, J Bircher *Gastroenterology*, 1975, **65** 556
9. W W Shreev, J D Shoop, D G Ott *Gastroenterology*, 1976, **71** 102
10. A P Sherr, M Sasaki, A Newman *N. Engl. J. Med.*, 1971, **285** 656
11. G W Hepner, E S Vessell *N. Engl. J. Med.*, 1974, **291** 1384
12. P Lepebere, A Lugak *Diabetologia*, 1978, **14** 39
13. J Bircher, A Küpfer, I Gikalon *Clin. Pharmacol.*, 1976, **29** 484
14. *Proc. I Intern. Conf. on Stable Isotopes in Chemistry, Biology, and Medicine, Argonne*, Acad. Press, New York, 1973
15. *Proc. II Intern. Conf. on Stable Isotopes, Oak Brook, 1975*, Acad. Press, New York, 1976
16. *Proc. III Intern. Conf. on Stable Isotopes, Oak Brook, 1978*, Acad. Press, New York, 1979
17. *Stable Isotopes in the Life Sciences*, IAEA, Vienna, 1977
18. M Benedict, T H Pigford *The Chemical Technology of Nuclear Materials* (Translated into Russian), Moscow, 1960
19. D E Wooldridge, F A Jenkins *Phys. Rev.*, 1936, **49** 404
20. D E Wooldridge, W R Smythe *Phys. Rev.*, 1936, **50** 233
21. G L Hertz *Z. Phys. Chem.*, 1932, **79** 108
22. R Sherr *J. Chem. Phys.*, 1938, **6** 251
23. G L Hertz *Z. Phys.*, 1934, **91** 810
24. P Capron, J M Delfosse, M I de Hemptinne, H C Taylor *J. Chem. Phys.*, 1938, **6** 656
25. P Capron, M I de Hemptinne *Phys. Radium.*, 1939, **10** 171
26. I G Gverdtsiteli, V K Tskhaka, in collected papers *Poluchenie Izotopov* (The Production of Isotopes), Izd. Akad. Nauk SSSR, Moscow, 1958, p. 113
27. I G Gverdtsiteli, V K Tskhaka *At. Energ.*, 1959, **6** 329
28. G F Barvikh, R Ya Kucherov, in collected papers *Poluchenie Izotopov* (The Production of Isotopes), Izd. Akad. Nauk SSSR, Moscow, 1958, p. 120
29. R Ya Kucherov, G A Tevzadze *At. Energ.*, 1959, **6** 207
30. K Clusius, G Dickel *Naturwissenschaften*, 1938, **26** 546
31. R C Jones, W H Furry *The Separation of Isotopes by Thermal Diffusion* (Translated into Russian), Izd. Inostr. Lit., Moscow, 1947
32. A O Nier *Phys. Rev.*, 1939, **56** 1009
33. A O Nier *Phys. Rev.*, 1940, **57** 30
34. G Dickel *Helv. Phys. Acta*, 1950, **23** 103
35. A O Nier, J Bardeen *J. Chem. Phys.*, 1941, **9** 690
36. W W Watson *Phys. Rev.*, 1939, **56** 29
37. A Bramley, A K Brewer *J. Chem. Phys.*, 1939, **7** 553

38. W Crotch *Chem. Tech.*, 1944, **17** 29
39. Y Horibe *J. Chem. Soc. Jpn., Pure Chem. Sect.*, 1952, **73** 75
40. Y Horibe *J. Chem. Soc. Jpn., Pure Chem. Sect.*, 1955, **76** 25
41. Y Horibe *J. Chem. Soc. Jpn., Pure Chem. Sect.*, 1959, **80** 1206
42. W M Rutherford, J M Keller *J. Chem. Phys.*, 1966, **44** 723
43. G D Rabinovich *Razdelenie Izotopov i Drugikh Smesei Termodiffuziei* (The Separation of Isotopes and Other Mixtures by Thermal Diffusion), Atomizdat, Moscow, 1981, p. 98
44. K Clusius, H H Bühler *Z. Naturforsch., A*, 1954, **9** 775
45. H Sakata, K Matsuda, E Takeda *J. Phys. Soc. Jpn.*, 1953, **8** 313
46. G M Panchenkov, V D Moiseev *Zh. Fiz. Khim.*, 1956, **30** 1602
47. N N Tunitskii, G G Devyatykh, M V Tikhomirov, et al., in collected papers *Poluchenie Izotopov* (The Production of Isotopes), Izd. Akad. Nauk SSSR, Moscow, 1958, p. 14
48. E C Anderson, W F Libby *Phys. Rev.*, 1947, **72** 931
49. P M Grootes, A E de Vries, W G Mook *Z. Naturforsch., A*, 1975, **30** 1
50. R Kretner, G Dickel *Z. Naturforsch., A*, 1975, **30** 554
51. D Staschewski *Chem. Tech.*, 1979, **8** 269
52. R A Schwind *Chem. Proc. Eng.*, 1969, (7) 75
53. W Groth, H Ihle, A Murrenhoff *Z. Naturforsch., A*, 1954, **9** 805
54. G G Devyatykh, A D Zorin *Zh. Fiz. Khim.*, 1956, **30** 1133
55. G A Yagodin, O V Uvarov, N M Zhavoronkov *Dokl. Akad. Nauk SSSR*, 1956, **111** 384
56. T E Johns *Proc. Intern. Symp. on Isotope Separation*, North Holland, Amsterdam, 1958, p. 74
57. O V Uvarov, N M Sokolov, V V Lyapin, N M Zhavoronkov, *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1962, 7 695
58. G G Devyatykh, A D Zorin, N I Nikolaev *Zh. Prikl. Khim. (Leningrad)*, 1958, **31** 368
59. N N Sevryugova, N M Zhavoronkov *Dokl. Akad. Nauk SSSR*, 1960, **134** 87
60. P Baertschi, W Kuhn *Z. Naturforsch.*, 1953, **171** 1018
61. N M Zhavoronkov, O V Uvarov, S N Babkov, in collected papers *Poluchenie Izotopov* (The Production of Isotopes), Izd. Akad. Nauk SSSR, Moscow, 1958, p. 145
62. Ya D Zel'venskii, V E Sokolov, V A Shalygin *Nauchn. Dokl. Vys. Shkoly, Khim. i Khim. Tekhnol.*, 1958, (2) 368
63. Ya D Zel'venskii, A A Efremov *Izv. Vys. Ucheb. Zaved. SSSR, Khim. i Khim. Tekhnol.*, 1962, (5) 727
64. W Kuhn, M Thürkauf, A Narten *Proc. UN Intern. Conf. Peaceful Uses of Atomic Energy (Geneva)*, 1958, Vol. 4, p. 371
65. A Narten, W Kuhn *Helv. Chim. Acta*, 1961, **44** 1474
66. M V Tikhomirov, N I Tunitskii *Zh. Prikl. Khim. (Leningrad)*, 1959, **32** 531
67. P Ya Asatiani, V A Kaminskii, E D Oziashvili *Isotopenpraxis*, 1968, **4** 275
68. P Ya Asatiani, A G Ganson, E D Oziashvili, et al. *Proizvodstvo Izotopov* (The Production of Isotopes), Atomizdat, Moscow, 1973, p. 487
69. P Ya Asatiani, Candidate's Thesis, Mendeleev Moscow Institute of Chemical Technology, 1981
70. W R Daniels, A O Edmunds, I M Lockhart *Stable Isotopes in the Life Sciences*, IAEA, 1977, p. 21
71. H London *Proc. Intern. Symp. on Isotope Separation*, North Holland, Amsterdam, 1958, p. 319
72. H C Urey, L J Greiff *J. Chem. Phys.*, 1935, **3** 321
73. H C Urey, A H W Aten, A S Keston *J. Chem. Phys.*, 1936, 622
74. D R Stranks, S M Harris *J. Am. Chem. Soc.*, 1953, **75** 2015
75. I A Semiokhin, A K Lynkova, A G Serenkova *Vestn. Mosk. Univ., Ser. Khim.*, 1963, (5) 29
76. G A Mills, H C Urey *J. Am. Chem. Soc.*, 1939, **61** 534
77. G A Mills, H C Urey *J. Am. Chem. Soc.*, 1940, **62** 1019
78. I A Semiokhin, G M Panchenkov, Yu A Zhurov *Vestn. Mosk. Univ.*, 1960, (5) 7
79. I A Semiokhin, G M Panchenkov, Yu A Zhurov *Zh. Fiz. Khim.*, 1959, **33**(11) 2633 [English translation in *Russ. J. Phys. Chem.*, 1959(11)]
80. I A Semiokhin, A G Serenkova, A K Lynkova *Vestn. Mosk. Univ., Ser. Khim.*, 1962, (1) 39
81. M K Shennikova, Candidate's Thesis, Gor'kii State University, Gor'kii, 1953
82. A L Shnerson, A G Leitush *Zh. Prikl. Khim.*, 1946, **19** 869
83. Yu K Shaposhnikov *Zh. Fiz. Khim.*, 1958, **32** 870
84. T I Taylor *J. Chem. Phys.*, 1963, **60** 154
85. J P Agrawal *Sep. Sci. Technol.*, 1971, 819
86. M R Ghate, T I Taylor *Sep. Sci. Technol.*, 1975, 547
87. J P Agrawal *Sep. Sci. Technol.*, 1971, 831
88. R A Schwind, W M Rutherford *Symp. New Devel. in Radiopharmaceuticals and Labelled Compounds*, IAEA, Copenhagen, 1973, p. 225
89. E D Oziashvili, A S Egiazarov, Sh I Dzhidzheishvili, N F Bashkatova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, **5** 247
90. E D Oziashvili, A S Egiazarov, Sh I Dzhidzheishvili, N F Bashkatova *Stable Isotopes in the Life Sciences*, IAEA, Vienna, 1977, p. 29
91. H C Urey *The Chemistry of Isotopes* (Translated into Russian), Izd. Inostr. Lit., Moscow, 1948, Part I, p. 86
92. I Roberts, H G Thode, H C Urey *J. Chem. Phys.*, 1939, 7 137
93. C A Hutchison, D W Stewart, H C Urey *J. Chem. Phys.*, 1940, **8** 532
94. D R Stranks, S M Harris *J. Am. Chem. Soc.*, 1953, **75** 2015
95. E W Becker, K Bier *Z. Naturforsch., A*, 1952, 7 651
96. L L Brown, J S Drury *Z. Naturforsch., A*, 1952, 7 664
97. L L Brown, J S Drury *J. Inorg. Nucl. Chem.*, 1973, **35** 2897
98. K A Piez, H Eagle *Science*, 1955, **122** 968
99. H Schütze, P Kulicke *Dritte Arbeitstagung über Stable Isotope*, Leipzig, 1963, p. 217
100. C N Davidson, C K Mann, R K Sheline *J. Am. Chem. Soc.*, 1961, **83** 2389
101. C N Davidson, C K Mann, R K Sheline *J. Phys. Chem.*, 1963, **67** 1519
102. K E Holmberg *Acta Chem. Scand.*, 1962, **16** 1045
103. M Ciric, E Krell *Isotopenpraxis*, 1969, **3** 21
104. K Wetzel *Kernenergie*, 1966, **9** 203
105. A A Palko, L Landau, J S Drury *Ind. Eng. Chem. Process. Des. Dev.*, 1971, **10** 79
106. G Stiehl, R Kiessling *Kernenergie*, **5** 322
107. USSR P. 154241; *Byull. Izobret.*, 1963, (9) 19
108. E M Belenov, E P Markin, A I Oraevskii, V I Romanenko *Zh. Eksp. Teor. Fiz.*, 1973, **18** 196
109. T J Manuccia M D Clark *Appl. Phys. Lett.*, 1976, **28** 372
110. I A Semiokhin, Yu P Andreev, G M Panchenkov *Zh. Fiz. Khim.*, 1963, **37**(12) 2782 [English translation in *Russ. J. Phys. Chem.*, 1963(12)]
111. Yu P Andreev, I A Semiokhin, G M Panchenkov *Zh. Fiz. Khim.*, 1964, **38**(4) 1032 [English translation in *Russ. J. Phys. Chem.*, 1964(4)]

112. Yu P Andreev, I A Semiokhin, G M Panchenkov *Zh. Fiz. Khim.*, 1964, **38**(12) 2087 [English translation in *Russ. J. Phys. Chem.*, 1964(12)]
113. V A Sirotkina, I A Semiokhin *Zh. Fiz. Khim.*, 1968, **42**(5) 1300 [English translation in *Russ. J. Phys. Chem.*, 1968(5)]
114. I A Semiokhin, V K Korovkin, G M Panchenkov, Kh S Bakhchevanskii *Zh. Fiz. Khim.*, 1964, **38**(8) 2072 [English translation in *Russ. J. Phys. Chem.*, 1964(8)]
115. I V Nikitin, E N Eremin *Zh. Fiz. Khim.*, 1962, **36**(3) 616 [English translation in *Russ. J. Phys. Chem.*, 1962(3)]
116. I A Semiokhin, Yu P Andreev, G M Panchenkov *Zh. Fiz. Khim.*, 1964, **38**(3) 794 [English translation in *Russ. J. Phys. Chem.*, 1964(3)]
117. I A Semiokhin, Yu P Andreev *Zh. Fiz. Khim.*, 1966, **40**(10) 2377 [English translation in *Russ. J. Phys. Chem.*, 1966(10)]
118. I A Semiokhin, V A Sirotkina, Yu V Filipov *Russ. J. Phys. Chem.*, 1968, **42**(6) 1536 [English translation in *Russ. J. Phys. Chem.*, 1968(6)]
119. N G Basov, E M Belenov, V A Isakov, et al. *Zh. Eksp. Teor. Fiz.*, 1975, **68** 2032
120. A S Egiazarov, T G Abzianidze, T M Burkhudarova, et al. *Izv. Akad. Nauk Gruz. SSR, Ser. Khim.*, 1978, **4** 354
121. T G Abzianidze, V N Andryushchenko, A B Bakhtadze, et al. *Stable Isotopes in the Life Sciences*, IAEA, Vienna, 1977, p. 69
122. G Liuti, S Dondes, P Harteck *J. Chem. Phys.*, 1966, **44** 4052
123. V N Bagratashvili, V S Letokhov, A D Makarov, E A Ryabov *Mnogofotonnye Protsessy v Molekulakh v Infrakrasnom Lazernom Pole* (Multiphoton Processes in Molecules in an Infrared Laser Field), Izd. VINITI, Moscow, 1981, Vol. 2, p. 83
124. A N Rozen *Teoriya Razdeleniya Izotopov v Kolonnakh* (The Theory of the Separation of Isotopes in Columns), Atomizdat, Moscow, 1960, p. 438
125. S N Bittenson, P A Houston *J. Chem. Phys.*, 1977, **67** 4819
126. M Drouin, M Gauthier, R Pilon, et al. *Chem. Phys. Lett.*, 1978, **60** 16
127. V N Bagratashvili, V S Dolzhikov, V S Letokhov, E A Ryabov *Pis'ma Zh. Eksp. Teor. Fiz.*, 1978, **4** 1181
128. M Gauthier, P A Hackett, M Drouin, et al. *Gen. J. Chem.*, 1978, **56** 2227
129. O N Avatkov, A B Bakhtadze, V S Dolzhikov, et al. *XI Vsesoyuznaya Konferentsiya po Kogerentnoi i Nelineinoi Optike. Tezisy Dokladov* (Summaries of Papers Presented at the Eleventh All Union Conference on Coherent and Non-linear Optics), Erevan, 1982.
130. V N Bagratashvili, V S Dolzhikov, V S Letokhov, E A Ryabov *Appl. Phys.*, 1979, **20** 231
131. J L Lyman, S D Rockwood *J. Appl. Phys.*, 1976, **47** 595
132. V V Vizhin, Yu N Molin, A K Petrov, et al. *React. Kinet. Catal. Lett.*, 1977, **7** 303
133. G N Abdushelishvili, O N Avatkov, A B Bakhtadze, et al. *Kvantovaya Elektronika* 1981, **8** 534
134. O N Avatkov, V M Vetsko, G G Esadze, et al. *Kvantovaya Elektronika*, 1981, **8** 1119
135. T G Abzianidze, A S Egiazarov, A K Petrov, Yu N Samsonov *Kvantovaya Elektronika* 1981, **8** 565
136. T G Abzianidze, A S Egiazarov, A K Petrov, Yu N Samsonov *Soobshch. Akad. Nauk Gruz. SSR*, 1980, **98** 93
137. G N Abdushelishvili, O N Avatkov, V N Andryushchenko, et al. *Pis'ma Zh. Eksp. Teor. Fiz.*, 1979, **5** 849
138. O N Avatkov, A B Bakhtadze, G G Esadze, et al., *Abstr. of Contributed Papers of the 2-nd Intern. Conf. on Multiphoton Processes, Budapest*, 1980, p. 1
139. G N Abduselishvili, A N Avatkov, V Yu Baranov, et al. *Materialy IV Mezhdunarodnogo Simpoziuma po Gazovym Protochnym i Khimicheskim Lazeram* (Proceedings of the Fourth International Symposium on Gas Flow and Chemical Lasers), Stresa (Italy), 1982, A-35
140. G I Abdushelishvili, O N Avatkov, V I Bagratashvili, et al. *Kvantovaya Elektron.*, 1982, **9** 743
141. O N Avatkov, A B Bakhtadze, V Yu Baranov, et al. *Appl. Optics*, 1984, **23** 26
142. T G Abzianidze, Candidate's Thesis, Moscow, State University, Moscow, 1983
143. A K Petrov, T G Abzianidze, A S Egiazarov, E D Oziashvili *Izv. Sibir. Otd. Akad. Nauk SSSR, Ser. Khim.*, 1983, (3) 101
144. R E Center *J. Quant. Electr.*, 1974, **OE-10** 203
145. M M Mann, D K Rice, R G Eguchi *J. Quant. Electr.*, 1974, **OE-10** 682
146. I V Kovsh *Trudy FIAN* (Proceedings of the Physical Institute of the Academy of Sciences of the USSR), Vol. 116, Izd. Nauka, Moscow,. 1980, p. 54
147. T G Abzianidze, V Yu Baranov, A B Bakhtadze, et al. *Kvantovaya Elektron.*, 1986, **13** 206
148. S V Izyumov, Candidate's Thesis, Moscow Physicotechnical Institute, Moscow, 1984

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Chemiluminescence in cryogenic matrices

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ABSTRACT. The literature data on chemiluminescence (CL) in cryogenic matrices have been classified and correlated for the first time. The role of studies on phosphorescence and CL at low temperatures in the development of cryochemistry is shown. The features of low-temperature CL in matrices of nitrogen and inert gases (fine structure of spectra, matrix effects) and the data on the mobility and reactivity of atoms and radicals at very low temperatures are examined. The trends in the development of studies on CL in cryogenic matrices, such as the search for systems involving polyatomic molecules and extending the forms of CL reactions, are followed. The reactions of active nitrogen with hydrocarbons that are accompanied by light emission and CL in the oxidation of carbenes at $T \geqslant 77$ K are examined.

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I. Introduction

During the last three decades a separate new branch of chemistry has been formed—cryochemistry. The impressive results obtained in low-temperature chemistry have been correlated in a number of monographs and review articles.[1-10] There are quite a number of theoretical models that examine the mechanisms of low-temperature reactions; but in representing the kinetics of such processes a number of problems still occur, which cannot be resolved without the collection and classification of experimental material. The kinetics and mechanism of low-temperature solid-state reactions have mainly been studied using spectroscopic methods, among which chemiluminescence (CL) plays an important role.

Every year hundreds of reports on new CL reactions, investigations of their mechanisms, and applied aspects of the phenomenon are published. In this stream of information, some studies on low-temperature solid-state CL, comparatively few in number but very interesting, get lost. It is appropriate to recall here that the CL method can be used to measure directly the rate of a chemical process. When the high sensitivity of the CL method, which under favourable conditions permits the monitoring of changes down to only thousands or even hundreds of molecules per second, which are inaccessible to calorimetry, EPR, and absorption spectroscopy, is taken into consideration, it becomes clear that there is future potential in using low-temperature CL to study those solid-state processes which, as a rule, occur at a low rate. It is a favourable circumstance that in cryogenic systems temperature quenching of luminescence is suppressed to a considerable degree, and there is a substantial increase in the number of particles which can exist in electronically excited states during the time required to record them.

Low-temperature CL reactions do not constitute an exotic class; they occur over a wide range of temperatures and in various media—from cryogenic matrices of nitrogen and inert gases to frozen aqueous[11,13-15,17,18] and nonaqueous[12,16,19,20] solutions. Chemiluminescence at low temperatures accompanies radical recombination, atom transfer reactions, and a number of redox reactions such as oxidation of sulphur with ozone,[11] uranium(IV) sulphate complexes with ozone and xenon difluoride and trioxide,[12] luminol with oxygen and hydrogen peroxide,[13,15,18] triethylaluminium with xenon difluoride,[16] and reduction of $[Ru(bipy)_3]^{3+}$ with sodium borohydride,[14] the hydrolytic reduction of XeF_2,[17] and several other reactions.[12,19,20]

In this review we will not examine frozen solutions but will confine ourselves to CL in cryogenic matrices. The CL method is used to study the stabilisation of free radicals in nitrogen and inert gas matrices, to simulate under laboratory conditions the photochemical reactions that occur on the surface of dust particles in interstellar space, and to monitor the course and kinetics of chemical reactions in low-temperature matrices. Up to the present time, however, there have been no reviews in the world literature on studies devoted to low-temperature CL.

The present article serves a double purpose: firstly, to draw the attention of cryochemists to the unique possibilities of the CL method and, secondly, to alert the specialists in the field of gas-phase and liquid-phase CL to a new extensive region for application of efforts—low-temperature solid-state chemical reactions.

II. Early studies of phosphorescence and chemiluminescence at low temperatures

Investigations into the problems relating to the phenomenon of low-temperature CL were undertaken by Becquerel, Dewar, Lewis, and Rayleigh. The progress made by the end of the last century in the preparation and storage of liquid gases made it possible to widen the scope of studies in low-temperature chemistry and physics. Phosphorescence was detected at the temperature of liquid air for a large number of organic compounds, such as alkaloids, hydrocarbons, acids, alcohols, ethers,[1] but the mechanism of the phenomenon remained uncertain up to the 1940's, when as a result of the efforts of Jablonski,[21] Lewis,[22] Terenin,[23] and Kasha[24] it was

established that phosphorescence spectra are due to triplet-singlet electronic transitions from the lowest excited triplet states of molecules.

It was Dewar[25] who first observed the phosphorescence of a number of compounds at the boiling point of hydrogen. Back in 1903 in conjunction with Moissan he carried out a study of the reaction of liquid hydrogen with solid fluorine at 20.5 K.[26] Dewar was the first to use low-temperature traps cooled with liquid air for the preservation of unstable compounds.[27,28] Moreover, in conjunction with Jones he was the first to observe flashes of light accompanying the low-temperature explosive polymerisation of carbon monosulphide, whose spectrum contained cyanogen lines and sulphur and hydrocarbon bands.[27,28] Even earlier, in 1894, Dewar had detected the accumulation of ozone in liquid oxygen when exposed to electric discharge and he observed the luminescence of molecular and atomic oxygen produced by electron bombardment.[29] In the luminescence spectrum of oxygen he recorded, in particular, a green line (557.7 nm), which caused many disputes 34 years later in attempts to determine the nature of the aurora borealis and the luminescence of the night sky.

In 1924 Vegard[30] put forward the suggestion that the aurora borealis is caused by the luminescence of crystals of nitrogen present in the upper atmospheric layers when exposed to intense cosmic radiation. In attempting to confirm experimentally his hypothesis about the mechanism of this natural phenomenon, Vegard detected and studied in detail the luminescence of solid nitrogen condensed on a surface cooled to 20.5–4.2 K and then subjected to bombardment with electrons or positive ions. He considered that the green line that he observed with wavelength 557.738 nm was due to radiation from an excited nitrogen molecule. Vegard's hypothesis proved to be incorrect. McLennan and co-workers[31] measured the wavelength of the green line of oxygen with a Fabry–Perot interferometer and obtained a value of 557.7341 ± 0.0004 nm, which was in excellent agreement with the value of 557.7350 ± 0.0005 nm determined from astronomical measurements by Babcock.[32] Thus, it was demonstrated that the green line at 557.7 nm was due to the radiative $^1S \rightarrow {}^1D$ transition of an oxygen atom formed in the upper atmosphere as a result of solar radiation on molecular oxygen.[33]

Vegard was responsible for a remarkable observation which to a large degree assisted an extensive study of free radicals started three decades later. He found that after bombardment of solid nitrogen has ceased, a bright luminescence occurs for several minutes. On increasing the temperature of the sample the luminescence appears again, and its intensity and spectroscopic composition undergo changes during warming. The luminescence is not phosphorescent in nature, as was clear even after the first experiments of Vegard, who observed the emission of light from the sample when it was warmed several hours after electron bombardment had ceased. Consequently, it was shown that the luminescence produced by warming an irradiated nitrogen matrix is CL caused by the recombination of nitrogen atoms. Thus, Vegard was the first to observe CL in cryogenic matrices and to undertake a spectroscopic study of it under experimental conditions with good reproducibility.

Also to Vegard's credit is that he was in fact the first to use the method of matrix isolation in low-temperature spectroscopy. A pioneer in the concept of matrix isolation was Schmidt.[34] By assuming that the phosphorescence of compounds in liquid solution is considerably reduced as a result of the loss of excitation energy through molecular collision, he attempted to reduce the deactivation effect of excited particles by diluting them with inert molecules, placing the compound being studied in a rigid matrix or crystal (gelatine, sugar, papaverine). It was the experiments of Schmidt that served as an impetus for studying the effect of temperature and viscosity of the solvent on phosphorescence.

At the end of the 1920's many spectroscopists who had tried to obtain radicals by electrical discharge observed an unusual luminescence in the low-temperature traps protecting vacuum pumps. In some cases condensed ozone, hydrogen peroxide, and other compounds were detected.[1] At that time radical chain reactions were of considerable interest to research workers, so evidently they made considerable efforts to elucidate the role of radicals in the luminescence observed in traps and in detonation of frozen products. Thus, Lavin and Bates[35] reported a blue-green luminescence in a trap at 93 K to which was admitted ammonia that had previously passed through a discharge zone. It was concluded that the luminescence was due to the formation of NH and NH_2 particles. Lunt and Mills[36] reproduced these experiments and observed CL by interacting the decomposition products of gaseous ammonia in an electrical discharge on a solid surface of NH_3 at 93 K, having thus confirmed the results of Lavin and Bates.[35] The authors[36] considered that the reaction of metastable NH particles with hydrogen molecules in the ground state was the most probable source of CL

$$2\ {}^1\Delta\,NH + {}^1\Sigma H_2 = N_2^*H_4 \rightarrow 2\overset{*}{N}H_2.$$

The reaction product—an excited hydrazine molecule—dissociates to give two electronically excited NH_2 particles, which emit the CL.

III. Chemiluminescence in solid nitrogen

In 1954 Broida and Pellam[37] detected considerable luminescence accompanying the condensation of active nitrogen on a surface cooled to 4.2 K. It was suggested that the solid inert gases and nitrogen could be used as media for matrix isolation.[38,39] Their selection was determined not only by their considerable inertness but also by their transparency over a wide range of wavelengths (from the far infrared region of the spectrum to the vacuum ultraviolet) and by their adequate rigidity at 4.2–20 K. The reader can find detailed information about the method of matrix isolation, the properties of the matrices, condensation of solid deposits, and generation of highly active particles in several studies.[2,6–9,40–47]

After the report of Broida and Pellam,[37] extensive studies were carried out on luminescence spectra recorded not only by depositing the products of microwave discharge in gaseous nitrogen[48–56] but also by stimulation of luminescence through a high-voltage discharge using a Tesla transformer,[57] electron bombardment,[58,59] and the action of X-ray emission.[60]

Problems concerning the stabilisation of nitrogen atoms were studied by Fontana.[61,62] He came to the conclusion that if the condensing gas contains more than 1–2 mol % of nitrogen atoms virtually all of them recombine when the solid condensate is formed. It transpired that not more than 0.01–0.04 mol % of nitrogen atoms were stabilised in the nitrogen matrix.

Subsequently, Edwards[2] attempted to interpret the main characteristics of CL in solid nitrogen. He suggested that when the condensate is warmed up, diffusion of nitrogen atoms is initiated, and they migrate and undergo recombination to form nitrogen molecules in the ground ($X^1\Sigma_g^+$) and electronically excited ($A^3\Sigma_u^+$) states:

$$N(^4S) + N(^4S) \rightarrow N_2; \quad N(^4S) + N(^4S) \rightarrow \overset{*}{N}_2.$$

It was later suggested that the heat evolved from these reactions causes an increase in temperature of the sample and thus stimulates subsequent chemical processes. It was therefore assumed[2] that the β-lines in the CL spectrum are due to oxygen atoms formed in an excited state by the reaction:

$$N+NO\rightarrow N_2+O^*;\ O^*\rightarrow O+h\nu.$$

The transfer of energy from an excited N_2^* molecule to an oxygen atom is also allowed

$$O+N_2^*\rightarrow O^*+N_2^{\neq};\ O^*\rightarrow O+h\nu\ (\beta\text{-line});$$
$$O^*(N_2^{\neq})\rightarrow O+N_2+h(\nu_{el}\pm\nu_{vib})(\beta\text{-, }\beta'\text{- and }\beta''\text{-lines}),$$

where $N_2^{\neq}$ is a vibrationally excited nitrogen molcule, $O^*(N_2^{\neq})$ is an intermediate state which decomposes with emission of β-lines. The appearance of α-lines was accounted for by the occurrence of similar processes, except that, instead of an oxygen atom, a nitrogen atom was assumed to take part in the reactions:

$$N+N_2^*\rightarrow N^*+N_2^{\neq};\ N^*\rightarrow N+h\nu\quad(\alpha\text{-line});$$
$$N^*(N_2^{\neq})\rightarrow N+N_2+h(\nu_{el}\pm\nu_{vib})(\alpha\text{-, }\alpha'\text{- and }\alpha''\text{-lines}).$$

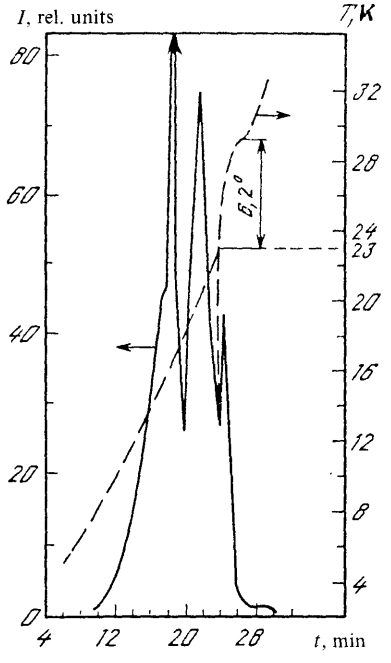


Figure 1. Dependences of the intensity of the α-band in the chemiluminescence spectrum (solid line) and the temperature of the sample (broken line) on time during the warming of a solid condensate of the products of ultra-high frequency discharge in gaseous nitrogen.[63]

In the mechanism examined a direct connection between CL and heat processes accompanying the recombination of atoms was assumed. Hemstreet and Hamilton[63] did not agree with such a treatment. They interpreted the dependence of the intensity of CL on time when the sample was warmed up (Fig. 1) by assuming the possible stabilisation of nitrogen atoms occurring not in the ground state but in an electronically excited state in the N_2 matrix.[63] This type of hypothetical stabilisation of excited particles, the life-time of which is several tenths of a second (we should remember that the radiative life-time of nitrogen atoms in the ^2D-state in a vacuum amounts to ~20 h, and in the ^2P-state to about 4 s), occurred, according to Hemstreet and Hamilton, via the formation of a weak complex between an electronically excited nitrogen atom and an N_2 molecule in the ground state. It was suggested that this complex inhibited the spontaneous deactivation of nitrogen atoms until it was destroyed on warming the matrix.

The presence of two maxima on the intensity curve (Fig. 1) was accounted for by Hemstreet and Hamilton[63] on the basis that there were two types of trap in ordered and disordered parts of the matrix respectively. It transpired that the maxima for CL and heat liberation did not necessarily coincide in time. Hemstreet and Hamilton saw that there was a discrepancy in the model of Edwards mainly because according to their data the luminescence peak occurred earlier than the heat liberation processes resulting from the recombination of nitrogen atoms in the ground state were recorded.

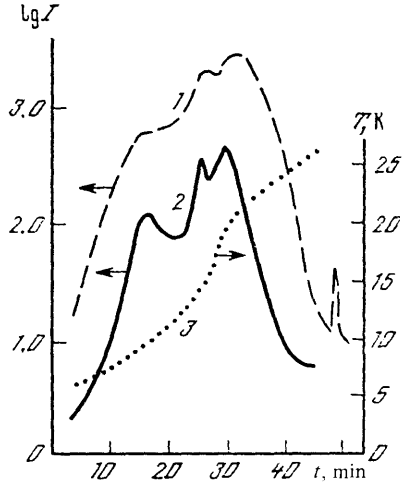


Figure 2. Dependence of the logarithm of the intensity of chemiluminescence on time (curves *1* and *2*) during warming and a thermogram of the sample in the case of irradiation with annealing (curve *3*). *1*, irradiation without annealing; *2*, irradiation with initial annealing.[64]

However, the results of Brocklehurst and Pimentel[64] based on quantitative thermometric and spectroscopic studies of solid nitrogen subjected to electron bombardment at 4.2 K contradicted the theory of Hemstreet and Hamilton. When the sample was warmed up the authors[64] observed three broad CL peaks and light emission at 35 K—the phase transition temperature (curve *1*, Fig. 2). When there was initial annealing of the sample, curve *2* was obtained with good reproducibility. The peaks were better resolved in the case of the annealed sample of solid nitrogen, which made it possible to exclude any of the observed CL maxima from being attributed to a process involving the ordering of imperfections in the crystal lattice

that develop when the condensate is formed. Thus, it remained to Brocklehurst and Pimentel to propose a mechanism for CL which would account for the presence of not two, as found by Hemstreet and Hamilton,[63] but three luminescence peaks.

In order to try and explain the presence of three luminescence peaks using the model of Hemstreet and Hamilton, it would be necessary to admit the existence of three complexes of excited atoms with molecules of the matrix, each of which would decompose irreversibly at a given temperature. Therefore, Brocklehurst and Pimentel returned to the model of Edwards, having modified it slightly. They proposed that each CL peak was due to the same active particles—this followed directly from the lack of change in the luminescence spectrum of a sample when its temperature was varied from 4–20 K. Subsequently, the authors,[64] by assuming that the given luminescence maxima were initiated by diffusion, postulated that the $N(^4S)$ nitrogen atoms were stabilised in the nitrogen matrix in three different positions (relative to the matrix environment), each of which was characterised by one of three values for its enthalpy of activation of diffusion. This model satisfactorily explained a number of features of CL in a nitrogen matrix, since the recombination reaction of $N(^4S)$ nitrogen atoms provides sufficient energy (225 kcal mol^{-1}) to excite the nitrogen atoms to the ^2D (54.7 kcal mol^{-1}) or ^2P (86.4 kcal mol^{-1}) states by exciton transfer.

However, despite the progress achieved by the beginning of the 1960's in understanding the nature of the CL of solid nitrogen, there were still considerable difficulties in attempts to interpret the fine structure of emission spectra. Complications arose because in order to obtain sharp and intense nitrogen luminescence spectra a very pure gas without contamination with oxygen was necessary since the latter quenches the luminescence of nitrogen and gives a series of broad emission bands in the exact spectroscopic region for observing nitrogen lines. In the study of Brocklehurst and Pimentel,[64] where the most complete theoretical analysis of the spectroscopic characteristics of the luminescence of solid nitrogen was carried out, gas of 99.995% purity was used.

In solid nitrogen that is free of impurities, the most intense band in the visible region of the spectra is the α-band. This component of luminescence is attenuated very slowly, and is caused by a very striking green afterglow with $\lambda = 523$ nm, due to the $^2D \rightarrow {}^4S$ transition of the nitrogen atom. The α′-band, as designated by Bass and Broida,[49] is much weaker than the α-band. It was established[52,54] that the difference in frequencies $\Delta\nu = \nu(\alpha)-\nu(\alpha') = 2300$ cm^{-1} is close to the vibration frequency of an N_2 molecule in the ground electronic state. On the basis of this, the α′-band was interpreted as the combination of a $^2D \rightarrow {}^4S$ electron transition of a nitrogen atom and a concurrent vibrational transition $v = 0 \rightarrow v = 1$ in a neighbouring N_2 molecule.

In the near IR region of the spectrum, the most intense emission comes from the so-called δ-band at 1044 nm, as detected by Peyron and co-workers,[55] and which they attributed to the $^2P \rightarrow {}^2D$ transition of an N atom.

Earlier, the fine structure of the α-band had been studied using spectrograms obtained photographically.[49,55,58] The difficulties which arose in the interpretation of this structure were overcome by Dressler and co-workers,[65] who for the first time obtained a photoelectric record of the α-band in the emission spectrum of solid nitrogen bombarded by electrons at 4.2 K (Fig. 3). It was shown that the spectrum of the α-band may be made up by a series of modified Lorentzian curves. The intensity ratio of lines *1–5* remains constant for different conditions of excitation and condensation of the samples. The overall pattern of these lines was interpreted as a dynamically induced electron-phonon band containing asymmetric molecular vibrations in the ground state, and the O_A and O_B lines were attributed to an unsymmetrically broadened, induced phonon-free band. This assignment was confirmed by a frequency analysis of the satellite vibration lines α′, α″, and α‴.

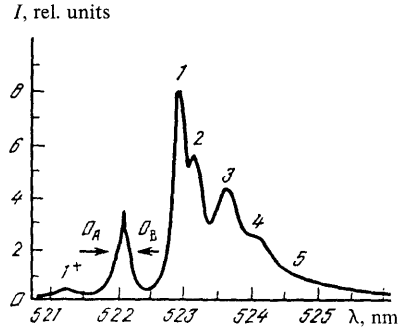


Figure 3. Structure of α-bands caused by the $^2D \rightarrow {}^4S$ transition in the low-temperature (4.2 K) luminescence spectrum of the nitrogen atom.[65]

Information about the structure of the traps containing active particles is of considerable importance for the correct interpretation of CL processes that occur when cryogenic matrices are warmed up. Such information was obtained even in the early studies on the EPR spectra of N atoms in a nitrogen matrix.[66,67] There is an interesting study,[68] in which in order to obtain data on the possible molecular environment of nitrogen atoms, an investigation was made as to how the EPR spectra were affected by the temperature of condensation of the products formed in an ultra-high frequency discharge in gaseous nitrogen. The occurrence of a single group of lines (spectrum *A*) at 7 K and three groups of lines (spectra *A*, *B*, and *C*) in the EPR spectrum of solid nitrogen at 14 K was related by Delannoy and co-workers[68] to the existence of one and three types of trap respectively in the matrix of molecular nitrogen. In an N_2 matrix the nitrogen atoms can occur in different stabilisation sites as a result of three processes (the position is characterised by the distance *R* between the centre of the structural defect occupied by the N atom and one of the adjacent nitrogen molecules):

1) substitution ($R_\alpha = 0.4$ nm);
2) insertion with an octahedral matrix environment ($R_\beta = 0.282$ nm)
3) insertion with a tetrahedral matrix environment ($R_\gamma = 0.244$ nm)

The capture centres of the $N(^4S)$ nitrogen atoms in an N_2 matrix were investigated in the study of Adrian.[69] With the theory he proposed it is possible to establish an interrelationship between the value of the hyperfine splitting constant and the number of neighbouring molecules and also the distance from the latter to the centre of the stabilised atom.

The next stage in studying the phenomenon of CL observed when condenstates of active nitrogen are warmed up was undertaken by Faure and co-workers.[70] Having used a combination of EPR and optical spectroscopy, they studied the effect of temperature on the capture of nitrogen atoms in traps of various types. When the condensate was warmed up from 5 to 40 K they observed three CL

peaks from the main component of the α-band for the $^2D \rightarrow {}^4S$ atomic transition (at 15.9, 20.3, and 23.5 K), which was consistent with earlier results.[63]

By analysing the changing features of the fine structure of the emitting α-band on varying the temperature, which revealed a different behaviour of the two components of luminescence in the region of the phonon-free band—O_A and O_B (Fig. 4)—Faure and co-workers[70] were able to conclude that N atoms were captured in two different types of trap. In fact, it is very clear from Fig. 4 that there is a relative decrease in intensity of the O_A lines (λ = 522.13 nm) when the temperature of the sample is increased. When a temperature of 18–20 K is reached, line O_A disappears. The observed changes in the spectra correspond, according to Dressler and co-workers,[65] to a change in the background structure due to an exchange of the types of trap in which the nitrogen atoms are stabilised.

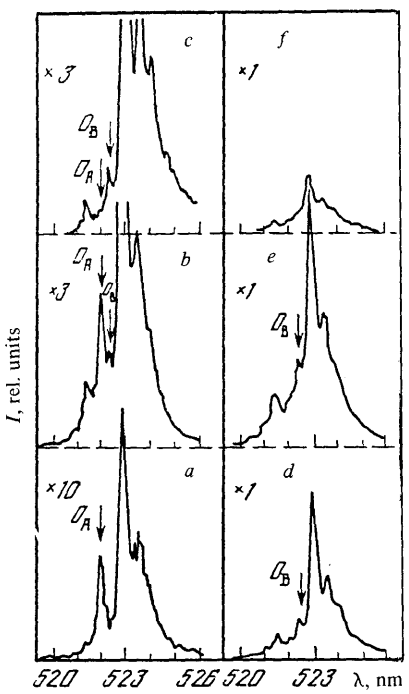


Figure 4. Fine structure of the $^2D \rightarrow {}^4S$ α-band emission obtained at different decomposition temperatures during warming (0.7 deg/min) of the condensate of products of gaseous nitrogen when exposed to ultra-high frequency discharge.[70] The rate of scanning the spectrum was 32 Å/min.
Temperature, K: *a*, 10–11.5; *b*, 14–15.5; *c*, 16–17.5; *d*, 20–21.5; *e*, 24–25.5; *f*, 26–27.5.

The studies started by Faure and co-workers[70] were continued by Tribbollet and Valadier,[71] who analysed the changes that occur in the fine structure of the α-band in the luminescence spectrum recorded during condensation of nitrogen at different fixed temperatures. The observed changes in the relative intensity of lines O_A, O_B, and O_C were interpreted on the basis of the existence of the three types of trap identified previously.[65]

The temperature dependencies of the intensity of the individual lines *1*, O_{AB} and O_C, as shown in Fig. 5, indicate that there can be several possible energy of activation values for each type of trap. Tribollet and Valadier[71] proposed that low-temperature CL is due to two different processes for excitation of nitrogen atoms: firstly, the recombination of atoms situated near each other (this process is responsible for the formation of the first maximum on the temperature curve of CL intensity and occurs in a similar manner to the recombination of electron–hole pairs by a tunnel mechanism); and secondly, the recombination of atoms with a diffusion mobility that is provided by thermal activation (the formation of the second CL peak is due to this mechanism, which has a bimolecular nature).

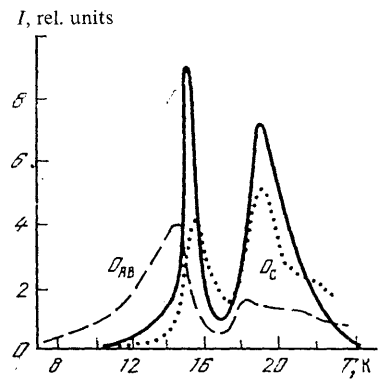


Figure 5. Temperature dependences of the intensity of three lines: *1*, O_{AB} and O_C, present in the luminescence spectrum of the nitrogen atom for $\alpha(^2D \rightarrow {}^4S)$.[71] O_{AB} is the sum of lines O_A and O_B.

In this study[71] the first event in the mechanism for stimulation of CL is assumed to be the recombination of two $N(^4S)$ atoms. The energy of the excited triplet molecule of N_2 is then transferred to nitrogen atoms, which emit light.

The suggestion that there were two mechanisms for excitation of nitrogen atoms was based on the results of an investigation of the kinetics of liberation of N atoms from traps at different temperatures. It transpired that in no single case could the attenuation of CL on removing the heating and stabilising the temperature of the nitrogen matrix containing nitrogen atoms be represented by an exponential decay typical of a first-order kinetic reaction. The decrease in luminescence at 20.3 K corresponds closely to $1/(1 + at)^2$. The intensity of CL at 15.9 and 23 K varies according to a hyperbolic relationship, $1/t$, which is characteristic of the recombination of electron-hole pairs occurring by a tunnel mechanism.

Tribbollet and Valadier[71] proposed two equations to represent the temperature dependencies of intensity obtained in their study for one of the components of the α-band (designated by them as line *1*) in the CL spectrum recorded on warming nitrogen which had condensed at 5 K after passage through a zone of ultra-high frequency discharge. The first expression was obtained by assuming

that the CL reaction occurs by a first-order kinetic mechanism, the second was obtained for the kinetics of a bimolecular reaction:

$$I_1 = n_0 S \exp(-E/kT) \cdot \exp\left(-\frac{S}{B}\int_{T_0}^{T} \exp(-E/kT')\,dT'\right),$$

$$I_2 = n_0 S' \exp(-E/kT) \cdot \left(1+\frac{S'}{B}\int_{T_0}^{T} \exp(-E/kT')\,dT'\right)^{-2},$$

where n_0 is a factor proportional to the number of particles responsible for luminescence at temperature T_0; E is the energy of activation; S is the pre-exponential factor; B is the rate of warming; T_0 is the initial temperature.

It may be mentioned that the theoretical curve that is plotted using the second expression is a better approximation to the experimentally obtained curve.

The problem of stabilising atoms and free radicals that occur in significant concentrations in solid matrices at low temperatures also remains important at the present time. The development of low-temperature physics has revived interest in metastable systems containing atoms stabilised at helium temperatures because of the possibility of finding unique quantum properties in such systems, namely, quantum diffusion, tunnel chemical reactions involving exchange of an atom with a molecule, superfluidly doped atoms, and superconductivity. These questions are among the most interesting and important problems of contemporary physics.

The fact that in the 1950's to 1960's it was only possible to stabilise atoms and radicals in very low concentrations was due to the thermal instability of systems containing considerable quantities of high-activity particles. It was suggested that atoms or free radicals were stabilised in structural traps in the matrix and the thermal instability was due to an increase in their diffusion capabilities caused by a temperature wave coming from the centre of a random recombination. This accounted for the weak dependence of the limiting concentrations of the stabilised atoms on the temperature of the matrix and depth of the structural traps.

Experiments carried out by a group of Soviet research workers[72–77] in which an original method was used for stabilisation of atoms based on the introduction of atom-molecule clusters into superfluid helium (He *II*) through its surface[72] showed that under good heat-exchange conditions and at a low temperature ($T_0 \approx 1.5$ K) the concentration of stabilised nitrogen atoms can reach 10%,[77] and the N atoms do not recombine for at least 1.8×10^3 s. It may be concluded from this that there is virtually complete stabilisation of the nitrogen atoms in He *II*. It was found that on increasing the temperature a significant proportion of the nitrogen atoms that accumulated at T < 2 K recombined in an explosive manner at the λ-point ($T_\lambda \simeq 2.19$ K). A powerful emission of CL is recorded at the same time.[72,73] Since at the λ-point there is only a sudden change in the thermal conductivity of liquid helium, the authors concluded that the effect was due to thermal explosion of particles of molecular nitrogen containing N atoms that were suspended in the liquid.

An analysis of the thermal stability of systems containing stabilised atoms was carried out by Gordon and co-workers.[73] They came to the conclusion that the limiting concentrations of the atoms stabilised at very low temperatures (T < 4 K) are determined by the stability of the system towards temperature-wave explosion and at higher temperatures towards thermal explosion. In the first case, the conditions for stabilisation require that the temperature wave coming from the centre of a random recombination does not succeed during its existence in inducing the recombination of neighbouring atoms in the matrix; in the second case the conditions require that the rate of heat removal from recombination provides a constant temperature of the medium.

The mechanisms examined above concerning the excitation of condensates of active nitrogen assumed the occurrence of two successive processes: the diffusion-controlled recombination of $N(^4S)$ atoms on the surface or in the bulk of a solid sample and the resonant transfer of energy from the $N_2(A\,^3\Sigma_u^+)$ molecule formed to an $N(^4S)$ atom, which is converted in the process to the electronically excited ^2D state.

Gordon and co-workers[74,75] studied the effect of isolating active nitrogen in a neon matrix on the fine structure of the α-band in the luminescence spectrum of solid nitrogen condensed in superfluid helium from a region of microwave discharge. They came to the conclusion that the α-emission of the nitrogen atoms at the moment of condensation was not due to the recombination of $N(^4S)$ atoms but to the de-excitation of excited $N(^2D)$ atoms trapped from the gas phase in the matrix of molecular nitrogen. The authors made use of the fact that even the lowest energy level of an excited neon atom (E = 16.6 eV) cannot be populated using the recombination reaction of $N(^4S)$ atoms (E = 9.8 eV). Consequently, the resonant transfer of energy from the triplet $N_2(A\,^3\Sigma_u^+)$ nitrogen molecule through the neon matrix is impossible. Therefore, if the mechanism for excitation of condensates of active nitrogen includes the recombination of nitrogen atoms in the ground state followed by transfer of energy from $N_2(A\,^3\Sigma_u^+)$ through the nitrogen matrix to an $N(^4S)$ atom, as N_2 is replaced by Ne the intensity of luminescence of the nitrogen atoms due to the $^2D \rightarrow {}^4S$ transition must decrease. If the main reason for the development of $N(^2D)$ atoms in the condensate is their capture from the gas phase, the matrix isolation with neon should not affect the intensity of the α-band in He *II*.

It transpired that when the ratio Ne/N_2 was varied from 0 to 20 the intensity of luminescence due to the transition $N(^2D \rightarrow {}^4S)$ in the nitrogen–neon condensate did not change.

In one study[76] the fine structure of the α-band in the luminescence spectrum of active nitrogen condensed in superfluid helium was examined, and it was concluded that the line with $\lambda \geqslant 523$ nm was due to a phonon wing transition and the I^+ line (λ = 521.2 nm) was not due to an anti-Stokes transition[65] but corresponded to the luminescence of nitrogen atoms captured on surface traps of a molecular nitrogen matrix.

IV. Chemiluminescence in cryogenic matrices of inert gases

A large contribution to the study of reactions in cryogenic matrices was made by Pimentel and co-workers. Back in 1958 Milligan and Pimentel[78] made a visual observation of the red luminescence during the warming up of solid nitrogen which had been subjected to UV photolysis at 20 K and which contained diazomethane. It was suggested that the CL was caused by one of three reactions:

Reaction	$-\Delta H$, kcal mol^{-1}
a) $CH_2 + CH_2N_2 = C_2^*H_4 + N_2$	101
b) $CH_2 + CH_2 = C_2^*H_4$	122
c) $CH_2N_2 + CH_2N_2 = C_2^*H_4 + 2N_2$	80

Subsequently, Goldfarb and Pimentel[79,80] undertook a more detailed spectrographic and visual study of the orange-red CL recorded at 20–40 K during the warming of a nitrogen or argon

matrix containing reactive residues of diazomethane or its deuterated analogues. On increasing the temperature the intensity of CL changed substantially—from a luminescence scarcely visible to the eye adapted to darkness to a bright orange-red emission which could be discerned even in a light sufficient for reading.

It should be noted that the photolytic method for obtaining active particles stabilised in cryogenic matrices proved very convenient and the majority of the subsequent studies concerned with low-temperature CL were carried out using UV photolysis. One of the studies of Goldfarb and Pimentel[79] is also of interest as a complex method for studying the mechanism of solid-state CL was used in it—IR absorption spectroscopy and emission spectroscopy and isotope substitution. Many subsequent studies were carried out using a similar approach.

Two decades after the discovery of CL in ethylene, Pimentel returned to cryogenic matrices containing diazomethane in order to study once again the luminescence spectrum, to elucidate the role of oxygen impurities, to obtain additional evidence for the presence of CH_2 radicals in a photolysed matrix, and to identify the emitter of chemiluminescence and the electronic transitions responsible for the emission of light.[81] During the intervening period there had been a considerable increase in the scope for recording low-temperature CL and knowledge about the energy levels of the excited states of ethylene had broadened. With the use of EPR and photoelectron spectroscopy new information about CH_2 radicals was obtained and an attempt was made to identify the possible products from the photolysis of diazomethane in matrices of inert gases.

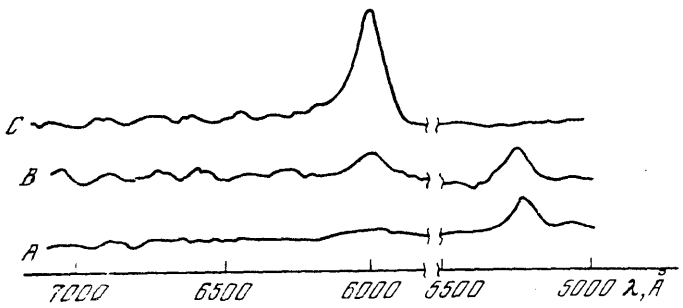


Figure 6. Luminescence spectrum recorded on warming a UV-irradiated nitrogen matrix containing CH_2NN (CH_2NN/N_2 = 1/300).[81]
Temperature, K: *A*, 8–10; *B*, 11–12; *C* 15–16.

Samples obtained by coprecipitation of diazomethane and argon (CH_2N_2 : Ar = 1 : 300) on a copper sheet at 6 K were irradiated with the full light of a medium-pressure mercury lamp for 2.5 h, and the CL spectra were recorded at a slow rate of warming (1–2 deg/min).[81] The early observations[79–80] were confirmed, and with better resolution of the spectroscopic apparatus used, additional structural features were detected in the spectrum. Below 10 K, a broad band with a maximum at 522.0 ± 0.4 nm (Fig. 6, spectrum *A*) predominated in the spectrum. At 11–12 K, a broad band appeared in the region 598.7 ± 0.5 nm, and there were also weak bands over the range 600–760 nm (Fig. 6, spectrum *B*). When the temperature was increased further the emission at 522.0 nm decreased and at 15 K was no longer recorded. At the same time the intensity of the band at 598.7 nm increased, reaching a maximum value at 18 K. This luminescence could be recorded up to about 35 K (Fig. 6, spectrum *C*).

The determination of the nature of the CL emitter was given prominence in this study.[81] Each of the maxima in the luminescence spectrum at 522.0 and 598.7 nm is a separate broad peak without any signs of vibrational structure. This type of spectrum is typical for a monoatomic emitter or a molecular transition between states with almost the same molecular geometry. The nitrogen atom and N_2, CH_2NN, CH_2NH, and C_2H_4 molecules were examined as probable sources of CL. The authors[81] considered the most probable CL emitter to be the ethylene molecule formed in reactions (a) and (b). This interpretation was confirmed not only by the observed correlation between the brightness of luminescence and the concentration of ethylene in the sample but also by the existence in a C_2H_4 molecule of electronic transitions between states with the same geometry. The latter circumstances accounts for the frequencies of the observed spectroscopic bands and the absence of vibrational structure in the CL spectrum. An argument in favour of a C_2H_4 molecule participating in the chemiluminescent reaction was the band detected in the IR region at 1115 cm^{-1}, which corresponded to the deformational vibration of the ground state of CH_2.[81] Consequently, on warming the matrix either diffusion and subsequent recombination of CH_2 radicals was possible or they could react with diazomethane [reactions (b) and (a) respectively]. The authors proposed that the long-wavelength CL maximum at 598.7 nm was due to electronic transitions from the second singlet ($^1A_1$, 43 000 cm^{-1}) or the first singlet ($^1B_2$, 43 769 cm^{-1}) state to the triplet ($^3A_2$, 24 700 cm^{-1}) state of the ethylene molecule. No definite conclusion was reached about the nature of the CL with a maximum at 522.0 nm.

At the start of the 1970's, owing to the efforts of inorganic chemists and organometallic chemists interest was once again stimulated in processes occurring in low-temperature matrices. The focus in studies of this type was shifted from the physical aspects of the chemistry towards synthesis, structure, and reactivity. Laser Raman spectroscopy, Mössbauer spectroscopy, magnetic circular dichroism, developed for application in matrix studies, proved a useful addition to the methods of EPR, absorption, and emission spectroscopy. CL also underwent further development.

Starting in 1974 a whole series of studies was published on low-temperature solid-state CL reactions involving sulphur atoms. In one of the first reports[82] there is information about a blue luminescence observed during the warming of Ar, N_2, or CO matrices which had previously been photolysed at 20 K and which contained hydrogen sulphide. The observed phenomenon was attributed to the formation of HS radicals, and hydrogen and sulphur atoms during photolysis. It was assumed that at 30 K diffusion of sulphur atoms starts, leading to their recombination and radiative deactivation of the excited sulphur molecule formed. The correctness of such an interpretation was confirmed by experiments involving photolysis of OCS.[83,84]

Direct evidence for the formation of S(^1S) atoms by photodecomposition of OCS in an argon matrix at 4 K on exposure to light with λ = 147 nm was obtained by Brom and Lepak.[83] They observed a broad emission band with a maximum at 775 nm, which was readily identified as the $^1S \rightarrow {}^1D$ transition in a sulphur atom.

The chemiluminescence of SO_2 on warming cryogenic matrices that had been irradiated with UV light and which contained SO_2 was first observed by French research workers,[85] who proposed that

the luminescence developed as a result of the reactions S + O_2 and O + SO. Long and Pimentel[86] interpreted the CL spectrum recorded on warming an argon matrix that had been photolysed at 8.5 K and which contained OCS and O_2 molecules by comparing it with the spectrum of the gas-phase phosphorescence of SO_2 and also by measuring the isotope shifts of the vibrational bands of the CL spectrum when $^{16}O_2$ was replaced by $^{18}O_2$. It was concluded that CL develops during the reaction of sulphur atoms with an oxygen molecule, which occurs with an energy of activation almost equal to zero at 10–40 K:

$$S(^3P_2) + O_2(X\,^3\Sigma_g^-) \rightarrow S{\cdot}O_2 \rightarrow SO_2(X\,^1A_1) + h\nu.$$

French research workers[84] detected a considerable diffusion of sulphur atoms in an argon matrix even at 6 K. This study was the extension of a previous one,[85] in which the occurrence of CL on warming a matrix containing SO_2 was attributed exclusively to the emission of SO_2 formed in an electronically excited state as a result of reaction in the lattice $S(^3P) + O_2(X^3\Sigma_g^-)$. However, the high intensity of SO_2 phosphorescence could have masked the emission of $S_2(B^3\Sigma_u^-)$ and in order to detect CL of the sulphur molecule, the French research workers turned to other sulphur-containing compounds giving sulphur atoms by photodissociation. In their later study[84] they observed two clearly distinguishable types of luminescence—the photoluminescence during photolysis at 5–6 K of Ar matrices containing OCS or CS_2 molecules, and CL when the temperature of the sample was increased after the completion of irradiation with light of wavelength 147 nm. Since the energy of the photons (8.3 eV) was insufficient for photoionisation of CS_2 or OCS, the observed luminescence was not due to recombination of charges, as occurs in radiothermoluminescence, but was due to the recombination of atoms, forming molecules in an electronically excited state, in other words, it was CL by its very nature.

It was also established that the CL emitter in matrices containing both OCS and CS_2 was an electronically excited molecule of sulphur, which emits light from the transition $(B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-)$. As well as emission from S_2, emission of SO_2 was recorded in the matrices containing OCS, which was borne out by the similar shape of the temperature curves of intensity of luminescence for S_2 and SO_2 molecules,[84,86] which was an indication of the identity of the particles responsible for luminescence (Fig. 7). In the case of CS_2, bands relating to CS particles $(a^3\Pi \rightarrow X^1\Sigma^+)$ were observed in the CL spectrum. These results indicate that carbon atoms can also diffuse for a considerable distance to form $CS(a^3\Pi)$ particles according to the reaction

$$C(^3P) + S(^3P) \rightarrow CS(a\,^3\Pi),$$

and the rate of diffusion of the carbon atoms is higher than that for the sulphur atoms—Cs bands are observed at lower temperatures than for S_2 bands.

The reliably established evidence for the formation of S_2[83,84] and O_2[87] molecules in an electronically excited state as a result of solid-state chemical reactions stimulated the study undertaken by Lee and Pimentel[88] on low-temperature matrices aimed at obtaining SO molecules in an electronically excited state; there was no information about the existence of these molecules in the gas phase. The authors introduced NO_2, O_2, and SO_2 molecules into an argon matrix for the photogeneration of oxygen atoms, and to obtain sulphur atoms they introduced OCS and SO_2. When the photolysed matrices ($OCS/O_2/Ar$; $OCS/NO_2/Ar$; SO_2/Ar) were warmed up, they observed CL, with a spectrum containing two emission bands—in the region 390–520 nm, due to the transitions $SO_2(\tilde{a} \rightarrow \tilde{X})$, and a progression in the region 520–770 nm. In the system $OCS/O_2/Ar$ the $S_2(\tilde{c}^1\Sigma_u^- \rightarrow \tilde{a}^1\Delta_g)$ was also observed.[89]

The progression in the region 520–770 nm was identified by Gordon and co-workers[74] as SO emission, which was identified from the proximity of ω_e'' to the vibrational frequency of the progression and arose from the low electronically excited states of the SO molecule. Experiments with $^{18}O_2$ showed that the CL emitter contained oxygen.

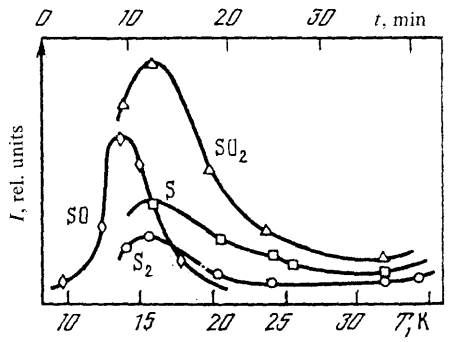


Figure 7. Dependences on temperature and time for the intensity of chemiluminescence of SO, S_2, S, and SO_2 molecules, recorded on warming UV-irradiated Ar matrices containing O_2 and COS ($COS:O_2:Ar = 1:1:200$).[88]

By analysing the experimentally obtained and calculated data on the energy levels of the SO molecule, Lee and Pimentel[88] were able to conclude that the chemiluminescence of SO was due to the radiative transition $\tilde{c}^1\Sigma^- \rightarrow \tilde{a}^1\Delta$. The $\tilde{c}^1\Sigma^-$ state is populated as a result of the reaction $S(^3P_2) + O(^3P_2)$ taking place either directly or via the higher $\tilde{A}''$ and/or $\tilde{A}'$ states, which rapidly relax to the $\tilde{c}$ state. Thus, in this study[88] spectroscopic information about the $\tilde{c}^1\Sigma^-$ state of the SO molecule was obtained for the first time.

In all the studies examined above CL spectra were recorded either photographically or by using a photoelectron multiplier (PEM). The main disadvantage of the latter system is the variation in the light flux, the intensity of which is proportional to the concentration of emitting particles such as SO_2^* or S_2^* during the interval of time necessary to record the spectrum. Consequently, the ratio of intensities of the bands at the limits of an emitting system can only be determined approximately.

This difficulty is eliminated when a photographic method is used, when all the emission distributed in the spectrum is recorded at the same time. However, because of the relatively low sensitivity and the logarithmic dependence of the degree of darkening of photoemulsions on the duration of exposure, it is only possible to use this method successfully with bright CL systems. These disadvantages are eliminated by an optical multichannel analyser in which the integral (multichannel) resources of a photographic plate are combined with the high sensitivity and linear characteristics of the PEM.

By using an optical multichannel technique it was possible for the first time to record simultaneously low-temperature CL spectra on warming cryogenic matrices.[90] The time of scanning a section of the spectrum with width 275 nm was 32.8×10^{-3} s. In each experiment up to 1000 individual scans were carried out using 500 channels. The studies were carried out over the spectroscopic range 200–650 nm. Frozen mixtures of inert gases (Ar, Kr, Xe) with added amounts of O_3, $H_2S + O_2$, and $O_3 + H_2S$ at 8 K were irradiated with UV light. The successive warming up of the irradiated samples over the range 8–20 K led to the appearance of intense chemiluminescence in the visible region of the spectrum.

In the CL spectrum observed on warming an irradiated matrix containing ozone there was the Herzberg I system due to $O_2(A\,^3\Sigma_u^+ \rightarrow X\,^3\Sigma_g^-)$ emissions. This system (340–640 nm) was observed by Broida and Peyron[56] when they studied the luminescence of solid condensates from ultra-high frequency discharge in gaseous N_2 containing traces of oxygen. However, in contrast to Broida and Peyron, who postulated an excitation mechanism that included the transfer of energy from an electronically excited N_2 molecule, Smardzewski[90] considered that excitation of O_2 occurred as a result of diffusion and emissive recombination of oxygen atoms formed by photolysis of ozone:

$$O(^3P) + O(^3P) + M \rightarrow O_2(A\,^3\Sigma_u^+ \rightarrow X\,^3\Sigma_g^-) + M.$$

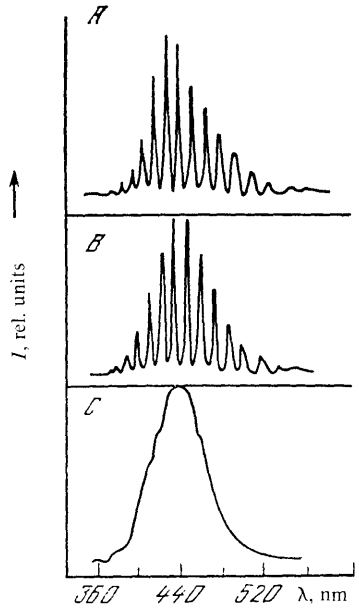


Figure 8. Chemiluminescence spectra observed on warming (from 8 to 13–15 K) H_2S-containing matrices subjected to UV-photolysis during their condensation at 8 K.[90] $M : H_2S = 100 : 1$; *A*, M = Ar; *B*, M = Kr; *C*, M = Xe.

By using different inert gases as matrices it was possible to study the effect of the matrix environment on the CL spectra. There could be two causes of such an effect—diffusion effects and the interaction of trace particles and atoms or molecules of the cryogenic matrix. In densely packed structures of solid inert gases, the dimensions of the interstices and vacancies increase with atomic weight. If the dimensions of trace particles having a low atomic (molecular) weight are comparable with the dimensions of the vacancies in the matrix, diffusion of such particles can take place at an appreciable rate.

It was shown,[90] in fact, that the $(A \rightarrow X)$ emitting system of O_2 molecules formed in an excited state by recombination of oxygen atoms has high intensity in solid argon, low intensity in krypton, and is not recorded at all in solid xenon. This was attributed to the fact that in matrices of heavy inert gases (Kr, Xe) the diffusion mobility of oxygen atoms is quite high even at the temperature of photolysis (8 K) so that even before the sample is warmed up the oxygen atoms have time to react with each other to give O_2 or O_3. Such an interpretation is consistent with an earlier study,[59] in which the radiative $(A\,^3\Sigma_u^+ \rightarrow X\,^3\Sigma_g^-)$ transition of molecular oxygen was observed during electron bombardment of Kr and Xe matrices containing O_2.

In experiments with matrices containing H_2S, Smardzewski[90] observed CL, the spectra of which are shown in Fig. 8. In the case of the Ar and Kr matrices, CL was due to $S_2(B\,^3\Sigma_u^- \rightarrow X\,^3\Sigma_g^-)$ emission in the region 365–560 nm. The same type of emission was observed[83,84] when photolysed Ar matrices containing OCS and CS_2 molecules were warmed up.

The recombination of sulphur atoms in the ground state was considered to be a fundamental part of the CL mechanism by both Smardzewski and other authors.[83,84] However, it was known from gas-phase studies that the $B\,^3\Sigma_u^-$ state of S_2 is not populated by direct reaction of two $S(^3P)$ atoms. In order to overcome this difficulty, it was assumed that when the $S(^3P)$ atoms recombine, S_2 is formed in the predissociative state 1_u, whose potential curve intersects the potential curve of the $B\,^3\Sigma_u^-$ state. The $B\,^3\Sigma_u^-$ state is then formed as a result of a nonradiative transition:

$$S(^3P) + S(^3P) \xrightarrow{M} S_2(1_u) \xrightarrow{M} S_2(B\,^3\Sigma_u^-,\ v' = 0).$$

The results of the study by Smardzewski[90] indicate that the effect of the matrix on the course of reactions involving recombination of O and S atoms varies substantially. In fact, the product of mass times radius of the sulphur atom is more than four times the corresponding value for an oxygen atom, and so naturally a lower mobility of S atoms compared to O atoms is to be expected. The diameter of the oxygen atom is ~1.2 Å, in other words, approximately equal to or slightly less than the average diameter of an interstice in solid krypton (1.28 Å) and considerably less than the corresponding distance in solid xenon (1.39 Å) at 4 K. The size of the sulphur atom (2.54 Å) and also its large mass impede the diffusion of the latter in all three matrices before the process of warming up the sample. Thus, the occurrence of chemiluminescence for S_2 and the absence of luminescence for O_2 in solid Xe is due to the different rate of diffusion of the S and O atoms in a Xe matrix at low temperatures.

Matrix effects of the second type, which are due to interaction of trace particles with the matrix material, are quite complex. Thus, in experiments concerned with studying CL in S_2 molecules, structured spectra were observed in Ar and Kr matrices, while for the Xe matrix an unexpected result was obtained—instead of a progression of sharp bands, the CL spectrum comprised a broad featureless band in the region 365–532 nm (Fig. 8, spectrum *C*).

Two possible causes of the broadening of the band were investigated.[90] One of these was fluorescence from vibrationally nonrelaxed states. In the Xe matrix, where the diameter of vacancies reaches 4.34 Å, two sulphur atoms could recombine on

warming the matrix to form an excited S_2 molecule, whose dimensions in the $B^3\Sigma_u^-$ state ($\sim$4.2 Å) would be less than the space occupied by a vacancy. If the radiative lifetime of such a particle is small, highly excited vibrational states ($v' \leqslant 9$) would not be attenuated and they would contribute to the emission spectrum. The absence of low-frequency bands and the short lifetime of S_2^* (45.0 $\pm$ 0.6 ns) are evidence for the possibility that $S_2(B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-)$ fluorescence takes place at the same time as nonradiative vibrational relaxation. In this particular case, superposition of $(n + 1)$ Franck–Condon emission maxima from each of the excited v_n' levels would give a total effect of broadening the S_2 fluorescence into the blue region of the spectrum. In the case of Ar and Kr matrices, which have smaller diameters for vacancies amounting to 3.76 and 3.99 Å respectively, vibrationally excited states will be attenuated as a result of collisions.

The alternative explanation for the broadening of the fluorescence lines, as proposed by Smardzewski,[90] assumes the formation of an S_2^*–Xe Van der Waals complex.

The CL emitters and electronic transitions that are responsible for the emission of bands in the regions 490–870 and 385–600 nm on warming matrices containing sulphur and oxygen atoms were established by Tevault and Smardzewski.[91] It was found that luminescence was due to the transitions $c\,^1\Sigma^- \rightarrow a\,^1\Delta$ and $A'\,^3\Delta \rightarrow X^3\Sigma^-$ from SO molecules formed in reactions involving recombination of sulphur and oxygen atoms. The interpretation of the spectra was based on the results of experiments with $^{18}O_2$ and ^2H isotopes, which showed that the emitting molecule did not contain hydrogen atoms and had one oxygen atom. An optical multichannel analyser was used as the primary photodetector,[91] so that it was possible to follow several CL systems simultaneously over a practicable time-scale.

Lee and Pimentel[89] extended the spectroscopic range for observing CL caused by reactions involving sulphur atoms to the near IR region. In the CL spectrum observed over the range 8–44 K on warming photolysed Ar, Kr, and SF_6 matrices containing CS_2 and COS molecules, three progressions were recorded. The progression in the region 340–552 nm was due to the familiar[83,84,86,90] $B^3\Sigma_u^-$ $(B''\,^3\Pi_u) \rightarrow X^3\Sigma_g^-$ radiative transition of the S_2 molecule, while the two new bands in the regions 558–689 and 668–875 nm were identified as $A'\,^3\Delta_u \rightarrow X^3\Sigma_g^-$ and $c\,^1\Sigma_u^- \rightarrow a\,^1\Delta_g$ transitions respectively.

Fluorescence spectra and recombination emission of S_2 molecules, recorded on photolysis with light at $\lambda = 257.3$ nm (frequency doubled pulsed Ar^+ laser) of CS_2/Ar mixtures frozen at 15 K were observed by Hamaguchi and Tasumi.[92] These spectra contained two series of vibrational bands attributed to transitions of the S_2 molecule—$B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$ and $B''\,^3\Pi_u^- \rightarrow X^3\Sigma_g^-$. The excitation mechanism includes the primary photodissociation of CS_2 molecules:

$$CS_2 + h\nu \rightarrow CS\,(a\,^3\Pi) + S\,(^3P)$$

followed by a process involving recombination luminescence:

$$S\,(^3P) + S\,(^3P) \rightarrow S_2^*\,(B''\,^3\Pi_u) \rightarrow S_2\,(X\,^3\Sigma_g^-) + h\nu.$$

CL systems containing nitrogen oxides[93] and carbon oxides[94,95] have been detected. When a photolysed argon matrix containing NO_2 and O_2 molecules was warmed up, two emitting systems from NO_2 and O_2 were recorded. Irradiation at 7.5 K of an Ar matrix containing N_2O with light of wavelength 147 nm was accompanied by emission of Vegard–Kaplan bands of the N_2 molecule $(A\,^3\Sigma_u^+ \rightarrow X\,^1\Sigma_g^+)$ and fluorescence of oxygen atoms $(^1S \rightarrow {}^1D)$ and nitrogen atoms $(^2D \rightarrow {}^4S)$.[94] It follows from this that the primary processes in the photolysis of N_2O are:

$$N_2\,(X\,^1\Sigma_g^+) + O\,(^1S); \quad N_2\,(A\,^3\Sigma_u^+) + O\,(^3P);$$
$$NO\,(X\,^2\Pi_{1/2}) + N\,(^2D).$$

On warming the irradiated samples, starting at 9 K, CL, resulting from the recombination of oxygen atoms was recorded

$$O\,(^3P) + O\,(^3P) \rightarrow O_2\,(A\,^3\Sigma_u^+ \rightarrow X\,^3\Sigma_g^-).$$

Under the experimental conditions of the study,[94] the distance between the oxygen atoms was estimated to be 50 Å; it would be necessary for the oxygen atoms to complete about 170 random jumps in order to cover the space separating them and undergo reaction.

In the presence of CO the CL spectrum changes. Instead of a radiative O_2 transition, a continuum is recorded in the region 380–500 nm, due to emission of CO_2 molecules excited in the reaction

$$CO\,(X\,^1\Sigma^+) + O\,(^3P) \rightarrow C^*O_2\,(^3B_2 \rightarrow X\,^1\Sigma_g^+).$$

The photolysis of CO_2 in Ne, Ar, and Kr matrices at 4.5 K with UV light ($\lambda = 147$ nm) and the reactions occurring when the samples were subsequently warmed up were studied.[95] The CL spectrum consisted of four bands of an $O_2(A\,^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-)$ Herzberg system, which were absent in the photoluminescence spectrum. It was shown that the recombination of $O(^3P)$ atoms on irradiation of CO_2 in solid Ar or Kr did not take place even when photolysis was carried out at 30 or 40 K. Increasing the temperature of the samples was a necessary condition. At the same time, in a Ne matrix the recombination of oxygen atoms, appearing as CL, took place under isothermal conditions even at 4.5 K. It was not possible to account for this behaviour on the basis of differing rigidities of the matrices since they are the same for Ne at 4.2 K and for Kr at 20 K. Fournier and co-workers[95] proposed a model according to which the oxygen atoms in the Ne matrix do not interact with the atoms of inert gas while in the case of Ar, Kr, and Xe matrices they are stabilised by formation of oxides of the respective inert gas.

The suggestion about the formation of Van der Waals complexes had been put forward previously,[96] when the luminescence stimulated by synchrotron irradiation was attributed to radiative transitions of ArO and KrO. The formation of XeO was detected in an argon matrix containing Xe, CO_2, or O_2 when it underwent UV photolysis with light at $\lambda = 121.5$ nm.[97] In the photoluminescence spectrum of a frozen mixture of Ar/Xe/CO_2, a system of bands was observed, corresponding to a XeO transition $(d^1\Sigma^+ \rightarrow a^1\Sigma^+)$ in the region 520–570 nm and Cameron bands due to CO.

The range of CL systems in cryogenic matrices is constantly expanding. There are interesting studies on the laboratory simulation of processes occurring in dust clouds in interstellar space. Studies of this type have theoretical importance for our understanding of chemical and prebiological evolution.[10] Thus, on warming argon matrices containing water vapour and/or ammonia which had been irradiated at 10 K with light from a hydrogen lamp ($\lambda = 150$–170 nm), CL from O_2, NO, N_2, and NH molecules was detected.[98] The occurrence of electronically excited diatomic molecules on warming the photolysed matrices for all cases except NH and the β-bands from NO was attributed to the diffusion and subsequent recombination of nitrogen and oxygen atoms in the

ground state. In similar experiments with $Ar/CH_4/H_2O$ mixtures, which also simulated the "dirty ice" on dust particles in dense nebulae, as well as an O_2 system in the CL spectrum, Cameron bands were observed, caused by $a^3\Pi \rightarrow X^1\Sigma^+$ transitions of CO, as were unidentified bands, which were later[99] identified as radiative $d^3\Pi_g \rightarrow a^3\Pi_u$ transitions from C_2 molecules.

There are many unresolved problems in the chemistry of atomic carbon, which is mainly due to the difficulty of obtaining C atoms and their high reactivity. The rate of a chemical process can be considerably reduced by cooling the reaction system. Krogh and co-workers[99] did precisely that, having used the method of matrix isolation to study the dynamics of reactions involving products from the UV photolysis of cyanazide. The highly active intermediates formed were identified from the results obtained using IR spectroscopy and low-temperature CL. The source of carbon atoms was NCN_3 which dissociated when photolysed. The first report about CL from warming an Ar matrix containing products from the photolysis of NCN_3 was produced by Milligan and co-workers,[100] who established that the primary product of the photodissociation of cyanazide is the NCN radical.

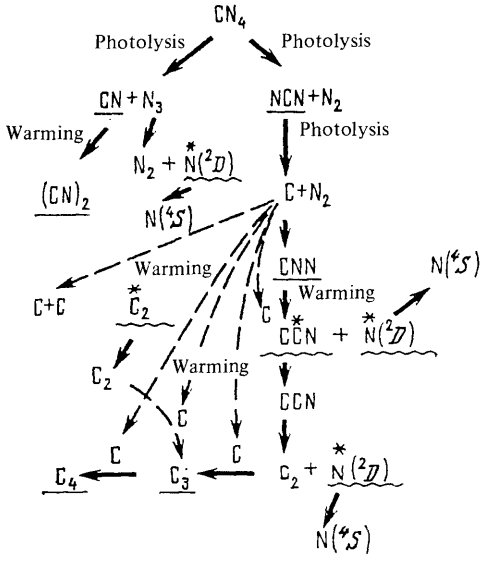


Figure 9. Mechanism for the reaction involving the photolysis products of NCN_3 in an argon matrix.[99] The data of IR measurements are emphasised with a straight line, the curved lines indicate the results obtained using an optical multichannel analyser.

In the CL spectrum[99] recorded using an optical multichannel analyser when a photolysed argon matrix containing NCN_3 was warmed up, 5 Swan bands from $C_2(d^3\Pi_g \rightarrow a^3\Pi_u)$ and bands due to emission by the CCN radical ($A^2\Delta_i \rightarrow X^2\Pi_i$) and the nitrogen atom ($^2D \rightarrow {}^4S$) were detected. It was shown that $N(^2D)$ atoms were mainly formed during thermal decomposition of N_3 radicals formed as a metastable cyclic isomer by photolysis. The reaction scheme occurring on photolysis of NCN_3 followed by warming of the matrix is depicted in Fig. 9. Krogh and co-workers[99] concluded that despite the complexity of the process, photolysis of cyanazide could serve as a powerful source of carbon atoms.

During the last ten years low-temperature solid-state chemiluminescence has been detected for several diatomic (O_2, S_2, CO, CS) and triatomic (NO_2, SO_2, CO_2, CCN) molecules which are formed as a result of the thermally induced diffusion and subsequent interaction of highly active particles stabilised in cryogenic matrices. There is a clear trend towards extending the CL method to study low-temperature reactions involving polyatomic molecules. The first results in this direction have already been obtained. Thus, in one study examined above[81] CL was detected in ethylene. Subsequently, when an Ar matrix which had undergone UV irradiation at 8 K and which contained diazomethane and oxygen was warmed up, CL was detected,[101] and in the spectrum two new progressions in the regions 310–360 and 390–490 nm were detected together with the known $O_2(A'^3\Delta_u \rightarrow X^3\Sigma_g^-)$ emission.

By analysing isotope shifts in experiments with $^{18}O_2$ it is possible to interpret the vibrational numbers v'' in two ways for both emission systems. The spectroscopic parameters obtained indicate that the observed progressions belong to the $a^3A'' \rightarrow X^1A'$ and $A'^1A' \rightarrow A^1A''$ transitions of the HCOOH molecule. This is the first observation (not only as luminescence but also when using any other methods of excitation) of such transitions in formic acid, whose molecules are excited in an argon matrix according to the reaction:

$$CH_2(^3B_1) + O_2(^3\Sigma_g^-) \rightarrow HCOOH.$$

In all of the previously examined reports on low-temperature CL in cryogenic matrices, reactions whose initial stage was recombination of radicals were studied. The recently discovered chemiluminescence of BaO, which is excited in the reactions

$$Ba + N_2O \rightarrow Ba^*O + N_2 \text{ and } Ba + O_3 \rightarrow Ba^*O + O_2,$$

presents a new class of CL reactions, with a mechanism that involves atom transfer.[88]

In the case of an argon matrix containing barium atoms and an oxidising agent (N_2O or O_3) a sharp increase in temperature of the sample is found when it is warmed up. Matrices containing Ba and N_2O (or O_3) at about 15 K warm up unexpectedly rapidly to 40 K, which results in evaporation of the sample. Chemiluminescence is usually recorded, starting at 8 K, then its intensity increases steadily as the temperature is raised. In the region 13–15 K a sharp increase in the intensity of luminescence occurs and the subsequent sudden jump in temperature of the sample is accompanied by an extremely bright emission. In the opinion of Pimentel and co-workers[102] the rapid rise in the temperature of the matrix is caused by decomposition of the unstable oxidising agents N_2O and O_3, catalysed by barium oxide or barium atoms.

Local warming and evaporation of even small sections of the matrix in such exothermic processes leads to a loss of vacuum in the space surrounding the sample and consequently results in warming and evaporation of the whole matrix. This phenomenon restricts the temperature region for recording CL spectra to 10–13 K. However, it transpired that emission spectra obtained during condensation of a sample were identical to the CL spectra from warming the matrix. Two molecular progressions of BaO with ν_{00} = 17 035 and 17 195 cm^{-1} and ω_e'' = 657 and 651 cm^{-1} were detected in the CL spectrum. They were related to radiative $\tilde{a}^3\Sigma^+ \rightarrow \tilde{X}^1\Sigma^+$ transitions of the BaO* molecule stabilised in different positions relative to the matrix environment. The possibility of an $\tilde{A}^1\Sigma^+ \rightarrow \tilde{X}^1\Sigma^+$ transition occurring was also not

ruled out. The proposed mechanism for excitation of BaO molecules involves population as a result of the chemical reactions of one or two singlet states ($\tilde{A}\,^1\Sigma^+$ and/or $\tilde{A}'\,^1\Pi$) followed by a rapid intercombination transition to the $\tilde{a}\,^3\Sigma^+$ state. The $(6s6p\,^1P) \rightarrow (6s^2\,^1S)$ radiative transition of the Ba atom was also observed. Excitation occurs by transfer of energy from the electronically excited BaO* molecule to a barium atom:

$$Ba^*O(\tilde{A}\,^1\Pi) + Ba(6s^2\,^1S) \rightarrow BaO(\tilde{X}\,^1\Sigma^+) + Ba^*(6s6p^1P).$$

There is a considerable difference between atom transfer reactions and radical recombination reactions. For the former the selection rules are less strict, which ensures the existence of several reaction pathways. In the case of a radical reaction the total excess of energy is concentrated in the excited product, while in an atom transfer reaction a redistribution of energy takes place between the products. The relaxation pathways of such excited products can be studied directly by CL.

V. Chemiluminescence in hydrocarbon matrices at 77 K and above

In addition to the investigation of CL reactions in cryogenic matrices, CL has also been studied in low-temperature systems. A series of studies has been published on CL occurring as a result of the interaction of a stream of active nitrogen on the surface of hydrocarbons frozen at 77 K.[103-103]

When the surface of frozen benzene, fluorobenzene, and chlorobenzene was treated with active nitrogen, Devolder[103,104] observed CL, with spectra that matched the phosphorescence spectra of benzonitrile, a mixture of the three isomers of fluorobenzonitrile, and an isomeric mixture of chlorobenzonitriles respectively.

Studies were also made on the CL spectra of polycrystalline benzene with added amounts of naphthalene, carbazole, acetonitrile, and benzaldehyde, for which the energy of the phosphorescent triplet state was lower than the corresponding energy for benzonitrile. The CL spectra observed were dependent on the concentration of the added components (guests). At high concentrations of guests ($\sim 10^{-1}$ M), only the phosphorescence spectrum of the guest was observed, whereas at low concentrations ($\sim 10^{-4}$ M), phosphorescence due to both the guest and benzonitrile was recorded. This indicates that the triplet states of the guests and benzonitrile are populated in concurrent processes and that the guest can play the role of quencher relative to the triplet state of benzonitrile. Since the intensity of CL proved to be proportional to the square of the concentration of $N(^4S)$ nitrogen atoms in a stream of active nitrogen and from the known fact that the $A\,^3\Sigma_u^+$ state of the N_2 molecule is a very effective energy donor the following two-stage mechanism for CL stimulation was proposed. Recombination of N atoms occurs on the cold surface of benzene with the formation of $N_2(A\,^3\Sigma_u^+)$ molecules in the triplet state followed by the transfer of energy to a phosphorescent state of the guest or to benzonitrile formed from benzene in a chemical reaction.

The initial studies[103,104] of CL reactions of active nitrogen with hydrocarbons were continued with a spectroscopic investigation.[105] The correlation of the CL spectra carried out in the earlier studies[103,104] was confirmed by the results of a parallel study of the reactions of active nitrogen with mixed polycrystals (an aromatic polycrystalline substrate activated with the corresponding benzonitrile derivatives). It was proposed that when benzonitrile is formed during reaction, a phenyl radical appears as an intermediate.

In another study[107] there is an investigation into the nature of the so-called delayed luminescence occurring as a result of the reaction between nitrogen and polycrystalline mixtures of aromatic compounds at 77 K. When hydrocarbons initially condensed on a cold surface are treated with a stream of active nitrogen, CL similar to that reported previously[103-105] is observed. If the supply of nitrogen is then cut off and a vacuum ($\sim 10^{-2}$ mm Hg) is created in the system, the luminescence diminishes exponentially for several minutes until a very low but still finite level is reached. This residual luminescence was called delayed luminescence by analogy with the very familiar delayed luminescence that occurs after ionisation of solids with UV or γ-radiation.

Three types of delayed luminescence were studied: isothermal luminescence at 77 K; isothermal luminescence stimulated by visible or IR light; and thermoluminescence.

The following mixtures (guest + matrix) were studied: naphthalene + benzene, naphthalene + benzene-d_6, acetonitrile + benzene-d_6, benzonitrile + fluorobenzene, *p*-cyanotoluene + toluene. It was found that the delayed luminescence spectrum matched the phosphorescence spectrum of the guest molecules.

When efficient electron acceptors—CCl_4 or benzyl chloride—were introduced into the sample, neither the intensity nor the composition of the CL spectrum obtained when active nitrogen was reacted with hydrocarbons changed, whereas the isothermal luminescence was very considerably reduced and the stimulated luminescence was not observed at all. The experimental results obtained were interpreted on the basis of ideas about the ionisation of mixed polycrystalline samples at 77 K during the primary reaction of active nitrogen with a cooled surface of hydrocarbons. Two possible mechanisms for chemiluminescence were proposed: either by energy transfer from high vibrational levels of $^3\Sigma_u^+$ nitrogen molecules to a high-energy triplet level (T_i) of molecules of the matrix (M) or guest (G):

$$N + N \rightarrow N_2(^3\Sigma_u^+, \text{high } \nu);$$
$$N_2(^3\Sigma_u^+, \text{high } \nu) + M \rightarrow N_2(^1\Sigma_g^+) + M(T_i)\ [\text{or } G(T_i)];$$
$$M(T_i)\ [\text{or } G(T_i)] \rightarrow M^+ (\text{or } G^+) + e^-,$$

or as a result of triplet-triplet annihilation of the guest with an $N_2(^3\Sigma_u^+)$ molecule which has relaxed to a state with low vibrational levels:

$$N_2(^3\Sigma_u^+, \text{low } \nu) + G(T_1) \rightarrow G^+ + e^- + N_2(^1\Sigma_g^+).$$

In a study by Devolder and co-workers,[107] together with the results already discussed in previous reports[103-106] there are additional data on the reactions of active nitrogen with hydrocarbons using chemiluminescence and EPR. It was established that the phase state of the matrix plays a substantial part in the mechanism for excitation of the triplet state in the guest. Thus, in polycrystalline matrices—both in aromatic (benzene, toluene, pyridine) and aliphatic (cyclohexane) matrices—the CL spectrum consists of phosphorescence from the guests (in the case of toluene, fluorescence from the benzyl radical was observed at the same time as phosphorescence from toluene). In vitreous matrices (ethanol, methylcyclohexane, isopentane) CL did not occur. In the EPR spectra mainly cyclohexadienyl-type radicals were detected.

The main difficulty in establishing the mechanism for the reaction of active nitrogen with organic compounds is principally connected with the existence of several reactive particles in active nitrogen generated by ultra-high frequency discharge in gaseous N_2. These particles are long-lived $N(^4S)$ atoms and $N_2(A\,^3\Sigma_u^+)$ molecules. There is one report[108] on a simple method for obtaining "pure" $N_2(A\,^3\Sigma_u^+)$ by passing active nitrogen through a trap filled with

liquid nitrogen. The removal of nitrogen atoms from $N_2(A^3\Sigma_u^+)$ is achieved in this method as a result of the recombination of the former on the cold surface of the trap. Dessaux[108] observed CL in the reaction of $N_2(A^3\Sigma_u^+)$ with benzene, chlorobenzene, and fluorobenzene at 77 K. The CL spectrum obtained in experiments with benzene matched the phosphorescence spectrum of benzene displaced to lower frequency, from which it was concluded that the CL emitter in this case is a charge transfer complex $N_2(A^3\Sigma_u^+)^{\pm} \ldots C_6H_6^{\mp}$.

This interpretation of the phenomenon was questioned by Mitsumori and Hiraoka.[109] They investigated the CL spectrum recorded at 77 K in reactions of $N_2(A^3\Sigma_u^+)$ with benzene and toluene, and also with given matrices containing biacetyl. If the luminescence emitter were the charged intermediate complex $N_2(A^3\Sigma_u^+)^{\pm} \ldots C_6H_6^{\mp}$ formed on the surface of solid benzene, as proposed by Dessaux, deactivation of its electronically excited state by energy transfer to guest molecules would be inefficient because of localisation of the complex in the benzene matrix. It was shown, however, that introduction of biacetyl into solid benzene substantially quenches the luminescence of pure benzene and leads to the appearance of characteristic phosphorescence from biacetyl.[109] This result indicates that there is migration of triplet excitation energy over a considerable distance in solid benzene. Mitsumori and Hiraoka[109] came to the conclusion that the CL accompanying the reaction of $N_2(A^3\Sigma_u^+)$ with solid benzene was caused by several products formed in the benzene matrix, possibly benzene isomers.

The absence of CL in reactions of $N_2(A^3\Sigma_u^+)$ with solid hexane or cyclohexane at 77 K and also the very weak (1000 times less than in benzene) phosphorescence of biacetyl (0.1 mol %) indicate either that there is no transfer of energy from $N_2(A^3\Sigma_u^+)$ to alkanes or that migration of triplet excitation energy does not occur in the solid matrices studied.

Chemiluminescence in a vitreous hydrocarbon matrix at temperatures above 77 K was first observed by Trozzolo and co-workers.[110] On warming a UV-irradiated glass containing diphenyldiazomethane and oxygen, emission of blue light was observed, with a spectrum that matched the phosphorescence spectrum of benzophenone. In samples that contained no oxygen, luminescence was absent. On the basis of the results obtained and also the fact that the matrices were warmed up several hours after irradiation, it was concluded that the observed luminescence belonged to CL accompanying the reaction of oxygen with the photolytically obtained diphenylmethylene. This CL reaction was observed on warming a 10^{-4} *M* solution of diphenyldiazomethane in 2-methyltetrahydrofuran which had been photolysed at 77 K.[111] Although the suggestion was made in these studies that the CL emitter was benzophenone in the triplet state, the CL spectrum was not published.

On freezing vitreous freon-113 (chosen because of the high solubility of oxygen in it) containing diphenylcarbene obtained photolytically at 77 K, Turro and co-workers[112] were the first to observe emission of light lasting 5–15 s which was visibie to the eye in a darkened room. Using an optical multichannel analyser it was established that CL occurs not only in the reaction between O_2 and diphenylcarbene but also in the oxidation of phenyltrifluoromethylcarbene or phenylchlorocarbene.

The CL spectrum corresponds qualitatively with the phosphorescence spectrum of the ketone which is a source of the carbene: benzophenone in the photolysis of diphenyldiazomethane, tetraphenyloxirane, 2,2,4,4-tetraphenyloxetanone, or diphenylketene; trifluoroacetophenone in the photolysis of phenyltrifluoromethyldiazirene; chlorobenzaldehyde in the photolysis of phenylchlorodiazirene. The CL spectra have an anomalous distribution of intensities of the components as compared with the photoluminescence of the corresponding ketones. The nature of this interesting phenomenon has not been determined, but in the opinion of Turro and co-workers[112] the rigid matrix of fluorocarbon glass, which inhibits the (0,0) transition because of the particular geometry of the chemically excited ketone, may be the cause.

It was established that CL may also occur at 77 K and not only when a vitreous matrix is warmed up.[112] This indicates that there is a low energy of activation for the process. It has been proposed that the reaction takes place via the formation (by a reaction between carbene and oxygen) of a $Ph_2C{=}O^+O^-$ Criegee intermediate, which reacts with oxygen to give the ketone (including that in an electronically excited state) and ozone. The latter has not been detected but is only postulated.

It was concluded[112] that CL from the reaction of carbenes with O_2 is a general phenomenon which does not depend on the multiplicity of the carbene or the source used to prepare it.

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Thus, in the studies on low-temperature CL important results have been obtained on the mobility and reactivity of a number of atoms and molecules at very low temperatures. The ability to diffuse proved very high for nitrogen, oxygen, sulphur, carbon, and barium atoms in matrices of inert gases; even at 5–10 K they diffuse over a distance of several tens of Ångstroms within comparatively short intervals of time (minutes-tens of minutes).

The increased interest shown in recent years towards CL in cryogenic matrices is due to the possibility of obtaining unique information. This primarily relates to the spectroscopic identification of new electronically excited states which often cannot be observed by other methods. It should be noted that CL spectra in matrices of inert gases have a fine structure that is similar to the spectra of gas-phase luminescence. This feature of low-temperature solid-state CL makes it possible to determine the luminescence emitter and reaction pathway and energetics with great accuracy. Chemiluminescence provides information on the population of excited states and makes it possible to assess the most precise details of the elementary event of a reaction and also the effect of matrices of varying types on relaxation processes. Thus, studies on low-temperature CL make a considerable contribution to the understanding of the role of excitation in exothermic reactions in solid matrices.

References

1. G J Minkoff *Frozen Free Radicals* (Translated into Russian) (Edited by V N Kondrat'ev, V L Tal'roze), Izd. Inostr. Lit., Moscow, 1962, p. 218
2. A M Bass, H P Broida (Editors) *The Formation and Stabilisation of Free Radicals* (Translated into Russian) (Edited by V N Kondrat'ev, V L Tal'roze), Izd. Inostr. Lit., Moscow, 1962, p. 622
3. V I Gol'danskii *Usp. Khim.*, 1975, **44** 2121 [English translation in *Russ. Chem. Rev.*, 1975(12)]
4. V I Goldanskii *Ann. Rev. Phys. Chem.*, 1976, **27** 85

5. G B Sergeev, V A Batyuk *Kriokhimiya* (Cryochemistry), Izd. Khimiya, Moscow, 1978, p. 296
6. S Cradock, A Hinchliffe *Matrix Isolation* (Translated into Russian) (Edited by O M Nefedov, R N Shchelokov), Izd. Mir, Moscow, 1978, p. 173
7. M Moskovits, G Ozin (Editors) *Cryochemistry* (Translated into Russian), Izd. Mir, Moscow, 1979, p. 594
8. R N Perutz *Chem. Rev.*, 1985, **85**(2) 77
9. R N Perutz *Chem. Rev.*, 1985, **85**(2) 97
10. V I Gol'danskii, L I Trakhtenberg, V N Flerov *Tunnel'nye Yavleniya v Khimicheskoi Fizike* (Tunnel Effects in Chemical Physics), Izd. Nauka, Moscow, 1986, p. 296
11. V P Kazakov, G S Parshin, S V Lotnik *Dokl. Akad. Nauk SSSR*, 1977, **236**(2) 379
12. V P Kazakov, G S Parshin, Yu K Gusev, et al. *Dokl. Akad. Nauk SSSR*, 1978, **239**(6) 1397
13. S V Lotnik, A M Kaplan, V P Kazakov *Fiz. Khim. Stekla*, 1982, **8**(5) 614
14. V P Kazakov, A D Karavaev, S V Lotnik, G S Parshin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, (8) 1924
15. S V Lotnik, A M Kaplan, V P Kazakov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, (3) 536
16. S V Lotnik, R G Bulgakov, V N Yakovlev, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, (3) 718
17. S V Lotnik, V P Kazakov, G A Tolstikov *Dokl. Akad. Nauk SSSR*, 1985, **284**(2) 382
18. A M Kaplan, A P Shvedchikov, S V Lotnik, V P Kazakov *Thermochim. Acta*, 1985, **93** 303
19. V P Kazakov, G A Tolstikov, S V Lotnik *Zh. Fiz. Khim.*, 1986, **60**(3) 788 [English translation in *Russ. J. Phys. Chem.*, 1986(3)]
20. S V Lotnik, V P Kazakov *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1987, **51**(3) 568
21. A Jablonski *Z. Phys.*, 1935, **94** 38
22. G N Lewis, D Lipkin *J. Am. Chem. Soc.*, 1941, **63** 3232
23. A N Terenin *Acta Phys. URSS*, 1943, **18** 210
24. G N Lewis, M Kasha *J. Am. Chem. Soc.*, 1944, **66** 2100
25. J Dewar *Proc. R. Soc. A*, 1901, **68** 360
26. H Moissan, J Dewar *C.R.*, 1903, **136**(11) 641
27. J Dewar, H O Jones *Proc. R. Soc. A*, 1910, **83** 526
28. J Dewar, H O Jones *Proc. R. Soc. A*, 1911, **85** 574
29. G D Liveing, J Dewar *Philos. Mag.*, 1894, **38** 235
30. L Vegard *Nature*, 1924, **113** 716
31. J C McLennan, J H McLeod *Proc. R. Soc. A*, 1927, **115** 209
32. H D Babcock *Astrophys. J.*, 1923, **57** 209
33. J C McLennan *Proc. R. Soc. A*, 1928, **120** 327
34. G C Schmidt *Ann. Phys.*, 1896, **58** 103
35. G J Lavin, J R Bates *Proc. Natl. Acad. Sci.*, 1930, **16** 804
36. R W Lunt, J E Mills *Trans. Faraday Soc.*, 1935, **31** 786
37. H P Broida, J R Pellam *Phys. Rev.*, 1954, **95** 845
38. E Whittle, D A Dows, G C Pimentel *J. Chem. Phys.*, 1954, **22** 1943
39. I Norman, G Porter *Proc. R. Soc. A*, 1955, **230** 399
40. *Matrix Isolation Spectroscopy* (Edited by A J Barnes, W J Orvill-Thomas, A Müller, R Gaufres), Reidel, London, 1981, p. 605
41. *Vibrational Spectroscopy on Trapped Species* (Edited by H E Hallam), Wiley, London, 1973, p. 430
42. B Meyer *Low Temperature Spectroscopy*, Elsevier, Amsterdam, 1971, p. 653
43. *Rare Gas Solids* (Edited by M L Klein, J A Venables), Vol. 1, Acad. Press, London, 1976, p. 607
44. D E Milligan, M E Jacox *Molecular Spectroscopy. Modern Research* (Edited by K N Rao, C W Matthews), Acad. Press, New York, 1972, p. 216
45. M E Jacox *Reviews of Chemical Intermediates* (Edited by O P Strausz), Vol. 2, Verlag Chem., Weinheim, 1978, p. 1
46. L Andrews *Annu. Rev. Phys. Chem.*, 1979, **30** 79
47. A J Downs, S C Peake *Mol. Spectrosc.* (Chem. Soc. London), 1973, **1** 523
48. C M Herzfeld, H P Broida *Phys. Rev.*, 1956, **101** 606
49. A M Bass, H P Broida *Phys. Rev.* 1956, **101** 1740
50. H P Broida, O S Lutes *J. Chem. Phys.*, 1956, **24** 484
51. H P Broida, M Peyron *J. Phys. Radium*, 1957, **18** 593
52. H P Broida, M Peyron *J. Phys. Radium*, 1958, **19** 480
53. H P Broida, M Peyron *J. Chem. Phys.*, 1958, **28** 725
54. M Peyron, H P Broida *J. Chem. Phys.*, 1959, **30** 139
55. M Peyron, E M Hörl, J Brown, H P Broida *J. Chem. Phys.*, 1959, **30** 1304
56. H P Broida, M Peyron *J. Chem. Phys.*, 1960, **32** 1068
57. L J Schoen, R E Rebbert *J. Mol. Spectrosc.*, 1958, **3** 417
58. E M Hörl *J. Mol. Spectrosc.*, 1958, **3** 425
59. L J Schoen, H P Broida *J. Chem. Phys.*, 1960, **32** 1184
60. D S Tinti, G W Robinson *J. Chem. Phys.*, 1968, **49** 3229
61. B J Fontana *J. Appl. Phys.*, 1958, **29** 1668
62. B J Fontana *J. Chem. Phys.*, 1959, **31** 148
63. R A Hemstreet, J R Hamilton *J. Chem. Phys.*, 1961, **34** 948
64. B Brocklehurst, G C Pimentel *J. Chem. Phys.*, 1962, **36** 2040
65. O Oehler, D A Smith, K Dressler *J. Chem. Phys.*, 1977, **66** 2097
66. T Cole, J T Harding, J R Pellam, D M Yost *J. Chem. Phys.*, 1957, **27** 593
67. T Cole, H M McConnell *J. Chem. Phys.*, 1958, **29** 451
68. D D Delannoy, B Tribbollet, F Valadier, A Erbeia *J. Chem. Phys.*, 1978, **68** 2252
69. F J Adrian *Phys. Rev.*, 1962, **127** 837
70. E Faure, B Tribbollett, F Vincent, et al. *J. Phys. Lett.*, 1979, **40**(21) 555
71. B Tribbollett, F Valadier *J. Phys. (France)*, 1981, **42** 673
72. E B Gordon, L P Mezhov-Deglin, O F Pugachev *Zh. Eksp. Teor. Fiz.*, 1974, **19**(2) 103
73. E B Gordon, L P Mezhov-Deglin, O F Pugachev, V V Khmelenko *Zh. Eksp. Teor. Fiz.*, 1977, **73**(3) 952
74. E B Gordon, V V Khmelenko, A A Pelmenev, O F Pugachev *Physics*, 1981, **108B** 1311
75. E B Gordon, A A Pelmenev, O F Pugachev, V V Khmelenko *Chem. Phys.*, 1981, **61**(1–2) 35
76. E B Gordon, A A Pel'menev, O F Pugachev, V V Khmelenko *Tezisy Dokladov Vsesoyuznogo Soveshchaniya po Molekulyarnoi Lyuminestsentsii i ee Primeneniyam* (Abstracts of Reports at the All-Union Conference on Molecular Luminescence and its Applications), Khar'kov, 1982, p. 69
77. E B Gordon, A A Pel'menev, O F Pugachev, V V Khmelenko *Tezisy Dokladov Vsesoyuznogo Soveshchaniya po Khimii Nizkikh Temperatur* (Abstracts of Reports at the All-Union Conference on Low-Temperature Chemistry), Izd. MGU, Moscow, 1985, p. 246.
78. D E Milligan, G C Pimentel *J. Chem. Phys.*, 1958, **29** 1405
79. T D Goldfarb, G C Pimentel *J. Chem. Phys.*, 1960, **33** 105
80. T D Goldfarb, G C Pimentel *J. Am. Chem. Soc.*, 1960, **82** 1865

81. Y-P Lee, G C Pimentel *J. Chem. Phys.*, 1981, **75** 4241
82. A J Barnes, H E Hallam, J D R Howells *J. Mol. Struct.*, 1974, **23** 463
83. J M Brom, E J Lepak *Chem. Phys. Lett.*, 1976, **41** 185
84. J Fournier, C Lalo, J Deson, C Vermeil *J. Chem. Phys.*, 1977, **66** 2656
85. C Lalo, L Hellner, J Deson, C Vermeil *J. Chim. Phys. Phys.-Chim. Biol.*, 1976, **73**(3) 237
86. S R Long, G C Pimentel *J. Chem. Phys.*, 1977, **66** 2219
87. J L Richards, P M Johnson *J. Chem. Phys.*, 1976, **65** 3948
88. Y-P Lee, G C Pimentel *J. Chem. Phys.*, 1978, **69** 3063
89. Y-P Lee, G C Pimentel *J. Chem. Phys.*, 1979, **70** 692
90. R R Smardzewski *J. Chem. Phys.*, 1978, **68** 2878
91. D E Tevault, R R Smardzewski *J. Chem., Phys.*, 1978, **69** 3182
92. H Hamaguchi, M Tasumi *Chem. Phys. Lett.*, 1982, **91** 406
93. J Fournier, J Deson, C Vermeil *J. Chem. Phys.*, 1977, **67** 5688
94. J Fournier, J Deson, C Vermeil, G C Pimentel *J. Chem. Phys.*, 1979, **70** 5726
95. J Fournier, H H Mohammed, J Deson, D Maillard *Chem. Phys.*, 1982, **70**(1–2) 39
96. R V Taylor, W F Scott, P R Findly, et al. *J. Chem. Phys.*, 1981, **74** 3718
97. W F Scott, W C Walker *J. Chem. Phys.*, 1984, **81** 4903
98. C E R M Van de Bult, L J Allamandola, F Baas, et al. *J. Mol. Struct.*, 1980, **61** 235
99. O D Krogh, C H Ward, J M Holenbeck *J. Phys. Chem.*, 1982, **86** 2892
100. D E Milligan, M E Jacox, A M Bass *J. Phys. Chem.*, 1965, **43** 3149
101. Y-P Lee, G C Pimentel *J. Phys. Chem.*, 1981, **74** 4851
102. S R Long, Y-P Lee, O D Krogh, G C Pimentel *J. Phys. Chem.*, 1982, **77** 226
103. P Devolder *J. Lumin.*, 1980, **21**(2) 177
104. P Devolder *J. Mol. Struct.*, 1980, **61** 111
105. P Devolder *Spectrochim. Acta, A*, 1980, **36**(8) 783
106. P Devolder, Ch Dupret *J. Chem. Soc. Faraday Trans., Pt. I*, 1981, **77** 1013
107. P Devolder, O Dessaux, P Goudmand *J. Photochem.*, 1981, **15**(4) 265
108. O Dessaux *J. Chim. Phys. Phys-Chim. Biol.*, 1970, **60** 1137
109. K Mitsumori, K Hiraoka *Bull. Chem. Soc. Jpn.*, 1983, **56**(2) 588
110. A M Trozzolo, R W Murray, E Wasserman *J. Am. Chem. Soc.*, 1962, **84** 4990
111. A M Trozzolo, W A Gibbons *J. Am. Chem. Soc.*, 1967, **89** 239
112. N J Turro, J A Butcher, G J Hefferon *Photochem. Photobiol.*, 1981, **34** 517

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Progress in the chemistry of thio derivatives of trivalent phosphorus acids

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ABSTRACT. The methods for synthesising thio derivatives of P(III) acids and their chemical behaviour in substitution and addition reactions are examined.

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I. Introduction

Thio derivatives of trivalent phosphorus acid (TTPA) have until recently remained one of the least studied classes of organophosphorus compounds. Although the first examples of this class of compounds were obtained more than 100 years ago, there were virtually no systematic studies of the chemical behaviour in their class for a long time. Only at the end of the 1950's and the beginning of the 1960's did TTPA start to attract more attention from research workers. This occurred because several TTPA were found to have practical application and continue to be of use as additives for lubricating oils,[1,2] stabilisers of polymeric materials,[3–6] heat-stable additives for organic products,[7,8] vulcanisation accelerators of rubbers,[9] etc. Moreover, with the discovery in the 1950's of the reaction between elemental phosphorus and disulphides,[10,11] the industrial synthesis of trialkyl phosphorotrithioites became a possibility. At the same time, the problem of finding ecologically preferable, 'chlorine-free' methods for synthesising various organophosphorus compounds based on phosphorotrithioites became important. Evidently the solution to these practical problems was not possible without a detailed study of the reactivity of TTPA.

By the mid-1970's investigations had been carried out on the synthesis and some chemical properties of esters and acid halides of P(III) thioacids had been studied, so that it was possible to find the first examples of the difference in chemical behaviour between TTPA and their oxygen analogues. These specific aspects of the chemistry of TTPA were partially covered in monographs[12,13] and a review[14] of that period and received the most attention in the review of Krasil'nikova,[15] which dealt with problems on the dual reaction of esters of P(III) thioacids with alkyl and acyl halides.

However, about 10 years has passed since it was published and during this time the chemistry of TTPA has undergone a new stage of development. Previously unknown classes and types of TTPA have been discovered, and an abundance of synthetic material has been collected on essentially new reactions involving TTPA, so it has been possible to establish the general mechanisms of these reactions. A wide range of physicochemical methods has been involved in structural and stereochemical studies of this class of compounds, which have recently been reviewed in a monograph.[16] Also at the present time it has become necessary to correlate and, as far as possible, classify the abundant and interesting material collected during the last few years in the world chemical literature.

In the review presented here, the findings of the last ten years, concerned with synthetic methods and properties of TTPA, have mainly been used.

II. Synthesis

By analysing the considerable flow of literature on the synthesis of TTPA, we have considered it practicable to limit ourselves to an examination of preparative methods based on those chemical conversions which lead to the formation of a P(III)–S bond in the molecule. The reactions which use trivalent phosphorus compounds that already contain a P(III)–S bond as starting materials will be examined when problems of the reactivity of the latter are discussed.

1. Synthesis based on elemental phosphorus

The direct synthesis of trialkyl phosphorotrithioites from elemental phosphorus and disulphides was developed back in the early 1950's:[10,11]

$$P_4+6RSSR\rightarrow 4(RS)_3P\,.$$

It was later shown[17,18] that phosphorotrithioites can be obtained in high yield by reaction of white phosphorus with thiols in the presence of sodium thiolate in CCl_4.

$$P_4+6RSH+6RSNa+6CCl_4\rightarrow 4(RS)_3P+6CHCl_3+6NaCl\,.$$

By using perfluorochloromethylsulphenyl chlorides in a reaction with elemental phosphorus it was possible to achieve the direct synthesis of perfluorochloromethyl phosphoromono- and phosphorodi-chloridothioites:[19]

$$P_4+CF_nCl_{3-n}SCl\rightarrow(CF_nCl_{3-n}S)_xPCl_{3-x}+(CF_nCl_{3-n}S)_2$$
$x=1, 2$ when $n=1, 2$; $x=1-3$ when $n=3$.

However, up to the present time phosphorylation of sulphur-containing compounds has continued to remain the most common method for obtaining TTPA.

2. Phosphorylation of sulphur-containing compounds

In recent years this method has been developed on the one hand by improving the reactions of this type that were already known and on the other hand by modifying them through expanding the range of both phosphorylating agents and reactants being phosphorylated.

The most widely used process is the phosphorylation of metal thiolates[20,21] and thiols[21–26] with P(III) acid halides.

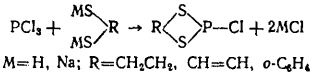
$$R_{3-n}PX_n + nR'SM \rightarrow R_{3-n}P(SR')_n + nMX$$

R = alkyl, aryl, RO, RS, Me_2N; X = Cl, Br, M = H, Na, Pb .

In the latter case a base is generally used, and in order to avoid an induction period in the reaction of P(III) halides with thiols it was proposed that the phosphorylation should be carried out in the presence of formamide[23] or other nitrogen-containing catalysts.[24]

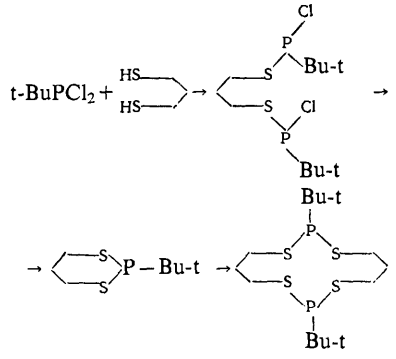
By using this reaction it was possible to obtain new types of bis-phosphorylated methylamines[27,28] and functionally substituted TTPA, including silicon-containing P(III) thioesters,[5,29,30] of γ- and ω-chloro-substituted phenylphosphonochloridothioites,[31] phosphorus(III)-containing dithiolothiadiazoles,[32] and *S*-phosphorylated derivatives of thioglycolic acid esters[33,34] and amides.[33]

By introducing *o*-dithiolobenzene, ethane- and *cis*-ethylene-dithiols, or their metal derivatives into a reaction with PCl_3, it was possible to synthesise a number of 1,3,2-dithiaphospholanes[35] and 1,3,2-dithiaphospholenes[36] containing an exocyclic P–Cl bond:



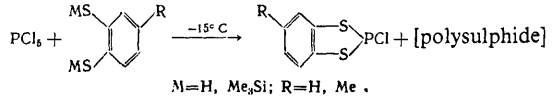
M = H, Na; R = CH_2CH_2, CH=CH, *o*-C_6H_4

At the same time, it is necessary to use a base in order to obtain 1,3,2-dithiaphospholanes with a P–C bond.[37] In the absence of the former the reaction of t-butyldichlorophosphine with 1,3-propanedithiol results in the formation of a twelve-membered ring containing phosphorus and sulphur atoms together with 2-t-butyl-1,3,2-dithiaphosphorinane.[38] The process takes place via an intermediate acyclic product:



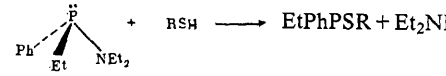
Recently[35,39] PCl_5 has also been used successfully as a phosphorylating agent for the synthesis of acyclic and cyclic TTPA:

$$PCl_5 + (C_6F_5S)_2Pb \rightarrow [(C_6F_5S)_5P] \rightarrow (C_6F_5S)_3P + (C_6F_5S)_2$$



M = H, Me_3Si; R = H, Me .

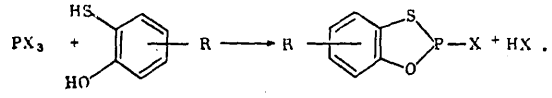
An attempt was made to utilise the phosphorylation of thiols with P(III) acid amides[40] in order to obtain optically active phosphinothioites.[40] However, when the optically active ethylphenylphosphinous diethylamide was treated with thiols, only the racemic thioester of this acid was formed:



When this reaction was extended to bis(trimethylsilyl) aminophosphine it was possible to synthesise the first example of a new class of TTPA—ethylthiophosphine:[41]

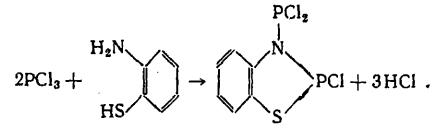
$$(Me_3Si)_2NPH_2 + EtSH \rightarrow EtSPH_2 + (Me_3Si)_2NH .$$

During the last ten years there has been a development of the phosphorylation of bifunctional reactants that have other proton-containing substituents in the molecule in addition to the thiol group; this is due to the growing interest of research workers in the chemistry of heterocycles. The reaction of phosphorus trihalides with certain 2-thiolophenols on heating gives the corresponding 2-halo-4,5-benzo-1,3,2-oxathiaphospholanes:[42,43]

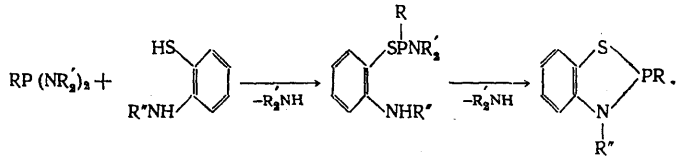


X = Cl, Br; R = H, alkyl, t-alkyl, OMe

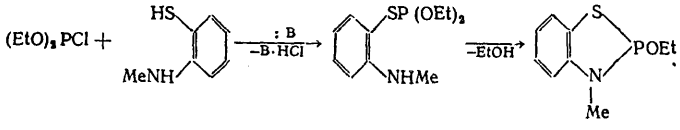
At the same time, attempts to synthesise 2-chloro-4,5-benzo-1,3,2-thiazaphospholane by phosphorylation of *o*-aminothiophenol with PCl_3 proved unsuccessful. In the presence of a base only a four-coordinate phosphorus derivative was isolated,[44] while in the absence of a base a halogenated *N*-phosphorylated 4,5-benzo-1,3,2-thiazaphospholane was formed:[45]



More successful was the use of alkyl- and aryl-phosphono-diamidites[46] and diethyl phosphorochloridite,[47] which made it possible to obtain a number of 1,3,2-thiazaphospholanes by reaction with *o*-aminothiophenol and its *N*-methyl derivative:



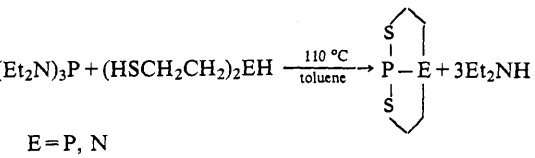
R = Me, Et, Ph; R′ = Me, Et; R″ = H, Me



It should be noted that in most cases the process takes place via the formation of linear products which are phosphorylated on the thiol group. In this case the factors (structure of reactants, temperature, presence of acidic catalysts, etc.) that affect the formation of products with a linear structure as well as cyclisation products have been determined.[46,47]

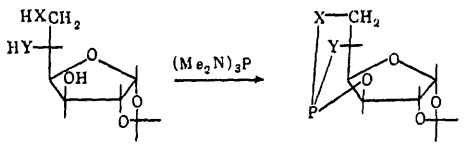
The temperature conditions of the reaction also govern the ratio of *S*- and *N*-phosphorylation products formed by reaction of indole-3-thiols with P(III) acid amides and chlorides,[48,49] the thiol group of indole-3-thiols being more active in reactions with chlorides.[49]

By using the reactions of polyfunctional compounds, in particular bis(β-thioloethyl)phosphine or bis(β-thioloethyl)amine, with triaminophosphine, a method has been developed for the preparation of bicyclic eight-membered heterocycles—2,8-dithia-1,5-diphospha- or 2,8-dithia-1-phospha-5-aza-bicyclo[3.3.0]octanes[50]



E = P, N

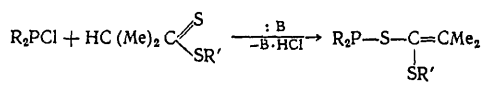
The reaction of thiolodeoxy-1,2-alkadiene-α-*D*-glucofuranose with PCl_3 [51] or hexamethyltriaminophosphine[52] was used for the synthesis of sugar bicyclophosphorothioites:



X = S, Y = O

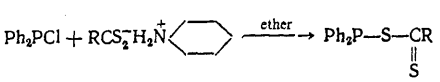
X = O, Y = S .

Phosphorylation has also been widely used to obtain TTPA that contain electron-withdrawing substituents on the sulphur atom. Thus, because the high mobility of the α-hydrogen atoms in dithiocarboxylic acid esters makes it possible to phosphorylate the latter on the sulphur atom of the thiocarbonyl group, a method based on the reaction of P(III) acid chlorides with dithioisobutyrate esters in the presence of a base could be developed for the synthesi of the previously unknown vinyl phosphorothioites:[53,54]



R = Cl, Et, EtO, Et_2N; R′ = Me, Et .

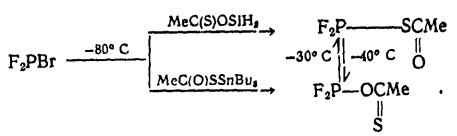
Piperidine salts of dithiocarboxylic acids proved to be convenient for the synthesis of the first examples of mixed anhydrides of diphenylphosphinothious acid and the respective dithiocarboxylic acid:[55]



R = Et, *p*-R′C_6H_4; R′ = Cl, Me, MeO.

These reactions were subsequently extended to dialkyl phosphorochloridites.[56]

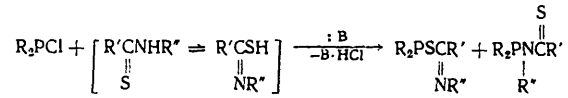
In a study of the phosphorylation of metal derivatives of thioacetic acid it was found[57] that *S*-acetyl phosphorodifluoridothioite is only formed when phosphorus difluorobromide reacts with the silyl ester of thioacetic acid at −80 °C:



At the same time, the reaction of phosphorus difluorobromide with tributylstannyl thioacetate gives the *O*-phosphorylation product—*O*-thioacetyl phosphorodifluoridite—which on heating to −30 °C is partially isomerised to *S*-acetyl phosphorodifluoridothioite.[57]

Phosphorylation of free thioacetic acid with PCl_5 only occurs on the sulphur atom and triacetyl phosphorotrithioite is formed.[58] The reaction of thioacetic acid with chlorophosphines in the presence of a base takes place in a similar manner.[58,59]

Taking into account the tendency of thiocarboxamides to form thiolimidoyl structures, studies were made of their phosphorylation with P(III) acid chlorides in the presence of a base.[60,61] While dialkyl phosphorochloridites react smoothly with thioacetamide to give only the *S*-phosphorylation product,[60] the reaction of diethyl phosphorochloridite with thiobenzoic acid *N*-methylamide gives *S*- and *N*-phosphorylation products in approximately equal proportions.[61] The phosphorylation of *N*,*N*′-diphenylthiourea occurs in a similar manner to that for the latter:[61]

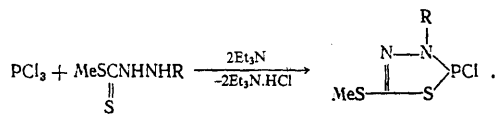


R = EtO, PrO, Et_2N; R′ = Me, Ph, NHPh; R″ = H, Me, Ph .

Reaction of phosphorodiamidochloridite with thiobenzoic acid *N*-methylamide again gives an imidoyl phosphorothioite as the sole product.[61]

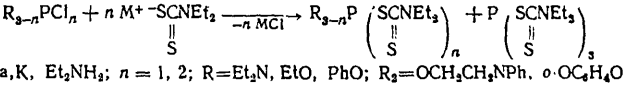
The products of *S*-phosphorylation-2-benzthiazolyl phosphorothioites—are also the only ones when Captax is reacted with trivalent phosphorus acid amides.[62]

Examples of new types of phosphorus-containing heterocycles—2-phenyl- and 2-acetyl-1-chloro-4-methylthio-1,5,2,3-phosphathiadiazoles—were synthesised by phosphorylation of the methyl esters of 3-substituted dithiocarbazic acids in the presence of triethylamine:[63]



R = Ph, MeCO

Treatment of alkali metal[64–66] or diethylammonium[66] *N*-diethyldithiocarbamates with P(III) acid chlorides gives phosphorylated derivatives of *N*-diethyldithiocarbamic acid:

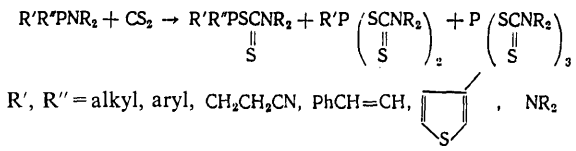


M = Na, K, Et_2NH_2; *n* = 1, 2; R = Et_2N, EtO, PhO; R_2 = OCH_2CH_2NPh, *o*-OC_6H_4O

It should be noted that compounds with a single dithiocarbamate group were only obtained in the case of 2-chloro-3-phenyl-1,3,2-oxaphospholane.[65,66]

Phosphorylated derivatives of dithiocarbamic acid can also be synthesised by reaction of P(III) acid amides with carbon disulphide, as was reported in detail back in 1963.[67] At the beginning of the 1980's this reaction once again drew the attention of research workers because a number of phosphorylated dithiocarbamates obtained from it proved to be effective vulcanisation accelerators for rubbers with polyfunctional action.[68–71] By studying new types of acyclic P(III) acid amides in reactions with carbon disulphide it was possible on the one hand to extend considerably the range of organophosphorus compounds containing one, two, or three dithiocarbamate groups[65,66,69,70] and on the other hand to determine the factors (nature of substituents, ratio of initial reactants, presence of acidic catalysts, etc.)[66,72] affecting the rate and direction of

reaction as well as the structure of the products formed and the composition of the reaction mixture:



R′, R″ = alkyl, aryl, CH_2CH_2CN, PhCH=CH, , NR_2

R = alkyl, $R_2=(CH_2)_n$, $(CH_2CH_2)_2O$; $n = 4,5$.

In the case of cyclic phosphoramidites containing both an exo- and endo-cyclic P–N bond, carbon disulphide is inserted selectively into the exocyclic phosphorus–nitrogen bond.[64,65]

In the last ten years a whole series of studies has been published on the synthesis of TTPA containing the heterosystem P–S–E (E = Si, Ge, P), information about which was previously restricted to individual studies.[73,74]

The possibility of forming *S*-silyl esters of P(III) thioacids was shown[75] when the reactions of different silylphosphines with elemental sulphur dissolved in hydrocarbons were studied:

$$RR'PSiMe_3 \xrightarrow{[S]} RR'PSSiMe_3$$

R=R′=Me, Me_3Si; R=Me_3Si, R′=Me, $P(SiMe_3)_2$.

In a study of the reaction of *bis*(difluorophosphine) sulphide with chlorogermane, *S*′-germyl phosphorodifluoridothioite was obtained for the first time:[76]

$$(F_2P)_2S + ClGeH_3 \xrightarrow{20^\circ C} F_2P{-}S{-}GeH_3 + F_2PCl\ .$$

However, it is not possible to synthesise the *S*-silyl or *S*-stannyl analogues of the latter by phosphorylation of disilathiane or bis(tributylstannyl) sulphide with difluorohalophosphines due to the high rate of the second stage of the reaction, resulting in the formation of bis(difluorophosphine) sulphide:[77]

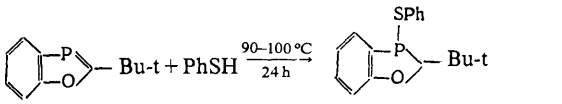
$$F_2PX + S(ER_3)_2 \xrightarrow[-XER_3]{} [F_2PSER_3] \xrightarrow[-XER_3]{F_2PX} F_2P{-}S{-}PF_2$$

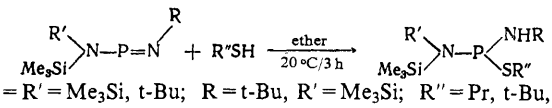
X = Cl, Br; E = Si, Sn; R = H, Bu.

Reaction of disilathiane with tetramethylphosphorodiamidochloridite also takes place in a similar manner.[78]

3. Synthesis of TTPA from bicoordinated phosphorus compounds

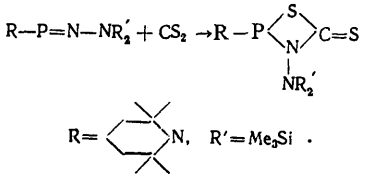
A new approach to the synthesis of previously unknown types of TTPA is opened up by the addition reactions of thiols to phosphaalkenes[79,80] and imidophosphenous acid amides:[81]





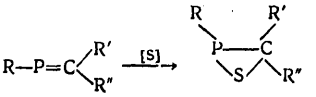
R = R′ = Me_3Si, t-Bu; R = t-Bu, R′ = Me_3Si; R″ = Pr, t-Bu, Ph.

It was possible to obtain a four-membered phosphorus-containing heterocycle by [2+2]-cycloaddition of carbon disulphide to 1-aminodiazaphosphene.[82]



R= , R′ = Me_3Si .

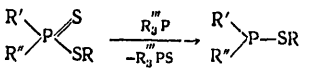
Certain phosphaalkenes reacted smoothly with sulphur by a [2+1]-cycloaddition to give the previously unknown 1,2-λ^3-thiaphosphiranes.[83,84]



R = $Me_3Si-C\equiv C$, R′ = R″ = Me_3Si; R = R″ = Bu-t, R′ = H.

4. Other methods for obtaining TTPA

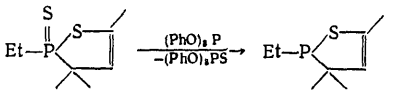
During the last ten years processes involving desulphurisation of four-coordinated phosphorus derivatives by treatment with tertiary phosphines and other P(III) derivatives have been used to an increasing extent for the synthesis of TTPA. Thus, the elimination of sulphur from phosphinodithioate esters,[85] including those that were optically active, with trialkylphosphines was successfully carried out, resulting in the isolation of the corresponding phosphinothioite esters:



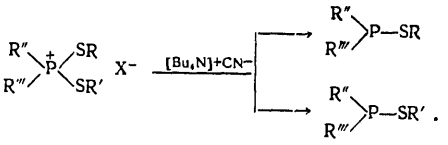
R = Me, R′ = R″ = Ph; R = *p*.$MeOC_6H_4$, R′ = Me, R″ = Ph; R‴ = Me, Bu .

However, optical activity cannot be retained in the reaction products due to the low pyramidal inversion barrier of phosphinothioites.[85]

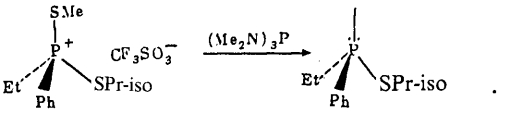
By using triphenyl phosphite to reduce 3,3,5-trimethyl-2-thione-2-ethyl-1,2-thiaphosphol-4-ene it was possible to synthesise the corresponding phospholene with a tricoordinated phosphorus atom:[86]



Phosphinothioite esters were obtained by P–S cyanolysis of quasiphosphonium salts containing an alkylthio group on the phosphorus atom:[87]

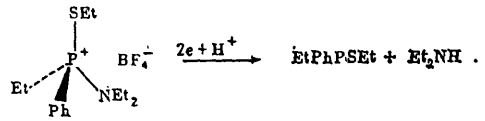


When this method was modified using hexamethyltriaminophosphine as the nucleophilic reagent it was possible to carry out the stereoselective synthesis of optically active phosphinothioites:[88]



For this reaction it was established in two studies[87,88] that, depending on the nature of the RS group, both its selective elimination giving only one phosphinothioite and the formation of a mixture of phosphinothioite esters were possible.

At the same time, electrochemical reduction of optically active ethylphenyl(diethylamino)ethythiophosphonium tetrafluoroborate in acetonitrile at 20 °C gives ethyl ethylphenylphosphinothioite that is optically inactive:[85]



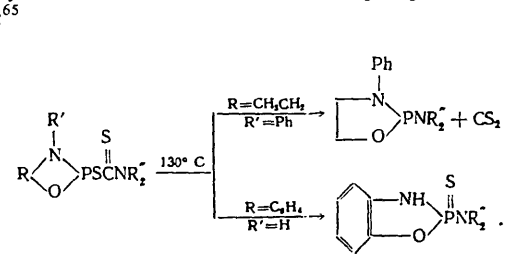
The formation of alkyl phosphorodichloridothioite occurred[89] on decomposition of certain diazadiphosphetidines, and a number of diphenylphosphinothioite esters were obtained by thermal decomposition of phosphorylated semimercaptals,[90] being accelerated in the presence of acidic catalysts.

III. Chemical properties

At the beginning of the 1970's the chemical conversions of TTPA were studied in the greatest detail in the case of reactions with alkyl and acyl halides, and in the course of these studies dual reactivity of P(III) acid thioesters was found.[15] In the last ten years the range of both electrophilic and nucleophilic reagents has been considerably extended, so it has been possible to determine the general mechanisms governing the chemical behaviour of TTPA in substitution and addition reactions and to establish the differences between the reactivity of the system $\geq\ddot{P}-\ddot{S}$ and that of other ambident systems with a heteroatom (N, O) on trivalent phosphorus.

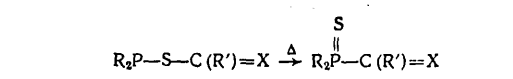
1. Thermal stability and isomerisation of TTPA

Studies on the thermal stability of P(III) acid thioesters using differential thermal analysis[20] indicate that the latter have quite a high stability when exposed to heat. In contrast to this, dialkyl phosphoranilidodithioites undergo thermal disproportionation even on distillation under vacuum or on heating in a sealed tube.[91] Products obtained from insertion of carbon disulphide into the exocyclic P–N bond of 2-dialkylamino-1,3,2-oxaphospholanes are also thermally unstable; on heating under vacuum they decompose to the original oxaphospholane with elimination of carbon disulphide.[65] At the same time, when 2-(*N*-dimethylthiocarbamoylthio)-4,5-benzo-1,3,2-oxaphospholane is exposed to heat, only 2-dimethylamino-2-thione-4,5-benzo-1,3,2-oxaphospholane is isolated:[65]



The change in the course of decomposition in this case is due to the presence of the condensed phenyl ring system.

The thermal thiol-thione isomerisation, due to *S,C*-migration of the phosphorus atom is of the greatest interest. Thus, phenyl diphenylphosphinothioite isomerises to triphenylphosphine sulphide only at 350 °C.[92] This type of rearrangement takes place much more readily in the case of ethyl phosphinothioites in the presence of iodosilane[93] and in a number of TTPA that contain electron-acceptor groups on the sulphur atom in the molecule, including those such as P(III) thioacid vinyl esters,[94] mixed thioanhydrides of P(III) acids and thioacetic[58,59] or dithiocarboxylic acids,[56] imidoyl phosphorothioites,[61] etc.



X = O, S, Nr'', CMe_3; R = alkyl, RO, R_2 R_2N, Ph;
R' = Me, iso-Pr, Ph, NHPh.

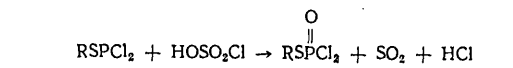
In the latter case it is necessary to isolate separately *S*-acetimidoyl phosphorothioites, which do not undergo thermal isomerisation but decompose to dialkyl phosphorothioites and acetonitrile, which is apparently due to the presence of a mobile proton on the imine nitrogen atom:[60]



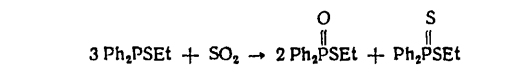
Thiol-thione isomerisation takes place on gentle heating of *S*-phosphorylated thioglycolic ester derivatives.[34]

2. Oxidation, addition of sulphur, and imination

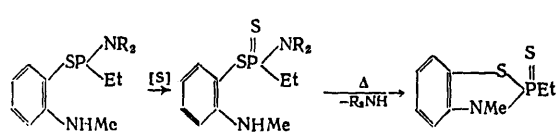
A characteristic feature of P(III) derivatives, including TTPA, is their tendency to undergo oxidation, addition of sulphur, and imination, which result in the formation of the corresponding P(V) derivatives. Thus, 2-benzthiazolyl phosphorothioites,[62] vinyl dialkyl phosphorothioite,[54] and *S*-thioacyl phosphorothioites[56] are readily oxidised with atmospheric oxygen to the corresponding phosphorothioates. Chlorosulphonic acid proved to be a convenient oxidising agent of TTPA such as alkyl phosphorodichloridothioite:[95]



The oxidation of diphenylphosphinothioite with sulphur dioxide[96] is accompanied by the formation of diphenylphosphinodithioate.

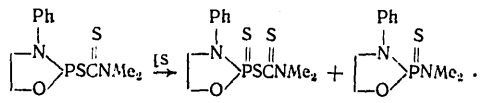


Reactions of elemental sulphur with TTPA have been studied quite extensively in recent years with the object of synthesising new types of P(V) acid derivatives, in particular, 3-thiophosphorylthioindoles,[49] 2-thiolobenzthiazolyl phosphorodithioates,[62] and optically active, *O,S*-dialkyl alkylphosphonodithioates.[97] The addition of sulphur to *S*-(*o*-methylaminophenyl) ethylphosphonamidothioite takes place in a similar manner.[46] However, in this case, the addition product cyclises during distillation to form 2-ethyl-2-thione-3-methyl-4,5-benzo-1,3,2-thiazaphospholane:

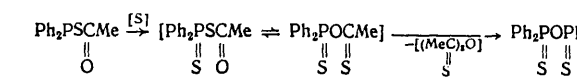


TTPA that contain electron-acceptor substituents react with sulphur in a more complex manner. Thus, as a result of the reaction of elemental sulphur with 2-dithiocarbamoyl-3-phenyl-1,3,2-oxazaphospholane, together with an addition product, 2-dimethylamino-2-thione-3-phenyl-1,3,2-oxaphospholane is also

formed by elimination of carbon disulphide from the dithiocarbamoyl derivative:[65]



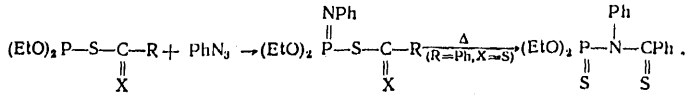
A dithionepyrophosphinate is obtained from *S*-acetyl diphenylphosphinothioite:[59]



It has been suggested[59] that at the first stage *S*-acetyl diphenylphosphinodithioate is formed, being converted to thioacetyl diphenylphosphinothioate as a result of phosphorotropic rearrangement; disproportionation of the latter gives the final product.

Trichlorophosphorus sulphide has been used in separate cases to introduce thione sulphur into TTPA molecules.[63]

Imination reactions of TTPA have in recent years only been studied in the case of the reaction of phenyl azide with vinyl phosphorothioites[54] and *S*-thioacyl phosphorothioites,[56] the corresponding phosphazo compounds being obtained:



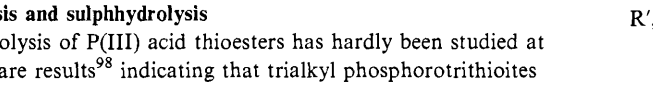
In the latter case[56] an imide-amide rearrangement can take place during distillation, which is due to migration of the thiocarbonyl group in the trio of atoms S–P–N.

3. Reactions of TTPA with proton-containing compounds

Substitution reactions on the trivalent phosphorus atom in a number of TTPA have been most effectively studied for reactions of the latter with compounds containing a mobile hydrogen atom. With these studies it was possible on the one hand to extend the methods for obtaining those TTPA already known in addition to new types and on the other hand to detect unusual pathways of particular reactions caused by the presence of alkylthio groups in the molecule.

(a) Hydrolysis and sulphhydrolysis

The hydrolysis of P(III) acid thioesters has hardly been studied at all. There are results[98] indicating that trialkyl phosphorotrithioites under normal conditions are stable to the action of water. At the same time, dialkyl phosphoramidodithioites are hydrolysed to ammonium salts of phosphorous acid and the corresponding phosphorotrithioites:[91,99]

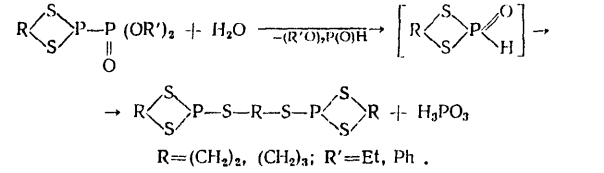


R=Et, Pr; R′=H, R″=Ph; R′=R″=Me .

It has been established that the rate of hydrolysis is dependent on the nature of the amide substituent on the trivalent phosphorus atom.[91,99]

In contrast to this, 2-benzthioazolyl phosphorodiamidothioites react with water and carbon disulphide with cleavage of the P–S bond and retention of the P–N bond[62] as a result of the pseudohalogen nature of the benzthiazolyl group.

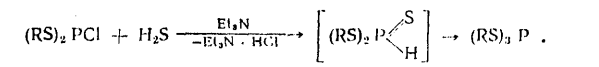
The nature of the substituents also governs the rate of hydrolysis of 2-dialkoxyphosphoryl-1,3,2-dithiaphospholanes and the analogous dithiaphosphorinanes;[100] this takes place with an initial cleavage of the P–P bond followed by disproportionation of the phosphorodithioic acid formed:



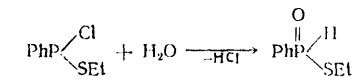
R=$(CH_2)_2$, $(CH_2)_3$; R′=Et, Ph .

It was shown[100] that hydrolysis can be accelerated by the action of acids and alkalis.

A similar disproportionation of intermediate dialkyl phosphorotrithioites has been suggested[101] in the sulphhydrolysis of cyclic and acyclic phosphorochloridodithioites.



Only when the reaction of *S*-ethyl phenylphosphonochloridothioite with water was studied by ^{31}P NMR spectroscopy was the formation of *S*-ethyl hydrogen phenylphosphonothioite detected for the first time:[102]

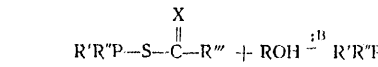


The latter decomposes during the reaction in a similar manner to other derivatives of this class of products.[103]

1-Chloro-1,5,2,3-phosphathiadiazole is readily hydrolysed by atmospheric moisture to give the initial dithiacarbazates.[63]

(b) Alcoholysis and thiolysis

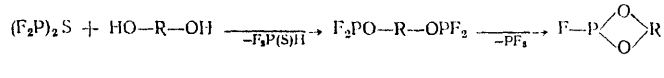
Alcoholysis reactions have been studied in a fairly detailed manner for a number of TTPA. The ready cleavage of the P–S bond by treatment with alcohols occurs in those TTPA containing benzthiazolyl,[62] dithioacyl,[55] thioacetimidoyl,[60] dithiocarbamate,[65] and other[86] groups with electron-withdrawing substituents on the sulphur atom.



R′, R″=RO, R_2N, Ph; R′R″=OCH_2CH_2NPh; R‴=alkyl, aryl, R_2N; X=S, NH.

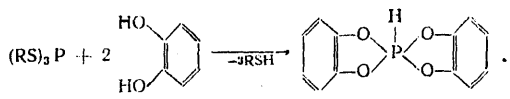
At the same time, alcoholysis of *tris*(*N*,*N*-dialkylaminothiocarbamoyl) phosphorotrithioite takes place under more severe conditions to give a complex mixture of products;[66] this is apparently due to the presence of intramolecular coordinate bonds in this type of TTPA.[72,104]

There has been extensive study of the reactions of bis(difluorophosphine) sulphide with alcohols, phenols, and diols, which give different types of phosphoromono- and phosphorodi-fluoridites:[105]



Cleavage of the P–S bond in trialkyl phosphorotrithioites is effected by sodium ethoxide[106] and also pyrocatechol.[107] In the latter case only *bis*(*o*-phenylenedioxy)phosphorane is formed,

whatever the ratio of the initial reactants.

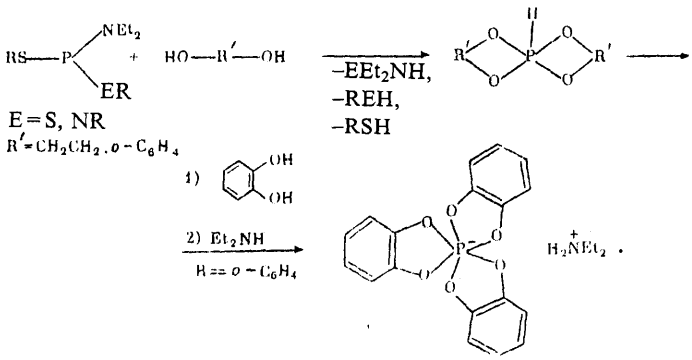


The reaction of dialkyl phosphoramidodithioites with alcohols takes place under severe conditions to give trialkyl phosphite and phosphorotrithioites:[99]

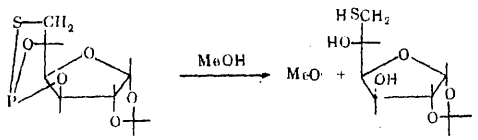
$$(RS)_3PNEt_2 + R'OH \xrightarrow{-Et_2NH} (RS)_2POR' \xrightarrow[-2RSH]{2R'OH} (R'O)_3P\,.$$
$$(RS)_2PNEt_2 + RSH \xrightarrow{-Et_2NH} (RS)_3P,\ R=R'=Et,\ Bu$$

Alcoholysis and phenolysis of bis(*N,N*-diethylcarbamoyl)diethylphosphoramidodithioite gives similar products.[66] It was established[99] that the amine generated at the first stage of the reaction catalyses the subsequent replacement of the alkylthio groups on the trivalent phosphorus atom by alkoxyl groups. When alcoholysis and phenolysis is carried out with removal of the amine, it is possible to stop the process at the stage where mixed *O,S,S*-phosphorodithioites are formed.[99] In this case the reaction is accelerated in the presence of acidic catalysts.

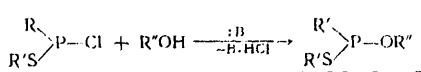
The reaction of phosphoromono- and phosphorodi-amidothioites with aliphatic and aromatic diols takes place with substitution of amide and alkylthio groups on the phosphorus atom, giving either a spirophosphorane with a P–H bond or compounds with a hexacoordinated phosphorus atom,[99] depending on the nature of the diol:



In a series of P(III) acid *O,S*-thioesters alcoholysis was only studied in the case of bicyclophosphorothioites of sugars:[51]



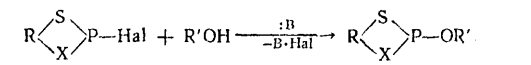
Anhydride derivatives of P(III) thioacids are widely used for the phosphorylation of alcohols and phenols. Thus, by alcoholysis of *S*-alkyl phosphonochloridothioites in the presence of the natural alkaloid, brucine, it was possible to obtain readily racemising optically active *O,S*-dialkyl phosphonothioites:[97]



R = Et, Bu; R′ = iso-Pr, iso-Bu, C_6H_{13}; R″ = Me, Et; B – brucine.

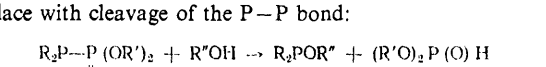
In the absence of a base, this type of reaction with phenylphosphonous acid derivatives does not stop at the stage where mixed *O,S*-thioesters are formed but gives partial *O*-alkyl phenylphosphonites by further phosphorylation of alcohol.[102]

A number of alkoxy derivatives of phosphorus-containing heterocycles have been obtained by phosphorylation of aliphatic alcohols and phenols with 2-halo-1,3-2-oxathiaphospholanes[42,43,108] and the analogous oxathiaphosphorinanes,[109] and also with 1-chloro-1,5,2,3-phosphathiadiazoles:[63]



R = $CH_2CH_2CH_2$, *o*-C_6H_4, RS–C=N, Hal = Cl, Br;
X = O, S, NR″; R′ = alkyl, Ph, *o*-FC_6H_4 etc.

Dialkyl acetyl phosphorodithioites,[110] 2-dialkyloxyphosphoryl-substituted 1,3,2-dithiaphospholanes or 1,3,2-dithiaphosphorinanes, and also their acyclic analogues can be used for the mild phosphorylation of aliphatic alcohols.[100] Alcoholysis of the latter takes place with cleavage of the P–P bond:

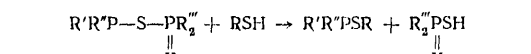


R_2 = S $(CH_2)_n$ S, $(BuS)_2$; *n* = 2, 3; R′ = Et, Ph; R″ = Me, Et .

For cyclic compounds the process is complicated by scission of the P–S bond in the ring, and the result depends on the structure of the compound, ratio of reactants, temperature, and reaction time.[100]

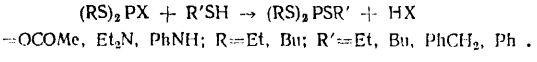
Phosphorylation of thiols with TTPA has not been studied very much. It was shown that the exocyclic P–Hal bond in 2-halo-1,3,2-dithia-[35,109] and 2-halo-1,3,2-oxathia-phospholanes[42,43] readily undergoes thiolysis in the presence of a base in a similar manner to the reactions with alcohols.

Information is also available on the thiolysis of P–S–P bonds:[105,111]



R′ = R″ = R‴ = F, X – unshared electron pair; R′ = Et, R″ = Ph, R‴ = EtO; X = S

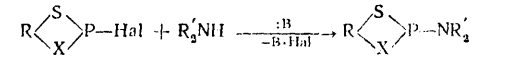
In recent years it has been established that acyclic acyl phosphorodithioites[110,112] and phosphoramidodithioites,[99,113] in contrast to their oxygen analogues which when treated with thiols are converted in most cases to thiophosphoryl compounds, can be successfully used to phosphorylate thiols:



X = OCOMe, Et_2N, PhNH; R = Et, Bu; R′ = Et, Bu, $PhCH_2$, Ph .

(c) Aminolysis

The synthesis of various P(III) thioacid amides is usually carried out by phosphorylation of primary and secondary amines with suitable P(III) halides. In recent years this method has been widely used to obtain 2-amino derivatives of 1,3,2-diheterophospholanes and 1-amido-1,5,2,3-phosphathiadiazoles.[63]



R = C_6H_4, RS–C=N; X = O, NR″; R′ = H, alkyl, Ph.

Together with dialkyl phosphorochloridodithioite,[113] acyl phosphorodithioites[112] and also mixed anhydrides of phosphorodithious and phosphorodithioic acids[114] have been proposed as

phosphorylating agents for the synthesis of acyclic phosphoramidodithioites:

$$(RS)_2PX + 2\,R'R''NH \rightarrow (RS)_2PNR'R'' + R'R''NH\cdot HX$$
X=Cl, OCOMe, (RO)$_2$P (S) S; R'=R''=Et; R'=H, R''=Ph .

The difficult-to-prepare aminodifluorophosphines can readily be obtained by reaction of primary and secondary amines with bis(difluorophosphine) sulphide.[105] The P–S bond also readily undergoes aminolysis in those TTPA containing benzthiazolyl,[62] dithioacyl,[55] thioacetimidoyl,[60] and dithiocarbamate[65] groups which have a pseudohalogen nature.

(d) Reactions with acids

Up to the end of the 1970's there was virtually no information in the literature about the reactions of TTPA with acids. At the beginning of the 1980's, as a result of a systematic study of the chemical behaviour of P(III) acid thioesters reacting with acids it was established[98] that in contrast to the oxygen analogues—phosphites—the pathway of the Arbuzov reaction is not followed but cleavage of the P–S bond occurs. Thus, the reactions of HCl with trialkyl phosphorotrithioite,[115] *S*-phosphorylated thioglycolates,[34] and *O,O*-dialkyl *S*-acetimidoyl phosphorothioites[60] occur with replacement of the alkylthio group on the trivalent phosphorus atom:

$$R_2'P-SR + HCl \rightleftharpoons R_2'P-Cl + RSH$$
R=Et, CH_2COOEt, C(Me)=NH; R'=EtS, RO, Cl .

Diphenylphosphinothioite esters react with HI in a similar manner,[116] but in this case the reaction is complicated by secondary processes.

Only in the case of *S*-germyl phosphorodifluoridothioite does cleavage of the S–Ge bond with hydrogen halides occur;[76] this is probably due to the greater electrophilicity of the germanium atom:

$$F_2PSGeH_3 + HX \rightarrow F_2P(S)H + XGeH_3$$
X=Cl, Br .

Studies of the reactions between P(III) acid thioesters and carboxylic acids showed[103,115] that they occur under severe conditions with cleavage of the P–S bond and formation of carboxylic acid thiol esters and *O*-containing phosphorus acids:

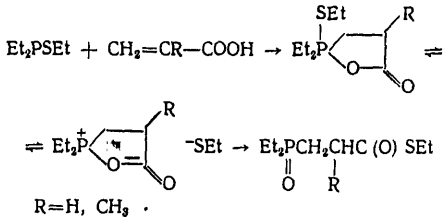
$$R'R''PSR + R'''COOH \xrightarrow{100-140^\circ C} R'R''POCOR''' + RSH$$
$$R'R''POCOR''' + R'''COOH \rightarrow R'R''P(O)H + (R'''CO)_2O$$
$$(R'''CO)_2O + RSH \rightarrow R'''C(O)SR + R'''COOH$$
R'=R''=SR; R=Et, Pr; R'''=Ph; R=R'=Et, R''=Ph, R'''=Me
R'=Et, Ph; R''=SR; R'''=Ph .

If there are alkylthio groups present on the phosphorus atom in the *O*-containing acids, they are unstable during the reaction and decompose with elimination of mercaptan to give P(III) acid anhydrides.[103]

Introduction of chlorine atoms into the acetic acid molecule has a substantial effect on the course of the reaction between the latter and P(III) acid thioesters.[117,118] In this case, instead of acidolysis, replacement of the alkylthio group on the trivalent phosphorus atoms by a chlorine atom takes place, giving the corresponding P(III) acid chlorides as well as oxidation products from the initial thioesters and products from dechlorination of carboxylic acids as the corresponding thiol esters:[118]

$$2\,\begin{matrix}R'\\R''\end{matrix}\!\!>\!PSR + CCl_nH_{3-n}COOH \rightarrow \begin{matrix}R'\\R''\end{matrix}\!\!>\!PCl + \begin{matrix}R'\\R''\end{matrix}\!\!>\!P(O)SR + CCl_{n-1}H_{4-n}C(O)SR$$
R'=R''=SR; R=Et, Pr; n=3; R'=Ph, R''=Et; n=3;
R'=Et, R''=Ph; R=Et, n=1–3 .

In studies on the reactions of phosphinothioites with α,β-unsaturated carboxylic acids, the previously unknown 1:1 addition products—diethyl-β-ethylthiocarbonylalkylphosphine oxides—were obtained:[119,120]

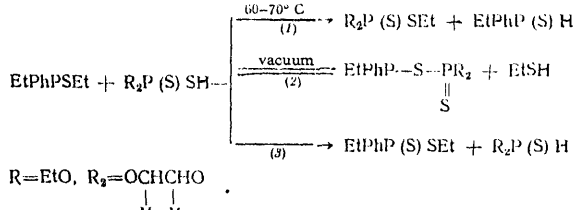


R=H, CH_3 .

When the reaction was monitored using IR and ^{31}P NMR spectroscopy[120] it was possible to detect an initially formed monocyclic phosphorane with a P–S bond, which probably then decomposes via an intermediate quasiphosphonium compound to the final phosphine oxide.

In contrast to phosphinothioites, phosphorotrithioites and phenylphosphonodithioites cause α,β-unsaturated carboxylic acids to polymerise.[120]

The reaction conditions have a significant effect on the course of the reaction between P(III) acid thioesters and organic acids. While ethylphenylphosphinothioite reacts with phosphorodithioic acids at 60–70 °C to form diethyl phosphorodithioate and ethylphenylphosphinothious acid [route (1)], at room temperature under vacuum a mixed anhydride of ethylphenylphosphinothious acid and the corresponding phosphorodithioic acid is obtained [route (2)]:[111]



R=EtO, R_2=OCHCHO (Me Me) .

It should be noted that whatever the method used to carry out the reaction it is accompanied by a subsidiary process involving desulphurisation of the phosphorodithioic acid by the initial phosphinothioite [route (3)].[111]

In a study of these reactions an unusual cleavage of the P–S bond in ethylphenylphosphinothioite on treatment with phosphorothious acid under vacuum was identified for the first time:[111]

$$EtPhPSEt + R_2P(S)H \xrightarrow[-EtSH]{vacuum} EtPhP(S)-PR_2 .$$

A similar route also occurs in the reaction of dialkyl phosphites with Schrader's anhydride[121] and related compounds[122] in the presence of a base:

$$R_2P(S)-P(OEt)_2 + (EtO)_2P(O)H \xrightarrow{Et_3N} R_2P(O)-P(OEt)_2 + (EtO)_2PSH\cdot NEt_3$$
R= (EtO)$_2$P (S) S; R_2=SCHMeCH$_2$S .

At the same time, dialkyl phosphoramidodithioites react with mineral[113] and organic[112,114] acids, retaining the P–S bond and replacing the amide group on the trivalent phosphorus atom to form

the corresponding P(III) thioacid anhydride derivatives:

$$(RS)_2PNR'R'' + 2HX \rightarrow (RS)_2PX + R'R''NH \cdot HX$$
R=Et, Pr; R'=R''=Et; R'=H, R''=Ph; X=Cl, OCOMe, $(RO)_2P(S)S$.

Acyclic[114,123,124] and cyclic[122] phosphorochloridodithioites in the presence of triethylamine react in a similar manner with organic acids:

$$(RS)_2PCl + HX \xrightarrow{Et_3N} (RS)_2PX + Et_3N \cdot HCl$$
R=Et, Pr; X=OCOMe, $(RO)_2P(S)S$, $(EtO)_2P(O)$.

In the absence of base, acidolysis of ethyl phosphorodichloridothioite takes place only on heating with removal of an alkylthio group and formation of ethyl thioacetate, acetyl chloride, and metaphosphorous anhydride:[125]

$$EtSPCl_2 + 2CH_3COOH \xrightarrow[-HCl]{70^\circ C} CH_3CSEt + CH_3CCl + 1/n\left[-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{P}}-O-\right]_n.$$

According to the findings of ^{31}P NMR spectroscopy, *S*-ethyl phenylphosphonochloridothioite reacts with acetic acid at 0 °C to form phenyldichlorophosphine and products derived from its stepwise acidolysis—phenylphosphonous acid and its monochloride.[102]

In their reactions with α,β-unsaturated acids dialkyl phosphorochloridodithioites behave similarly to other P(III) acid chlorides, being converted to the corresponding diethyl β-chloroformylalkylphosphonodithioates:[126]

$$(EtS)_2PCl + CH_2{=}CR{-}COOH \rightarrow (EtS)_2P\underset{\underset{O}{\|}}{C}H_2\underset{\underset{R}{|}}{C}HC(O)Cl$$
R=H, Me.

In studies on the reactions of acyl phosphorodithioites with mineral and organic acids[123,127] it was established that, in contrast to their oxygen analogues which react with acids according to the Arbuzov reaction mechanism, in these compounds replacement of the acetoxyl group on the trivalent phosphorus atom occurs with retention of its coordination:

$$(RS)_2POCOMe + HX \rightleftarrows (RS)_2PX + MeCOOH$$
R=Et, Pr; X=Cl, OCOPh, $(RO)_2P(S)S$

In this case the possiblity of transacylation of the acetoxyl group in acyl phosphite was demonstrated experimentally for the first time.[123]

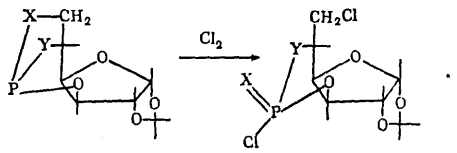
4. Reactions of TTPA with halogens and halogenated electrophilic reagents

The discovery by A E Arbuzov of the rearrangement of trivalent phosphorus acid esters to pentavalent phosphorus acid esters by treatment with alkyl halides formed the start of a systematic study of P(III) derivatives in reactions with halogenated electrophilic reagents. It is obvious that these studies could not also cover TTPA. By studying the chemical behaviour of the latter in reactions with alkyl and acyl halides in the 1960's and 1970's, with the most detailed treatment given in one review,[15] it was possible to establish some of these reaction mechanisms. It was found that in a number of cases the classical Arbuzov reaction route does not occur but the alkylthio group on the trivalent phosphorus atom is replaced and its coordination is retained. Moreover, there was a complete range of halogenated electrophilic reagents used up in this connection and there were virtually no studies on the reactions of TTPA with other compounds containing a halogen atom. At the beginning of the 1980's both in the USSR and abroad studies were published on the chemical behaviour of TTPA in reactions with halogens and halogenated reagents. Of particular interest are the results of those studies in which, as in the case of alkyl and acyl halides, there are deviations from the classical route of the Arbuzov reaction.

It was shown in 1980[76] that chlorine cleaves the S–Ge bond in *S*-germyl phosphorodifluoridothioite.

$$F_2P\underset{\underset{S}{\|}}{S}GeH_3 + Cl_2 \rightarrow F_2P\underset{\underset{S}{\|}}{C}l + ClGeH_3.$$

An interesting mechanism was found[128] in a study of the chlorination of 3,5,6-bicyclophosphorithioites of sugars:



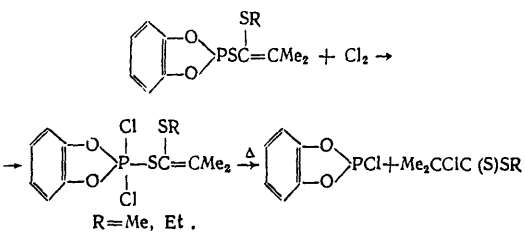
It was shown that the direction of chlorination is determined stereochemically, in all cases nucleophilic substitution being most favourable on the sterically accessible primary C(6) carbon atom.[128]

On mixing equimolar quantities of diphenylphosphinothioite ester and iodine, unstable quasiphosphonium compounds were subsequently obtained.[116]

$$Ph_2PSR + I_2 \xrightarrow[CH_2Cl_2]{-30^\circ C} Ph_2\overset{\overset{I}{|}}{\overset{+}{P}}SRI^- \xrightarrow[-EtI]{(R=Et)} Ph_2P\underset{\underset{S}{\|}}{I}.$$

When R = Et, the quasiphosphonium compound decomposes in accordance with the second stage of the Arbuzov reaction.

Quasiphosphonium compounds[35] as well as chlorophosphoranes[43] are also formed by chlorination of 2-chloro-4,5-benzo-1,3,2-diheterophospholanes that contain an endocyclic P–S bond. As a result of the reaction between chlorine and *S*-vinyl pyrocatechyl phosphorothioite, the first examples of vinylthiochlorophosphoranes were obtained, partially decomposing when distilled under vacuum.[129] In this case products from replacement of the vinylthio group on the trivalent phosphorus atom—pyrocatechyl phosphorochloridite and methyl α-chloroisobutyrodithioate—are isolated:



R=Me, Et.

Chlorination and bromination of phosphorotrithioites take place with the formation of substitution products—dialkyl phosphorohalodithioites:[130]

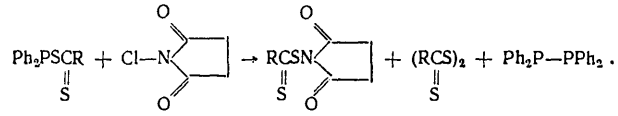
$$2(RS)_3P + Hal_2 \rightarrow (RS)_2PHal + (RS)_3PS + RHal$$
R=Me, Et, Pr; Hal=Cl, Br.

In this reaction phosphorotetrathioate and the respective alkyl halides are formed as by-products.[130]

The chlorination of trialkyl phosphorotrithioites with phosphorus pentachloride takes place in a similar manner:[130]

$$2(RS)_3P + PCl_5 \rightarrow (RS)_2PCl + (RS)_3PS + RCl + PCl_3$$
R=Et, Pr

The reaction of thioacyl phosphinothioites with *N*-chlorosuccinimide probably also leads to replacement of the *S*-thioacyl group by a chlorine atom, but products derived from further reactions are isolated in this case:[55]



The possibility that TTPA take part in exchange reactions with sulphenyl chlorides was first shown in 1980:[19]

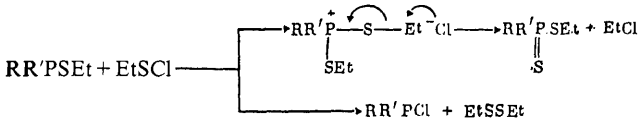
$$(CF_nCl_{3-n}S)_xPCl_{3-x} + xCF_nCl_{3-n}SCl \xrightarrow{-PCl_3} x(CF_nCl_{3-n}S)_2 .$$

The rate of this reaction decreases as the degree of chlorination of the reaction partners increases.

It was later found[131] that in the reaction between methyl phosphorodichloridothioite and trifluoromethylsulphenyl chloride the Arbuzov rearrangement does not occur and *S*-(trifluromethylthiomethyl) phosphorodichloridothioite is unexpectedly formed:

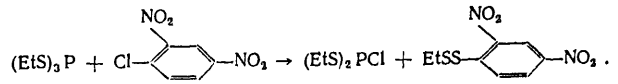
$$CH_3SPCl_2 + CF_3SCl \rightarrow CF_3SCH_2SPCl_2 + HCl .$$

Retention of the same coordination of the phosphorus atom together with an Arbuzov rearrangement also take place for the reactions of phosphorothioites and phosphinothioites with ethylsulphenyl chloride:[132]

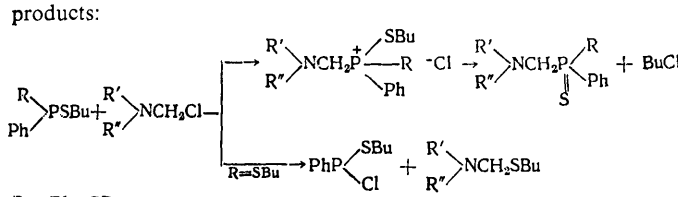


R=R'=SEt; R=Et, R'=Ph .

The course of the reaction is determined by the temperature, use of solvents, presence of acidic catalysts, and the nature of the sulphenyl chloride.[132] In particular, replacement of ethylsulphenyl chloride by 2,4-dinitrophenylsulphenyl chloride in a reaction with triethyl phosphorotrithioite has the result that the Arbuzov reaction pathway does not occur in this case but an alkylthio group on the trivalent phosphorus atom is replaced by a chlorine atom to give phosphorochloridodithioite and 2,4-dinitrophenyl ethyl disulphide:[132]



During the last ten years the study of the chemical behaviour of TTPA in reactions with alkyl and acyl halides has been continued. It transpired that chloromethyl derivatives of amines behave in a similar manner to alkyl halides in reactions with P(III) acid thioesters.[133] While phosphinothioites react with them on the phosphorus atom to form Arbuzov reaction products, phosphonodithioites give products from substitution of the alkylthio group on the trivalent phosphorus atom as well as Arbuzov rearrangement products:

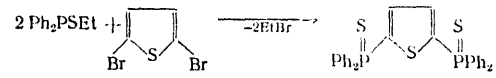


R = Ph, SBu.

The course of the reaction is determined by the polarity of the C—Cl bond; as the latter increases there is a greater tendency towards a substitution reaction.[133]

Phosphoramidothioites also react with alkyl halides by two routes—the Arbuzov reaction pathway and replacement of an alkylthio group.[134] The occurrence of a particular route is determined by the nature of the initial reactants and the presence of a catalyst ($ZnCl_2$).

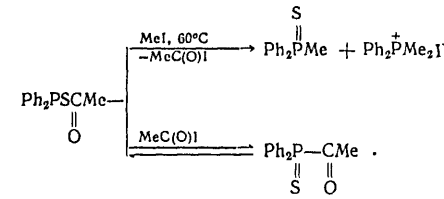
Mixed P(III) acid *O,S*-thioesters react with alkyl halides[36] and 2,5-dibromothiophene[135] in a complex and unclear manner.[135] Only in the case of reaction of the latter with *S*-ethyl diphenylphosphinothioite was it possible to isolate 2,5-bis(diphenylphosphinothioyl)-thiophene:[135]



New data has been obtained on the reactions of phosphorotrithioites with alkyl halides. Until recently it was generally thought[15] that these reactions occur with retention of the same coordination of the phosphorus atom. However, the first example of the formation of only classical Arbuzov reaction products was recently found:[136]

$$(EtS)_3P + MeI \rightarrow (EtS)_2P(=S)Me + EtI .$$

S-Acetyl diphenylphosphinothioite reacts with methyl iodide in an interesting manner.[59] Depending on the process conditions, either methyldiphenylphosphine sulphide and dimethyldiphenylphosphonium iodide or acetyldiphenylphosphine sulphide can be obtained, with the latter formed by a reversible isomerisation of the initial acetyl phosphinothioite under mild conditions by the action of trace quantities of acetyl iodide:[59]



In contrast to this, in the reaction between *S,S*-dialkyl acetyl phosphorodithioites and carboxylic acid halides the coordination of the phosphorus atom remains the same:[123,137]

$$(RS)_2POCOMe + R'C(O)X \rightarrow (RS)_2PX + R'C(O)OC(O)Me$$
R=Et, Pr; R'=Me, CCl_3, Ph; X=Cl, Br .

Dialkyl phosphoramidodithioites also react in a similar manner:[138]

$$(RS)_2PNEt_2 + R'C(O)X \rightarrow (RS)_2PX + R'C(O)NEt_2$$
R=Et, Pr; R'=Me, Ph; X=Cl, Br .

The Arbuzov reaction route, which is typical for the oxygen analogues, namely, acyl phosphites and phosphoramidites, does not occur in a single case, and the functional group is replaced by a halogen atom to give the corresponding phosphorohalodithioites.

In studies on the reactions of TTPA with acyl halides,[123,138,139] the effect of different factors, including the presence of acidic catalysts, on their rate was determined, and it was possible[140] to propose a general acid-catalysed mechanism for the reaction between TTPA and carboxylic acid halides.

$$(RS)_2P—A + HX \rightleftharpoons (RS)_2P—X + HA \xrightarrow{R'C(O)X} (RS)_2PX + R'C(O) + HX$$
A=SR, NR_2, OCOR'

Retention of the same coordination of the phosphorus atom also occurred in reactions of TTPA with polyhalomethanes. Thus, trialkyl phosphorotrithioites undergo a reaction with CCl_4 to form trichloromethylphosphonodithioite, phosphorochloridodithioite, and disulphide:[134,141]

$$2\,(RS)_3P + CCl_4 \rightarrow (RS)_2PCCl_3 + (RS)_2PCl + RSSR$$
$$R=Et,\ Pr,\ Bu\ .$$

At the same time, trichlorobromomethane under similar conditions gives phosphorotetrathioate and alkyl bromide together with trichloromethylphosphonodithioite:[134]

$$2\,(EtS)_3P + CCl_3Br \rightarrow (EtS)_2PCCl_3 + (EtS)_3PS + EtBr\ .$$

This contrast in the final reaction products is due to the different routes of side reactions.[134]

When phosphoramidothioites react with CCl_4 the alkylthio group on the trivalent phosphorus atom is also replaced and the coordination remains the same.[134,142] However, in this case the sole reaction products are the corresponding P(III) acid chlorides and trichloromethyl alkyl sulphide.

$$\begin{matrix} R' \\ Et_2N \end{matrix}\!\!>\!P\!-\!SR + CCl_4 \rightarrow \begin{matrix} R' \\ Et_2N \end{matrix}\!\!>\!P\!-\!Cl + CCl_3SR$$
$$R' = Et_2N,\ SR;\ R = Et,\ Pr\ .$$

In the case of phosphoramidothioites this reaction takes place only in the presence of Lewis acids.[142]

It was recently established that, in contrast to trialkyl phosphites, phosphorothioites[143] and phosphonothioites[144] reacted with dichloroacetylene not by the classical Arbuzov rearrangement route but they formed the previously unknown products derived by 'insertion' of dichloroacetylene into the P–S bond:

$$R'P(SR)_2 + Cl\!-\!C{\equiv}C\!-\!Cl \rightarrow \begin{matrix} R' \\ RS \end{matrix}\!\!>\!P\!-\!C(Cl){=}C(Cl)\!-\!SR$$
$$R' = Et,\ Ph,\ SR;\ R = Et,\ Pr\ .$$

5. Addition of TTPA to multiple bonds and to olefin oxides

Addition reactions of TTPA to C=O, C=C, C=N, N=N, and other multiple bonds have until recently constituted a little-studied area of organophosphorus chemistry; this was related to the low nucleophilicity of the trivalent phosphorus atom in TTPA. The preparation of new types of TTPA and the use of a number of synthetic procedures, in particular, the introduction of a third reagent into the reaction mixture, have made it possible in recent years to extend considerably the range of addition reactions involving TTPA.

(a) Addition to a carbon–oxygen multiple bond

Reactions with aldehydes and ketones. Phosphorotrithioites react with benzaldehyde at 130 °C in a complex manner to give α-alkylthiobenzylphosphonodithioates, trialkyl phosphorotrithioates, and 1-phenyl-1,1-bis(alkylthio)methanes:[145]

$$(EtS)_3P + PhCHO \xrightarrow{180^\circ C} (EtS)_2P(O)\!-\!CHPh(SEt) + (EtS)_3PO + (EtS)_2CHPh$$
$$(EtS)_3P + PhCHO \xrightarrow{200^\circ C} (EtS)_3PS + EtSCH_2Ph$$

It was shown[145] that the course of the reaction depends on the temperature. When this is increased to 200 °C, phosphorotetrathioate and ethyl benzyl sulphide are formed.

An effective synthetic procedure that made it possible to add on P(III) acid thioesters to aldehydes and ketones under mild conditions was the introduction of a third electrophilic reagent which served as an activator into the reaction mixture. Thus, phosphonothioites and phosphorothioites in the presence of an equimolar quantity of dry HCl underwent reaction with benzaldehyde[145] and acetone[146] even at room temperature to form α-alkylthio-substituted phosphonodithioates and phosphinothioates. The latter are formed as complexes with HCl, dissociating on distillation to give the final products;

$$RP(SEt)_2 + R'R''C{=}O + HCl \rightarrow \left[\begin{matrix} R & O\cdots HCl \\ & \| \\ & P\!-\!CR'R'' \\ EtS & SEt \end{matrix}\right] \xrightarrow[-HCl]{\Delta} \begin{matrix} R & O \\ & \| \\ & P\!-\!CR'R'' \\ EtS & SEt \end{matrix}$$
$$R = EtS,\ Et$$

Complex-formation apparently inhibits these reactions in the presence of catalytic quantities of HCl by deactivating the latter, so an equimolar quantity is required.[146]

At the same time, the reaction of *S*-acetyl diphenylphosphinothioite with benzaldehyde in the presence of HCl gives bis[α-(diphenylphosphoryl)benzyl] sulphide, which is isolated from the reaction mixture as a complex with two moles of HCl. In addition to that, α-acetoxybenzyldiphenylphosphine sulphide is formed in small quantity:[147]

$$Ph_2P(O)SCMe + PhCHO + HCl \rightarrow (Ph_2P(O)CHPh)_2S\cdot 2HCl + Ph_2P(S)\!-\!CHPh(OCOMe)$$
$$(Ph_2P(O)CHPh)_2S\cdot 2HCl \xrightarrow[-2Et_4N\cdot HCl]{2Et_4N} (Ph_2P(O)CHPh)_2S$$

This reaction route involves the initial replacement of the thioacetyl group by the action of HCl.[147]

When equimolar quantities of trimethylhalosilanes are used as activating agents in the reactions of phosphinothioites with benzaldehyde, two types of reaction take place depending on the nature of the halosilane. Benzaldehyde reacts with *S*-ethyl diphenylphosphinothioite in the presence of trimethylchlorosilane under mild conditions (–60 to –50 °C), resulting in the isolation of α-siloxybenzylphosphine sulphide as an addition product:[149]

$$Ph_2PSEt + PhCHO + Me_3SiCl \xrightarrow{200^\circ C} Ph_2P(S)\!-\!CHPh(SEt) + Ph_2PCl + (Me_3Si)_2O\ .$$

In contrast to trimethylchlorosilane, trimethyliodosilane can be used to carry out the reaction of phosphinothioites with benzaldehyde under mild conditions (–60 to –50 °C), resulting in the isolation of α-siloxybenzylphosphine sulphide as an addition product:[149]

$$\begin{matrix} Ph \\ R \end{matrix}\!\!>\!P\!-\!SEt + PhCHO + Me_3SiI \rightarrow \left[\begin{matrix} Ph & OSiMe_3 \\ & | \\ R & P\!-\!CHPh\ I^- \\ & | \\ & SEt \end{matrix}\right] \xrightarrow{-EtI} \begin{matrix} Ph & S \\ & \| \\ R & P\!-\!CHPh \\ & | \\ & OSiMe_3 \end{matrix}$$
$$R = Et,\ Ph$$

The formation of an intermediate quasiphosphonium compound has been detected by studying this reaction using ^{31}P NMR spectroscopy at different temperatures.[149] It was suggested[149] that coordination of the silicon atom with the oxygen of the carbonyl group must precede nucleophilic attack by the phosphorus atom.

By using PCl_3 as a third electrophilic reagent in the reaction of phosphorotrithioites with ketones it was possible to obtain a number of α-alkylthioalkylphosphonodichloridates:[150]

$$(RS)_3P + 3R'R''C{=}O + 2PCl_3 \rightarrow 3Cl_2P(O)CR'(SR)R''$$

R = Et, Pr; R′ = R″=Me; R′=Et, R″=Me .

The formation of the latter is evidently due to an initial exchange reaction between phosphorotrithioite and PCl_3 which is already known in the literature[12] followed by addition of the resulting alkyl phosphorodichloridothioite to the carbonyl compound. It has been established[151] that the reaction of *S*-alkyl phosphorodichloridothioites with aldehydes and ketones takes place with retention of the P–Cl bond and cleavage of the P–S bond, in contrast to other P(III) acid chlorides:

$$Cl_2PSEt + RR'C{=}O \rightarrow Cl_2P(O)CRR'(SEt)$$

R=R′=Me; R=H, R′=Ph .

Hydrogen chloride catalyses this reaction.

It should be noted that before the study of Al'fonsov and co-workers[151] there was only information in the literature about the reactions of P(III) thioacid chlorides with carbonyl compounds in the presence of proton-containing reactants. Thus, reaction of P(III) thioacid chlorides with aldehydes and ketones in the presence of an equimolar quantity of water gives *S*-alkyl esters of α-hydroxy-substituted phosphinothioates and phosphonodithioates:[102]

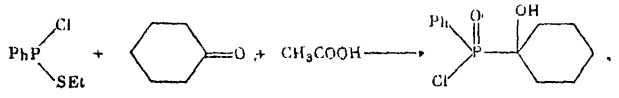
$$(RS)(R')P(O)Cl + H_2O \xrightarrow{-HCl} (RS)(R')P(O)H \xrightarrow{R'''R''C{=}O} (RS)(R')P(O)CR''R'''(OH)$$

R′ = Et, Ph, RS; R = Me, Et, Pr; R″ = H, Me

R‴ = Me, Pr, $(CH_2)_4$, $(CH_2)_5$, CCl_3, Ph, *o*-$O_2NC_6H_4$.

A detailed study of this reaction using ^{31}P NMR spectroscopy formed the basis of the proposal by Kardanov and co-workers[102] that the reaction takes place via hydrolysis of the acid chlorides followed by addition of the resulting P(III) thioacids to the carbonyl compound.

Replacement of water by acetic acid results in the formation of a product that does not contain sulphur:[102]



Recently[152] a simple and convenient method for the preparation of alkythio-substituted phosphinothioates and phosphonodithioates was developed on the basis of the reaction of P(III) thioacid chlorides with carbonyl compounds in the presence of thiols:

$$(R)(EtS)P(O)Cl + R'R''C{=}O + EtSH \rightarrow (R)(EtS)P(O)CR'(SEt)R'' + HCl$$

R = Et, EtS; R′=R″=Me; R′=H, R″—Ph .

However, compounds with an activated carbonyl group, in particular, acetyl phosphonates, do not undergo this reaction.[153] At the same time, the latter react with diethyl phosphorochloridodithioite in the presence of triethylamine to form α-(diethoxyphosphoryl)vinyl phosphorodithioites:[154]

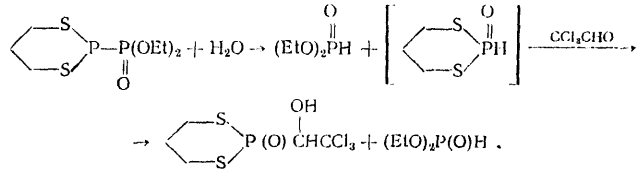
$$(EtS)_2PCl + (EtO)_2P(O)CH_3 \xrightarrow[-Et_3N\cdot HCl]{Et_3N} (EtS)_2POC(OEt)_2{=}CH_2 .$$

Other anhydride derivatives of P(III) thioacids have only been studied in a reaction with chloral. Thus, cyclic[155] and acyclic[110] acyl phosphorodithioites react with it to form new α-acetoxy-β,β,β-trichloroethylphosphonodithioates:

$$R_2POCOCX_3 + CCl_3CHO \rightarrow R_2P(O)CH(OCOCX_3)CCl_3$$

R=EtS, X=H; R_2 = SCH_2CH_2S, X=F .

2-Diethoxyphosphoryl-1,3,2-dithiaphosphorinane does not react with chloral even on boiling, but when water is added to the reaction mixture the P–P bond is cleaved even at room temperature to form 2-oxo-2-(β,β,β-trichloro-α-hydroxyethyl)-1,3,2-dithiaphosphorinane:[156]



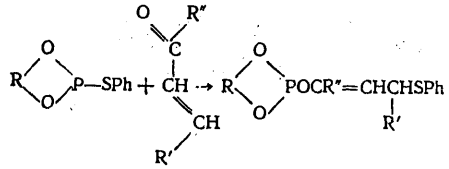
In a study of the addition of P(III) thioacid amides to carbonyl compounds it was established that the nature of the latter has no effect on the course of their reaction with phosphoranilidodithioites, in which α-anilidoaralkylphosphonodithioiates are formed:[157]

$$(EtS)_2PNHPh + n\text{-}XC_6H_4CHO \rightarrow (EtS)_2P(O)CH(NHPh)C_6H_4X\text{-}n$$

X = H, NO_2 .

There was not a single case where products with a P=N bond, namely, phosphonimidodithioates, which are characteristic for reactions of dialkyl phosphoranilidites with carbonyl compounds containing electron-withdrawing substituents, were formed.[157]

Reactions with conjugated carbonyl compounds. The reactions of TTPA with conjugated carbonyl systems, usually giving pentavalent phosphorus compounds, had by the end of the 1970's been studied in quite a detailed manner.[158] At the beginning of the 1980's, Ragulin and co-workers[159] showed that retention of the same coordination of the trivalent phosphorus atom in these reactions was possible by insertion of α,β-unsaturated aldehydes and ketones into the exocyclic P–S bond of phenyl ethylene- and 1,3-propylene-phosphorothioites:[159]

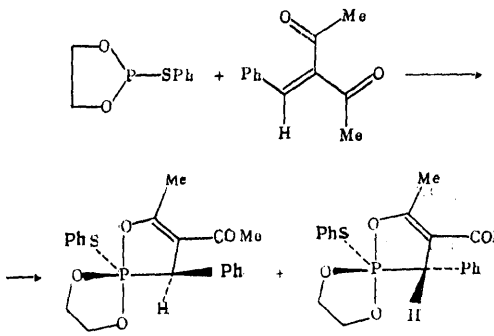


R = CH_3CH_2, $CH_2CH_2CH_2$; R′ = H, Me, Ph; R″ = H, Me .

The rate of condensation decreases when the β-carbon atom of the conjugated system is shielded.

At the same time, insertion of 3-benzylideneacetylacetone in a reaction with phenyl ethylenephosphorothioite results in the formation of a mixture of diastereomeric spirophosphoranes

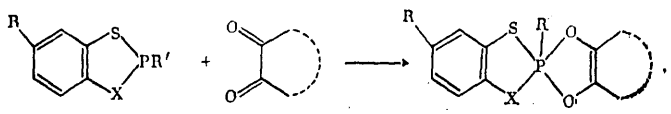
containing a P–S bond:[160]



anti – *syn* –

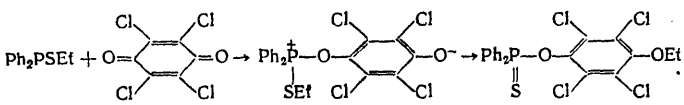
In this case the stereoisomer with the *syn*-configuration is the kinetically favourable product and the *anti*-isomer is the thermodynamically favourable reaction product. The fact that a thermodynamically nonequilibrium mixture of diastereomers is formed was taken by Ragulin and co-workers[160] as positive evidence for an almost synchronous 1,4-cycloaddition mechanism.

Spirophosphoranes containing a P–S bond are also obtained by reaction of α-dicarbonyl compounds with 1,3,2-dithia-[37] and 1,3,2-thiaza-phospholanes:[46]



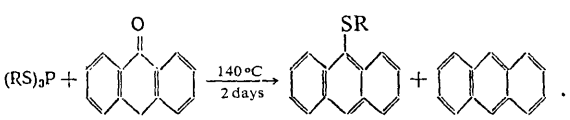
R=H, Me ; R′=Et, Ph ; X=S, NH

Ethyl diphenylphosphinothioite reacts with chloranil in benzene to form *p*-ethoxytetrachlorophenyl diphenylphosphinothioate:[161]



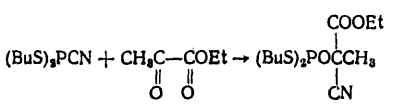
When benzene is replaced by the more polar DMSO and DMF it is possible to stop the process at the stage where a bipolar ion is formed, probably by stabilisation of the quasiphosphonium centre with solvent molecules. A study of this reaction by means of chemically induced polarisation of ^{31}P nuclei showed that there was also a radical route for formation of the final product.[161]

The reaction of trialkyl phosphorotrithioite with anthrone gives 9-alkythioanthracene and anthracene:[162]



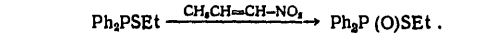
R = Et, Pr, iso-Pr, Bu, iso-Bu

P(III) thioacid cyanides react with ethyl pyruvate, retaining the same coordination of the phosphorus atom and forming α-cyanoalkyl esters of P(III) thioacids.[163]



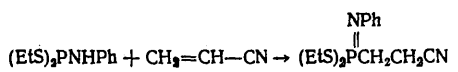
(b) Addition to other multiple bonds

Up to the present time there have been only isolated reports in the literature about the reactions of TTPA with compounds containing C=C, C=N, N=N, and other multiple bonds, which generally take place with retention of the P–S bond. When *S*-ethyl diphenylphosphinothioite reacts with 1-nitro-1-propene, instead of attack by the phosphorus atom on the β-carbon atom of the nitroolefin as occurs in the case of the oxygen analogues, only oxidation of the initial phosphinothioite occurs:[164]

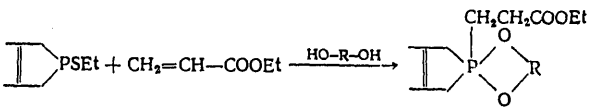


Using ^{31}P NMR spectroscopy, chemically induced polarisation of ^{31}P nuclei was detected on the initial and final products, so it could be assumed[164] that the reaction took place according to a one-electron transfer mechanism.

It was established[165] that cyclic phosphonodithioites do not react with acrylonitrile, while dialkyl phosphoranilidodithioites slowly add on to the latter with the formation of β-cyanoethylphosphonimidodithioates:[113]

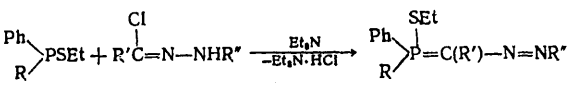


In reactions of phosphinothioites with ethyl acrylate in the presence of aliphatic and aromatic glycols the formation of cyclic phosphoranes was demonstrated:[165]



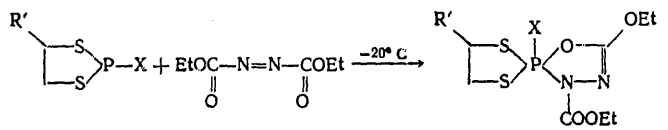
In this case there is probably an initial substitution of the alkythio group on the phosphorus atom.

The first examples of azomethylenephosphoranes containing a P–S bond were obtained in a study of the reaction of P(III) acid thioesters with nitrilimines in the presence of a base:[166,167]



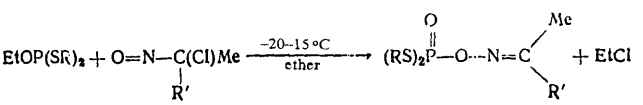
R=Ph, SEt; R′=MeC(O), PhC(O), EtOC(O)
R″ = Ph, *p*-CrC_6H_4, *p*-$O_2NC_6H_4$

A new approach to the synthesis of certain spirophosphoranes containing a dithiophospholane residue is the reaction of cyclic amides and esters of phosphorodithious acid with diethyl azodicarboxylate in chloroform:[168]



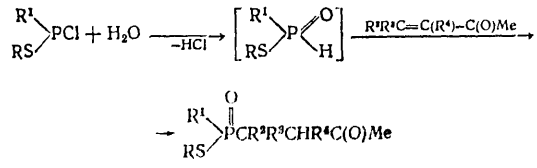
X=NMe_2, OMe; R′=H, Me

The previously unknown *O*-iminophosphonodithioates were readily formed by opening of the N=O bond in α-chloronitrosolkanes on treatment with mixed *O*,*S*-phosphorodithioites:[169]



R=Et, Pr, Bu; R′=Cl, Me

P(III) acid chlorides add on to a C=C bond in the presence of H_2O [170] in a similar manner to the reaction with carbonyl compounds:[102]

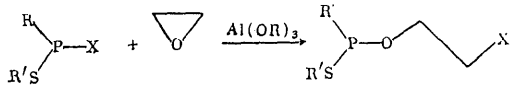


R = Et, Pr, Ph; R^1 = Et, Ph; R^2 = R^3 = R^4 = H, Me.

In the reaction of *S*-phenyl phenylphosphonochloridothioite the formation of a cyclic product—1,2-oxaphosphol-4-ene—occurs together with γ-ketophosphinothioates.[170] The proposed spontaneous cyclisation of γ-ketophosphinothioate was not confirmed experimentally.

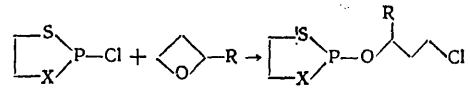
(c) Addition to olefin oxides

In the mid-1970's there were reports[171,172] in the patent literature about the development of a method for hydroxyalkylation of P(III) thioacid chlorides with olefin oxides in the presence of organoaluminium catalysts:



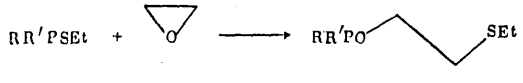
X = Cl, Br; R' = alkyl, R'S, R'O, R'_2N.

This reaction was subsequently extended to cyclic P(III) thioacid chlorides and oxetanes and it transpired that scission of the 2-methyloxetane ring occurs on the C–O bond through the primary carbon atom in the absence of catalysts:



X = O, S, NBu-t; R = H, Me.

Only in the mid-1980's was the possibility shown for the first time that olefin oxides could be inserted into the P–S bond of phosphinothioites[174] and phosphoramidothioites:[175]



R = Et, R' = Ph; R = R' = Ph, NEt_2; R = EtS, R' = Et_2N.

The reactions are catalysed by organic acids, Lewis acids, and bases.

6. Exchange reactions in a number of TTPA

Exchange reactions in a number of TTPA can be successfully used for the synthesis of various organophosphorus compounds. However, these studies were only elaborated at the end of the 1970's, as a result of which it was established that exchange can be accompanied by processes leading to a change in coordination of the P(III) atom together with retention of the same valency for phosphorus. In this case the effect of different factors (nature of the reactants, temperature, presence of catalysts) on the rate and course of these reactions was shown.

P(III) acid thioesters have been studied in the greatest detail in reactions with phosphorus trihalides,[176,177] which provided the basis for the development of synthetic methods not only for P(III) thioacid chlorides as already reported in the literature but also for the previously unknown phosphoromono-[177] and phosphorodi-bromidothioites.[178]

$$(RS)_3P + 2PX_3 \rightarrow 3RSPX_2;\quad 2(RS)_3P + PX_3 \rightarrow 3(RS)_2PX$$

R = Me, Et, Bu; X = Cl, Br.

It was later shown[179] that a similar reaction of tribenzyl phosphorotrithioite with phosphorus tribromide at 180 °C is accompanied by a change in coordination of the phosphorus atom and culminates in the formation of benzylphosphonothioic dibromide, although initial exchange products have been detected by ^{31}P NMR spectroscopy:

$$(PhCH_2S)_3P + 2PBr_3 \rightarrow 3PhCH_2P(S)Br_2.$$

In contrast to the reaction with phosphorus trihalides, the reaction between phosphorotrithioites and ethylphenylchlorophosphine is a reversible process:[177]

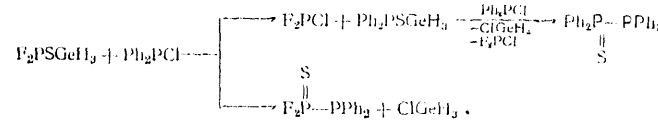
$$(RS)_3P + EtPhPCl \rightleftharpoons (RS)_2PCl + EtPhPSR$$

R = Me, Et, Pr.

At the same time, ethyl diphenylphosphinothioite reacts with diphenylchlorophosphine under severe conditions to form a complex mixture consisting of tetraphenyldiphosphine, ethyldiphenylphosphine sulphide, and diphenylchlorophosphine sulphide:[92]

$$Ph_2PSEt + Ph_2PCl \xrightarrow{250^\circ C} Ph_2P{-}PPh_2 + Ph_2P(S)Et + Ph_2PCl.$$

The reaction of *S*-germyl phosphorodifluoridothioite with diphenylchlorophosphine is also complex; cleavage of the S–Ge bond occurs together with formation of exchange products:[76]



At the beginning of the 1960's it was shown[176] that the reaction between trimethyl and tributyl phosphorotrithioites in the presence of trace amounts of HCl gives an equilibrium mixture consisting of four phosphorothioites:

$$(RS)_3P + (R'S)_3P \rightleftharpoons (RS)_2PSR' + RSP(SR')_2$$

R = Me; R' = Et, Bu.

It was established later[106] that the exchange of alkylthio groups in a number of phosphorotrithioites occurs only in the presence of catalytic quantities of acids and bases, the rate of exchange increasing on changing from acidic to basic catalysts.

The reaction of P(III) thioesters with trialkyl phosphites has only been studied in the case of Schrader's anhydride reacting with triethyl phosphite,[121] as a result of which a compound with a $P^{(III)}-P^{(V)}$ bond—*tris*(diethylphosphoryl)phosphine—is formed:

$$[(EtO)_2PS]_3P + 3(EtO)_3P \rightarrow [(EtO)_2P]_3P + 3(EtO)_2PSEt.$$

There is no information in the literature about the exchange of groups between P(III) acid thioesters and triaminophosphines, but the reactions of the latter with phosphoromono- and phosphorodichloridothioites[177] and also with 1,3,2-thiazaphospholanes containing an exocyclic P–Cl bond[180] have been studied, so it was possible to

obtain P(III) acid derivatives containing both a P–S bond and a P–N bond in the molecule:

$$(EtS)_2PCl + (Et_2N)_3P \underset{-40\,^\circ C}{\overset{20\,^\circ C}{\rightleftharpoons}} \begin{cases} (EtS)_2PNEt_2 + (Et_2N)_2PCl \\ (EtS)_2P{-}\overset{+}{P}(NEt_2)_3Cl^- \end{cases}.$$

More recently, in a study[181] of the reaction between diethyl phosphorochloridodithioite with hexaethyltriaminophosphine at low temperatures using ^{31}P NMR specroscopy it was possible to identify the formation of a quasiphosphonium compound with a P–P bond, which on increasing the temperature decomposed with the subsequent formation of exchange products. A quasiphosphonium compound with a P–P bond is also formed by reaction of diethyl phosphorochloridodithioite with tripropylphosphine;[181] this compound is converted at 0 °C to tripropylethylphosphonium chloride:

$$(EtS)_2PCl + Pr_3P \underset{0\,^\circ C}{\overset{-60\,^\circ C}{\rightleftharpoons}} \begin{cases} (EtS)_2P{-}\overset{+}{P}Pr_3\ Cl^- \\ Pr_3\overset{+}{P}SEt\ Cl^- \end{cases}.$$

Products with a P–P bond were also obtained in the case of the reaction between diethyl phosphorochloridodithioite and silyl phosphites:[124]

$$(EtS)_2PCl + (RO)_2POSiMe_3 \xrightarrow{-Me_3SiCl} (EtS)_2P{-}\underset{\underset{O}{\|}}{P}(OR)_2$$

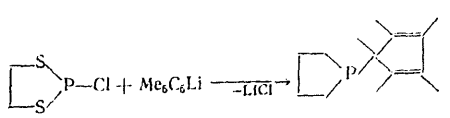
R=Et, Me_3Si.

The reaction takes place under mild conditions and is accompanied by the liberation of heat.

7. Reactions of TTPA with organometallic and complex compounds

In recent years studies on the reactions of TTPA with organometallic and complex compounds have been published in the literature. This is related to the fact that a number of metal-complex compounds containing TTPA as ligands have been used as catalysts for liquid-phase hydrogenation[182] and hydroformylation.[183] Moreover, new types and classes of organophosphorus compounds, including those with an unusual structure and coordination of the phosphorus atom, have been obtained from reactions of TTPA with organometallic compounds.

Thus, in the reaction of pentamethylcyclopentadienyllithium with 2-chloro-1,3,2-dithiaphospholane, 2-(pentamethyl-2,4-cyclopentadiene-1-yl)-1,3,2-dithiaphospholane is formed, having a 'fluxional' structure as a result of a 1,5-sigmatropic rearrangement of the dithiaphospholane residue:[184]



Previously unknown compounds with a pentavalent tricoordinated phosphorus atom—*bis*(methylene)phosphoranes—were synthesised from alkyl or aryl phosphorodichloridothioites and lithium *bis*(trimethylsilyl)methanide:[185,186]

$$RS{-}PCl_2 + 3LiCCl(SiMe_3)_2 \xrightarrow[-3LiCl\ -Cl_2C(SiMe_3)_2]{-110\,^\circ C} RS{-}P\!\left(\!=\!C(SiMe_3)_2\right)\!C(SiMe_3)_2$$

R = iso-Pr, C_5H_{11}, Ph.

Cleavage of the P–S bond in TTPA on treatment with organolithium compounds was shown only in the case of the reaction between *S*-thiobenzoyl diphenylphosphinothioite and phenyllithium:[55]

$$Ph_2PSCPh + PhLi \rightarrow Ph_2P + PhCS_2^-Li^+,$$
$$\qquad\qquad\quad \|\ S$$

The cleavage of the P–S bond in P(III) acid thioesters by organic hydrides of Group 4b metals was studied in greater detail.[187,188] On the basis of these investigations, for the first time a general method was developed for the synthesis of a new class of organophosphorus compounds—alkyl- and phenyl-alkylthiophosphines[189] and the previously unknown acyclic thioesters of hypophosphorous acid:[190]

$$RP(SR')_2 + Bu_3SnH \rightarrow RP\!\begin{cases} SR' \\ H \end{cases} + Bu_3SnSR'$$

R = Me, Et, iso-Bu, Ph, SR'; R' = Me, Et, Pr.

It is interesting that in the reaction of trialkylstannanes with trichloromethylphosphonodithioite the P–S bond is retained while a C–Cl bond in the trichloromethyl group is cleaved:[188]

$$CCl_3P(SEt)_2 + R_3SnH \rightarrow CHCl_2P(SEt)_2 + R_3SnCl$$
$$R = Et,\ Bu.$$

At the same time, it is not possible to use complex alkali metal hydrides, in particular, lithium aluminium hydride, as reducing agents in reactions with TTPA for carrying out a selective reduction, since all the P–S bonds are cleaved in phosphinothioites, phosphonothioites,[191,192] and phosphorodiamidothioites,[192] resulting in the formation of the corresponding primary or secondary phosphines and hypophosphorous acid diamides:

$$PhP(SEt)_2 \xrightarrow[\text{dibenzo-18-crown-6}]{LiAlH_4} PhPH_2$$
$$(Et_2N)_2PSR \xrightarrow[\text{ether}]{LiAlH_4} (Et_2N)_2PH.$$

It was shown for the first time[191,192] that the use of crown ethers as phase-transfer catalysts in these reactions considerably increases the rate of reduction and the yields of the final products.

During the last ten years there has been a considerable increase in interest concerning metal derivatives of TTPA, particularly in transition metal complexes. A number of mono- and di-substituted phosphinothioite and phosphonodithioite complexes of chromium,[193–196] molybdenum,[194,195,197] and tungsten[194,195] have been obtained from transition metal carbonyl complexes containing readily detachable ligands such as tetrahydrofuran (THF) or norbornadiene (NBD):

$$M(CO)_5THF + R_2PSR' \xrightarrow{-THF} M(CO)_5PR_2SR'$$
$$cis\text{-}M(CO)_4NBD + 2RP\!\begin{cases} S \\ S \end{cases}\!R'' \xrightarrow{-NBD} cis\text{-}M(CO)_4\left(RP\!\begin{cases} S \\ S \end{cases}\!R''\right)_2$$
M=Cr, Mo, W; R, R'=CH_3, CF_3; R''=CH_2CH_2, *o*-C_6H_4.

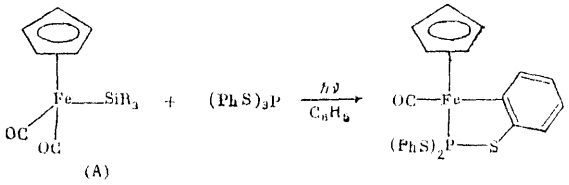
It was established that in all cases phosphorus coordinates with the metal atom, and the rate of ligand exchange depends on the nature of the substituents and the metal atom.[194,195] It should be noted that in the case of disubstituted complexes the compound with a *cis*-configuration that is formed initially can be converted to the *trans*-isomer, with the rate of isomerisation depending on the nature of the substituents, the metal atom, and the temperature.[195,196] The reaction of tetracarbonyl(norbornadiene)molybdenum with *S*-germyl phosphorodifluoridothioite takes place in a similar manner.[76]

More recently the synthesis of phosphinothioites of binuclear manganese carbonyl complexes has been carried out[198] by direct displacement of carbon monoxide from manganese carbonyls:

$$Mn_2(CO)_{10} + (CF_3)_2PSR \xrightarrow{90\text{-}130^\circ C} Mn_2(CO)_8P(CF_3)_2SR$$

R = alkyl, aryl, perfluoroalkyl, perfluoroaryl, $P(CF_3)_2$

Cyclometallated iron complexes with a triphenyl phosphorotrithioite ligand are readily formed by UV irradiation of a complex of the type (A) in the presence of triphenyl phosphorotrithioite:[199]



The replacement of ligands in platinum complexes with the involvement of *S*-germyl phosphorodifluoridothioite has been studied.[76]

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Thus, the introduction of alkythio groups on to the trivalent phosphorus atom produces a substantial change in the reactivity of P(III) acid derivatives. The Arbuzov reaction route, which is typical for oxygen analogues of TTPA, does not occur in the majority of cases and substitution at the trivalent phosphorus atom with retention of the same coordination takes place. This trend is particularly marked in the reactions of TTPA with acids and halogenated electrophilic reagents. The addition of TTPA to carbonyl compounds resulting in the cleavage of a P—S bond, as a rule, only occurs in the presence of a third reagent which assumes the role of activator for the process.

The effect of different factors, including acidic catalysts, on the rate of substitution and exchange reactions involving TTPA has been established, placing them in the same series with other trivalent phosphorus acid derivatives.

The mechanism established for the chemical behaviour of TTPA in substitution and addition reactions now make it possible not only to carry out the directed synthesis of compounds with a predetermined structure and properties but also to predict the course of TTPA reactions that have not yet been studied. Everything that has been reported above and the existence of a considerable number of convenient methods for obtaining TTPA mean that further studies of this class of compounds will have future potential.

References

1. US P. 3 360 573
2. USSR P. 293 039; *Byull. Izobret.*, 1971, (5) 111
3. Japanese Appl. 52-74 660; *Ref. Zh. Khim.*, 1978, 10T53
4. Japanese Appl. 52-109 547; *Ref. Zh. Khim.*, 1978, 23T100
5. French Appl. 2 375 243
6. USSR P. 317 286; *Byull. Izobret.*, 1981, (34) 320
7. B. Appl. 1 377 282; *Izobr. v SSSR za Rubezhom*, 1975, (19) No. 9
8. Japanese Appl. 53-20 798; *Izobr. v SSSR i za Rubezhom*, 1979, (57) No. 1
9. USSR P. 825 538; *Byull. Izobret.*, 1981, (16) 101
10. US P. 254 370; *Chem. Abs.*, 1951, **45** 57
11. C Wu *J. Am. Chem. Soc.*, 1965, **87** 2522
12. E E Nifant'ev *Khimiya Fosfororganicheskikh Soedinenii* (The Chemistry of Organophosphorus Compounds), Izd. MGU, Moscow, 1971
13. D Purdela, R Vilchanu *The Chemistry of Organophosphorus Compounds* (Translated into Russian), Izd. Khimiya, Moscow, 1972
14. B E Ivanov, V F Zheltukhin *Usp. Khim.*, 1970, **39**(5) 779 [English translation in *Russ. Chem. Rev.*, 1970(5)]
15. E A Krasil'nikova *Usp. Khim.*, 1977, **46**(9) 1638 [English translation in *Russ. Chem. Rev.*, 1977(9)]
16. V A Naumov, L V Vilkov *Molekulyarnaya Struktura Fosfororganicheskikh Soedinenii* (The Molecular Structure of Organophosphorus Compounds), Izd. Nauka, Moscow, 1986
17. C Brown, R Hudson, G Wartew *Phosphorus Sulfur*, 1978, **5** 121
18. C Brown, R Hudson, G Wartew *J. Chem. Soc., Perkin Trans. I*, 1979, 1799
19. A Haas, D Winkler *Z. Anorg. Allg. Chem.*, 1980, **468** 68
20. F A Mamedov, F N Mamedov, M A Mirzoeva *Azerb. Khim. Zh.*, 1981, (5) 33
21. W Zeiss, A Pointner, C Engelhardt, H Klehr *Z. Anorg. Allg. Chem.*, 1981, **475** 256
22. Japanese Appl. 55-39 557; *Izobr. v SSSR i za Rubezhom*, 1981, (55) No. 7
23. US P. 4 237 075; *Izobr. v SSSR i za Rubezhom*, 1981, (55) No. 14
24. French Appl. 2 383 190; *Izobr. v SSSR i za Rubezhom*, 1979, (55) No. 6
25. S Pastor, J Spivack, L Eteinhuebe *Phosphorus Sulfur*, 1985, **22** 169
26. USSR P. 757 538; *Byull. Izobret.*, 1980, (31) 93
27. J I Calquhoun, W McFarlane *J. Chem. Soc., Dalton Trans.*, 1977, 1674
28. C C Chang, R C Haltiwinger, A D Norman *Inorg. Chem.*, 1978, **17** 2056
29. BRD Appl. 2 658 368
30. B. Appl. 1 581 079
31. S Kobayashi, M Suzuki, T Saegusa *Bull. Chem. Soc. Jpn.*, 1985, **58** 2153
32. US P. 4 107 168; *Izobr. v SSSR i za Rubezhom*, 1979, (55) No. 8
33. BRD P. 2 809 492; *Chem. Abs.*, 1979, **90** 103 401
34. A R Burilov, M A Pudovik, L N Usmanova, A N Pudovik *Zh. Obshch. Khim.*, 1985, **55** 2401
35. D Denney, D Denney, L Lin *Khuasyue Syuebao, Acta Chim. Sin.*, 1984, **42** 340; *Ref. Zh. Khim.*, 1984, 23Zh365
36. C H Chen, B A Donatelli, N Zumbulyadis *Synthesis*, 1978, 667
37. A Sua, R Holmes *J. Organomet. Chem.*, 1978, **156** 253
38. J-P Dutasta, J Martin, J-B Robert *J. Org. Chem.*, 1977, **42** 1662
39. D Denney, D Denney, L Lin *Phosphorus Sulfur*, 1982, **13** 1
40. L Horner, M Jordan *Phosphorus Sulfur*, 1980, **8** 235
41. E Niecke, R Rüger *Angew. Chem.*, 1982, **94** 70
42. A M Kuliev, Sh R Aliev, F N Mamedov, et al. *Zh. Obshch. Khim.*, 1977, **47** 2492
43. D Stolberg, J Gloede, K Andrä *Z. Anorg. Allg. Chem.*, 1985, **527** 180
44. P Dalla Groce, S Maiorana *Synthesis*, 1984, 980
45. M A Pudovik, Yu B Mikhailov, L K Kibardina, et al. *Zh. Obshch. Khim.*, 1985, **55** 2185

46. M A Pudovik, Yu B Mikhailov, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1108
47. M A Pudovik, Yu B Mikhailov, A N Pudovik *Zh. Obshch. Khim.*, 1983, **53** 2468
48. P A Gurevich T V Komina, G Yu Klimentova, et al. *Khim.-Farm. Zh.*, 1984, **18** 833
49. P A Gurevich, A I Razumov, T V Komina, et al. *Zh. Obshch. Khim.*, 1985, **55** 1327
50. K Iurkschat, C Mügge, A Tzschach, et al. *Tetrahedron Lett.*, 1982, **23** 1345
51. E E Nifant'ev, M P Koroteev, S A Ermishkina, et al. *Zh. Obshch. Khim.*, 1978, **48** 1904
52. E E Nifant'ev, M P Koroteev, S A Lysenko, N K Kochetkov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 1441
53. Yu G Gololobov, M N Danchenko *Zh. Obshch. Khim.*, 1979, **49** 2623
54. M N Danchenko, Yu G Gololobov *Zh. Obshch. Khim.*, 1982, **52** 2205
55. S Kato, M Goto, R Hattori, et al. *Chem. Ber.*, 1985, **118** 1668
56. M N Danchenko, A D Sinitsa *Zh. Obshch. Khim.*, 1986, **56** 1773
57. E A V Ebsworth, M C Huntley, D W H Rankin *J. Chem. Soc., Dalton Trans.*, 1984, 2301
58. V A Al'fonsov, D A Pudovik, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1985, **55** 932
59. V A Al'fonsov, D A Pudovik, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1985, **55** 2203
60. V A Al'fonsov, D A Pudovik, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1985, **55** 559
61. D M Malenko, A D Sinitsa *Zh. Obshch. Khim.*, 1986, **56** 1654
62. E E Nifant'ev, A P Tuseev, A I Val'dman, et al. *Zh. Obshch. Khim.*, 1978, **48** 1473
63. N I Shvetsov-Shilovskii, D P Nesterenko, A A Stepanova *Zh. Obshch. Khim.*, 1979, **49** 1896
64. M A Pudovik, I A Aleksandrova, L K Kibardina, et al. *Zh. Obshch. Khim.*, 1980, **50** 1199
65. M A Pudovik, L K Kibardina, I A Aleksandrova, et al. *Zh. Obshch. Khim.*, 1981, **51** 28
66. M A Pudovik, L K Kibardina, I A Aleksandrova, et al. *Zh. Obshch. Khim.*, 1981, **51** 530
67. H Vetter, H North *Chem. Ber.*, 1963, **96** 1308
68. USSR P. 765303; *Byull. Izobret.*, 1980, (35) 151
69. S Kh Nurtdinov, S V Khairullina, V K Khairullin, et al. *Zh. Obshch. Khim.*, 1983, **53** 785
70. M A Vasyanina, I K Pokrovskaya, N P Safina, V K Khairullin *Khimiya i Tekhnologiya Elementoorganicheskikh Soedinenii i Polimerov* (The Chemistry and Technology of Heteroorganic Compounds) (Edited by P A Kirpichnikov), Izd. Kazan. Khim.-Tekhnol. Instituta, Kazan', 1983, p. 3
71. USSR P. 643509 (1977); *Byull. Izobret.*, 1979, (3) 88
72. R Light, L Hutchins, R Paine, C Compana *Inorg. Chem.*, 1980, **19** 3597
73. K Gosling, J Miller *Inorg. Nucl. Chem. Lett.*, 1973, **9** 355
74. C Glidewell *J. Organomet. Chem.*, 1977, **142** 171
75. G Fritz, D Hanke *Z. Anorg. Allg. Chem.*, 1986, **537** 17
76. E A W Ebsworth, E K Macdonald, D W H Rankin *Monatsh. Chem.*, 1980, **111** 221
77. D Arnold, E Gromie D W H Rankin *J. Chem. Soc., Dalton Trans.*, 1977, 1999
78. E P Lebedev, M D Mizhiritskii, V A Baburina, E N Ofitserov *Zh. Obshch. Khim.*, 1979, **49** 1730
79. J Heinicke, A Tzschach *Phosphorus Sulfur*, 1984, **20** 347
80. J Grobe, D Le Van, J Nientiedt *Z. Naturforsch., B*, 1986, **41** 149
81. V D Romanenko, A V Ruban, N N Kalibabchuk, et al. *Zh. Obshch. Khim.*, 1981, **51** 1726
82. U Dressler, E Niecke, S Pohl, et al. *Chem. Commun.*, 1986, 1086
83. R Appel, C Casser *Chem. Ber.*, 1985, **118** 3419
84. E Niecke, E Symalla *Chimia*, 1985, **39** 320
85. L Horner, M Jordan *Phosphorus Sulfur*, 1980, **8** 221
86. S Kh Nurtdinov, N M Ismagilova, T A Fakhrutdinova, T V Zykova *Zh. Obshch. Khim.*, 1983, **53** 1045
87. L Horner, M Jordan *Phosphorus Sulfur*, 1980, **8** 215
88. J Omelanczuk, M Mikolaiczyk *Tetrahedron Lett.*, 1984, **25** 2493
89. A Schmidpeter, K Karaghiosoff, C Cleve, D Schomburg *Angew. Chem.*, 1985, **97** 125
90. V A Al'fonsov, I S Nizamov, E S Batyeva, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2619
91. V P Kostin, O G Sinyashin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1982, **52** 2698
92. V A Al'fonsov, D A Pudovik, E S Batyeva, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 851
93. V A Al'fonsov, I S Nizamov, E S Batyeva, A N Pudovik, *Zh. Obshch. Khim.*, 1983, **53** 1713
94. M N Danchenko, I Yu Budileva, A D Sinitsa *Zh. Obshch. Khim.*, 1985, **55** 939
95. J Grosse, W Pieper, H Neumaier *Angew. Chem.*, 1982, **94** 560
96. F Ando, J Koketsu, Y Ishii *Bull. Chem. Soc. Jpn.*, 1978, **51** 1481
97. M N Dimukhametov, I A Nuretdinov *Zh. Obshch. Khim.*, 1984, **54** 1913
98. O G Sinyashin, Candidate's Thesis in Chemical Sciences, Kazan' University, Kazan', 1981
99. V P Kostin, O G Sinyashin A A Karelov, et al. *Zh. Obshch. Khim.*, 1985, **55** 2175
100. L V Ermanson, N N Godovikov, V S Blagoveshchenskii *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 423
101. E E Nifant'ev, A S Chechetkin, V E Blagoveshchenskii, A M Sokurenko *Zh. Obshch. Khim.*, 1983, **53** 2695
102. N A Kardanov, N P Provotorova, P V Petrovskii, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 2114
103. E N Ofitserov, O G Sinyashin, N V Ivasyuk, et al. *Zh. Obshch. Khim.*, 1980, **50** 1217
104. D S Yufit, Yu T Struchkov, M A Pudovik, et al. *Dokl. Akad. Nauk SSSR*, 1980, **255** 1190
105. E Gromie, G Hunter, D W H Rankin *Angew. Chem.*, 1980, **92** 323
106. O G Sinyashin, E S Batyeva, A N Pudovik, E N Ofitserov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 2133
107. V P Kostin, O G Sinyashin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1984, **54** 218
108. M Movsum-zade, S R Aliev, F N Mamedov *Zh. Obshch. Khim.*, 1980, **50** 2698
109. US P. 4140514; *Chem. Abs.*, 1979, **91** 91340
110. V P Kostin, O G Sinyashin, E S Batyeva, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 703
111. E N Ofitserov, O G Sinyashin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1981, **51** 738
112. V P Kostin, O G Sinyashin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1982, **52** 2701

113. V P Kostin, O G Sinyashin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1982, **52** 498
114. E S Batyeva, E N Ofitserov, O G Sinyashin, et al. *Zh. Obshch. Khim.*, 1980, **50** 2396
115. E N Ofitserov, O G Sinyashin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1980, **50** 222
116. V A Al'fonsov, G U Zamaletdinova, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1982, **52** 2199
117. O G Sinyashin, Sh A Karimullin, E S Batyeva, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1671
118. O G Sinyashin, Sh A Karimullin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1984, **54** 540
119. E N Ofitserov, O G Sinyashin, N V Ivasyuk, et al. *Zh. Obshch. Khim.*, 1981, **51** 468
120. O G Sinyashin, T N Sinyashina, E S Batyeva, et al. *Zh. Obshch. Khim.*, 1982, **52** 2438
121. L V Ermanson, V S Blagoveshchenskii, N N Godovikov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 1689
122. L V Ermanson, V S Blagoveshchenskii, N N Godovikov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 2788
123. O G Sinyashin, V P Kostin, E S Batyeva, et al. *Zh. Obshch. Khim.*, 1983, **53** 1706
124. V A Al'fonsov, G U Zamaletdinova, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1985, **55** 704
125. E N Ofitserov, O G Sinyashin, E S Batyeva, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 691
126. V A Al'fonsov, I S Nizamov, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1985, **55** 1253
127. O G Sinyashin, V P Kostin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1983, **53** 472
128. E E Nifant'ev, M P Koroteev, S A Lysenko *Carbohydr. Res.*, 1982, **111** 67
129. M N Danchenko, A D Sinitsa *Zh. Obshch. Khim.*, 1984, **54** 473
130. O G Sinyashin, Sh A Karimullin, D A Pudovik, et al. *Zh. Obshch. Khim.*, 1984, **54** 2458
131. A Haas, W Kortmann *Z. Anorg. Allg. Chem., 1983,* **501** 79
132. O G Sinyashin, Sh A Karimullin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1984, **54** 2463
133. B E Ivanov, S S Krokhina, T V Chichkanova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 178
134. O G Sinyashin, Sh A Karimullin, V P Kostin, et al. *Zh. Obshch. Khim.*, 1986, **56** 1700
135. E A Krasil'nikova, O L Nevzorova, V V Sentemov *Zh. Obshch. Khim.*, 1985, **55** 1283
136. V A Al'fonsov, G U Zamaletdinova, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1986, **56** 713
137. V P Kostin, O G Sinyashin, E S Batyeva, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1673
138. O G Sinyashin, V P Kostin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1983, **53** 502
139. V A Al'fonsov, G U Zamaletdinova, E S Batyeva, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1386
140. E S Batyeva, O G Sinyashin, V A Al'fonsov, et al. *Trudy VII Konferentsii 'Khimiya i Primenenie Fosfororganicheskikh Soedinenii'* (Proceedings of the VIIth Conference on the Chemistry and Use of Organophosphorus Compounds), Izd. Nauka, Leningrad, 1986
141. O G Sinyashin, Sh A Karimullin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1985, **55** 453
142. V F Kostin, O G Sinyashin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1985, **55** 1183
143. O G Sinyashin, V A Subanov, E S Batyeva, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1209
144. USSR P. 1 249 019; *Byull. Izobret.*, 1986, (29) 99
145. V A Al'fonsov, I S Nizamov, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1986, **56** 709
146. V A Al'fonsov, I S Nizamov, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1985, **55** 1634
147. V A Al'fonsov, D A Pudovik, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1986, **56** 1905
148. V A Al'fonsov, I S Nizamov, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1983, **53** 689
149. V A Al'fonsov, I S Nizamov, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1984, **54** 535
150. I S Nizamov, V A Al'fonsov, A G Trusenev, et al. *Zh. Obshch. Khim.*, 1986, **56** 216
151. V A Al'fonsov, I S Nizamov, E S Batyeva, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2413
152. USSR P. 1 177 305; *Byull. Izobret.*, 1985, (33) 85
153. I S Nizamov, Abstract of Candidate's Thesis in Chemical Sciences, Kazan' University, Kazan', 1985
154. V A Al'fonsov, G U Zamaletdinova, I S Nizamov, et al. *Zh. Obshch. Khim.*, 1984, **54** 1485
155. I V Konovalova, V F Mironov, E N Ofitserov, A N Pudovik *Zh. Obshch. Khim.*, 1983, **53** 690
156. L V Ermanson, N N Godovikov, V S Blagoveshchenskii *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 427
157. V P Kostin, O G Sinyashin, E S Batyeva, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1643
158. N A Razumova, A A Petrov, Zh L Evtikhov, et al. *Trudy IV Konferentsii 'Khimiya i Primenenie Fosfororganicheskikh Soedinenii'* (Proceedings of the IVth Conference on the Chemistry and Use of Organophosphorus Compounds), Izd. Nauka, Moscow, 1972, p. 100
159. V V Ragulin, N A Razumova, V I Zakharov, A A Petrov *Zh. Obshch. Khim.*, 1980, **50** 462
160. V V Ragulin, V I Zakharov, A A Petrov, N A Razumova *Zh. Obshch. Khim.*, 1981, **51** 34
161. V A Al'fonsov, O M Dianova, E I Gol'dfarb, et al. *Zh. Obshch. Khim.*, 1982, **52** 924
162. M Tomano, T Ikeda, J Koketsu *J. Chem. Soc. Jpn., Chem. Ind. Chem.*, 1984, 1158
163. A N Pudovik, G V Romanov, V N Volkova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 934
164. V A Al'fonsov, R D Gareev, E I Gol'dfarb, et al. *Zh. Obshch. Khim.*, 1982, **52** 441
165. P Beer, R Edwards, D Hall, et al. *Phosphorus Sulfur*, 1983, **17** 283
166. V I Namestnikov, L A Tamm, V N Chistokletov *Zh. Obshch. Khim.*, 1985, **55** 695
167. V I Namestnikov, L A Tamm, V N Chistokletov *Zh. Obshch. Khim.*, 1985, **55** 710
168. J-P Majoral, R Kraemer, T N'Gando M'Pondo, J Navech *Tetrahedron Lett.*, 1980, **21** 1307
169. I V Martynov, L A Chepakova, V K Brel', V B Sokolov *Zh. Obshch. Khim.*, 1986, **56** 2420
170. F S Mukhametov, R M Eliseenkova, N I Rizpolozhenskii *Zh. Obshch. Khim.*, 1980, **50** 222
171. BRD Appl. 2 407 006
172. B. Appl. 1 458 851
173. L Z Nikonova, O I Nuretdinova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 918

174. O G Sinyashin, Sh A Karimullin, E S Batyeva, A N Pudovik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 726
175. V P Kostin, O G Sinyashin, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1985 **55** 1860
176. K Moedritzer, G Burch, J Van Wazer, H Hofmeister *Inorg. Chem.*, 1963, 1152
177. O G Sinyashin, E N Ofitserov, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1981, **51** 2410
178. V A Naumov, O N Kataeva, O G Sinyashin *Zh. Strukt. Khim.*, 1984, **25**(3) 79
179. P S Khokhlov, L S Berseneva, N S Savenkov *Zh. Obshch. Khim.*, 1984, **54** 972
180. M A Pudovik, Yu B Mikhailov, T A Malykh, et al. *Zh. Obshch. Khim.*, 1980, **50** 1677
181. V A Al'fonsov, G U Zamaletdinova, K M Enikeev, et al. *Zh. Obshch. Khim.*, 1986, **56** 1697
182. US P. 3 110 747; *Chem. Abs.*, 1964, **60** 7504
183. US P. 3 351 666; *Chem. Abs.*, 1968, **68** 42 004
184. P Jutzi, H Saleske *Chem. Ber.*, 1984, **117** 222
185. R Appel, K Dunker, E Gaitzsch, T Gaitzsch *Z. Chem.*, 1984, **24** 384
186. R Appel, E Gaitzsch, K Dunker, F Knoch *Chem. Ber.*, 1986, **119** 535
187. P Dehnert, J Grobe, D Le Van *Z. Naturforsch., B*, 1981, **36** 48
188. O G Sinyashin, I Yu Gorshunov, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1985, **55** 2198
189. USSR P. 1 122 668; *Byull. Izobret.*, 1984, (41) 88
190. USSR P. 1 114 680; *Byull. Izobret.*, 1984, (35) 60
191. O G Sinyashin, I Yu Gorshunov, E S Batyeva, A N Pudovik *Zh. Obshch. Khim.*, 1984, **54** 1917
192. O G Sinyashin, I Yu Gorshunov, N V Ivasyuk, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1394
193. J Grobe, D Le Van *Z. Naturforsch., B*, 1979, **34** 1653
194. J Grobe, D Le Van *Z. Anorg. Allg. Chem.*, 1984, **518** 36
195. J Grobe, M Köhne-Wächter, D Le Van *Z. Anorg. Allg. Chem.*, 1984, **519** 67
196. J Grobe, D Le Van, J Szameitat *J. Organomet. Chem.*, 1985, **289** 341
197. J Grobe, D Le Van *Z. Naturforsch., B*, 1980, **35** 694
198. J Grobe, J Vatter, D Rehder *Z. Naturforsch.*, 1985, **40** 975
199. G Cervean, G Chanviere, E Colomer, R Corrin *J. Organomet. Chem.*, 1981, **210** 343

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Pentacoordinate fluorosilicate anions

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ABSTRACT. The literature data on the synthesis and properties of salts with pentacoordinate fluorosilicate anions have been classified and correlated. The geometric structural features of the pentafluorosilicate anion and its substituted derivatives are analysed, taking into account the hypervalent nature of the bonding in silicon(IV) complexes.
The bibliography includes 94 references.

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I. Introduction

From the date of publication of Sommer's well-known monograph[1], which correlated the main results on the dynamic stereochemistry of organosilicon compounds, research workers have taken a greater interest in pentacoordinate fluorosilicate anions. Compounds of this type are potential intermediates in various reactions involving tetra- and hexa-coordinate silicon fluoro-complexes. In particular, the pentafluorosilicate anion and its substituted derivatives may be regarded as stable 'models' of S_N2 Si intermediates in nucleophilic substitution reactions involving the respective tetrahedral fluorosilanes.[1] The formation of pentacoordinate silicon fluoro-complexes as intermediates was postulated in a discussion of the probable mechanism of the dehydro-fluorination of octahedral complexes of silicon tetrafluoride with nitrogen- and oxygen-containing donor ligands giving organofluorosilicon compounds such as fluorosilylamines, fluorosilazanes, and alkoxysilanes with a valuable set of physicochemical properties.[2]

Two reviews[3,4] have been devoted to various aspects of the chemistry of pentacoordinate silicon fluoro-complexes, but a limited amount of correlation of the information on pentacoordinate fluorosilicate anions is only presented in one study.[3] Moreover, in recent years a considerable number of interesting studies in this field have been published, and evidently the time was ripe for a new review. The aim of the present review is to classify and correlate the information published during the last decade on the synthetic methods, geometric structure, dynamic stereochemistry and ligand exchange processes in solution, properties, and use of pentacoordinate anions of silicon fluoro-complexes in preparative synthesis.

II. Synthetic methods

The earliest information about the preparation of pentafluorosilicates—salts of the simplest pentacoordinate fluorosilicate anion—was published in 1967. Clark et al.[5] discovered that the reaction of *trans*-$[PtHCl(Et_3P)_2]$ with tetrafluoroethylene in a Pyrex tube gave *trans*-$[PtCl(CO)(Et_3P)_2]SiF_5$. In subsequent reports[6,7] a simple method for the synthesis of pentafluorosilicates was proposed, being based on the reaction of equimolar quantities of tetraalkylammonium chloride or bromide with silica in an aqueous methanol solution of HF. This method was used to obtain $(R_4N)SiF_5$, where R = Et, n-Pr, n-Bu. A similar method has been reported by Behrends and Kiel.[8] It is interesting that the product of the reaction between SiF_4 and $Pt(PPh_3)_3$, which was first identified[9] as the complex $SiF_4.Pt(PPh_3)_3$, according to later results[10] is hydrido-tris(triphenylphosphine)platinum pentafluorosilicate $[PtH(PPh_3)_3].SiF_5$. A similar reaction between BF_3 and $Pt(PPh_3)_3$ leads to the formation of tetrafluoroborate salts. Bird et al.[10] stressed the need to make a critical assessment of the results of a synthesis based on covalent fluorides and basic metal complexes when the reactions are carried out in a glass apparatus.

Dehydrofluorination of complexes of silicon tetrafluoride with alcohols and primary amines in the presence of tertiary amines were used[11,12] for the synthesis of a number of trialkylammonium pentafluorosilicates:

$$5SiF_4 + 4ROH + 4R_3N \rightarrow Si(OR)_4 + 4(R_3NH)SiF_5,$$
$$3SiF_4 + RNH_2 + 2R_3N \rightarrow 1/n(RNSiF_2)_n + 2(R_3NH)SiF_5.$$

Gel'mbol'dt et al.[13,14] proposed a method for the synthesis of dialkyl- and trialkyl-ammonium pentafluorosilicates based on dehydrofluorination in the system SiF_4–acetone–amine, where the enol form of acetone acts as a proton donor:

$$5SiF_4 + 4Me_2CO + 4R_nNH_{3-n} \rightarrow \left(CH_2{=}\overset{\overset{Me}{|}}{C}{-}O\right)_4 Si + 4(R_nNH_{4-n})SiF_5, \quad n = 2, 3.$$

This method was recently used to obtain *N*,*N*-dialkylanilinium pentafluorosilicates $(PhNHR_2)SiF_5$ (R = Et, n-Pr, n-Bu).[15]

As was demonstrated in two studies,[12,16] a fairly general method for the synthesis of trialkyl- and tetraalkyl-ammonium pentafluorosilicates consists of the treatment of the respective hexafluorosilicates or 'complex' fluorosilicates containing anions of the stoichiometric composition $Si_2F_{11}^{3-}$ and $Si_3F_{16}^{4-}$ with an excess of silicon tetrafluoride in a suitable solvent (benzene, acetonitrile, methylene chloride). Since fluorosilicates of the type $(R_3NH)_3Si_2F_{11}$

or $(R_3NH)_4Si_3F_{16}$ are the double salts $(R_3NH)_2SiF_6.n(R_3NH)SiF_5$ (n = 1, 2),[17-20] the chemical nature of the conversion of fluorosilicates higher in fluorine to pentafluorosilicates can be represented by the general scheme:

$$SiF_6^{2-} + SiF_4 \rightarrow 2SiF_5^-.$$

The use of this method in the preparative synthesis of pentafluorosilicates may only be limited by the poor solubility of the initial hexafluorosilicates or double fluorosilicates in aprotic solvents.

A general method for the synthesis of pentafluorosilicates and also mixed pentacoordinate tetraalkylammonium alkyl- and aryl-fluorosilicates has been proposed. It is based on the reaction between SiF_4 or R_nSiF_{4-n} (n = 1, 2) and R_4NF in methanol:[21]

$$R_nSiF_{4-n} + F^- \rightarrow [R_nSiF_{5-n}]^-.$$

Despite the complexity of obtaining a tetraalkylammonium fluoride that is free of impurities, the latter method has been widely applied. In particular, it has been used in the synthesis of virtually all samples of salts with pentacoordinate fluorosilicate anions for X-ray diffraction studies.

There has been a report on a similar method for obtaining mixed anions of the type $[XSiF_4]^-$ by reaction between silicon tetrafluoride and Me_4NX (X = CF_3COO^-, $MeCOO^-$, $HCOO^-$, NO_2^-, CN^-, etc.) in liquid sulphur dioxide or methylene chloride:[22]

$$SiF_4 + X^- \rightarrow [XSiF_4]^-.$$

An excess of silicon tetrafluoride reacted with acetate ion leads to the formation of a binuclear anion with a bridging fluorine atom and an equatorial configuration of the monodentate $MeCOO^-$ groups:

$$5SiF_4 + 4MeCOO^- \rightarrow 2[Si_2F_7(MeCOO)_2]^- + SiF_6^{2-}.$$

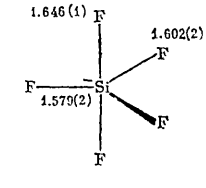
A proposed[21,22] route for the synthesis of pentacoordinate fluorosilicate anions was further developed by Ault and Tandoc,[23,24] who used the technique of low-temperature matrix isolation in order to obtain caesium salts with SiF_5^-, $[SiF_{5-n}Cl_n]^-$ (n = 1-4), and $[Me_nSiF_{5-n}]^-$ (n = 1, 2) anions. The compound $KSiF_5$ was also obtained. The synthetic method consisted of evaporating the respective metal fluoride (CsF, KF) followed by its cocondensation with samples of SiF_4, $SiF_{4-n}Cl_n$ (n = 1-4) or Me_nSiF_{4-n} (n = 1, 2) in an argon matrix at low temperatures.

In conclusion we should mention a simple method for synthesising tripropylammonium pentafluorosilicate by reaction of tripropylamine with a solution of fluorosilicic acid (molar ratio 1 : 3).[25] Unfortunately, this method is not a general one and when other tertiary amines are used, double trialkylammonium hexa- and penta-fluorosilicates are formed.

III. Electronic structure and stereochemistry

It was pointed out[2,3] that the specific nature of the structure and reactivity of fluoro-complexes of non-transition elements is most adequately expressed in terms of hypervalent bonds.[26] The elements of Subgroup IVB are not formally classified among the types of hypervalency as proposed by Musher for the electron-rich elements of Subgroups VB–VIIB. The scope of Musher's ideas[26] was extended by Voronkov et al.,[27-30] who modified the initial scheme for formation of a four-electron, three-centre bond [unshared electron pair (UEP) of the central atom and two unpaired electrons from ligands] for representing the mechanism of axial bonding in pentacoordinate silicon(IV) complexes such as silatranes, (aroyloxymethyl)trifluorosilanes, and related compounds. In the complexes $X-Si(OCH_2CH_2)_3N$ and $XC_6H_4COOCH_2SiF_3$ the coordination of the silicon polyhedron is a slightly distorted trigonal bipyramid. The formation of the hypervalent axial fragments X–Si ← N and F–Si ← O occurs as a result of intramolecular coordination using the UEP of the ligand (a nitrogen or oxygen atom). Out of the four valence atomic orbitals of silicon, three ($3s$, $3p_x$, $3p_y$) participate in equatorial bonding as sp^2 hybrids, forming three two-electron two-centre bonds. The bond in the linear X–Si ← N fragment and the slightly bent F–Si ← O fragment ($\angle$FSiO = 175–179°) arises from the $3p_z$ atomic orbital of silicon and the atomic orbitals of the axial ligands (one from each atom), in other words, it is a three-orbital three-central or hypervalent-II bond according to Musher.[26] This scheme for axial bonding has been extended to the pentafluorosilicate anion and its substituted derivatives.

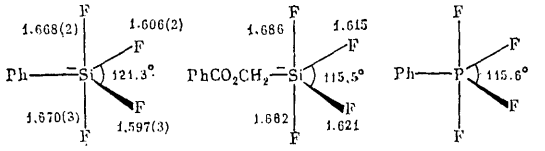
The first arguments in favour of a trigonal bipyramidal structure for the SiF_5^- anion were based on the results of spectroscopic studies.[7,21] In particular, according to the results of one study,[7] in the Raman spectrum of an acetonitrile solution of tetra-n-propylammonium pentafluorosilicate there was an intense polarised band at 708 cm^{-1} (A_1 mode), which was inactive in the IR spectrum; this was consistent with the SiF_5^- anion having D_{3h} symmetry. The marked similarities in the IR and Raman spectra of SiF_5^- and PF_5 (a trigonal bipyramidal configuration has been reliably established for the latter compound) support such a conclusion. An attempt to determine the structural parameters of the pentafluorosilicate anion in crystals of the salt $(Ph_4As)SiF_5$ proved unsuccessful because of the complex form of crystallographic randomisation.[31] More recently the results of an X-ray diffraction analysis of the complex salt $[IrH_2CO(PPh_3)_3]SiF_5$ were published.[10] The geometry of the SiF_5^- anion differed only slightly from the ideal trigonal bipyramidal form, but the accuracy in determining the structural parameters was limited by the intense vibrational movements of the anion and it amounted to 0.04 Å for the bond lengths and 4° for the bond angles. The lengths of the axial and equatorial Si–F bond coincided within the limits of experimental error and constituted 1.69 Å on average. A precise determination of the molecular structure of the SiF_5^- anion in the salt $(PhCH_2NMe_3)SiF_5$ was carried out only comparatively recently.[32] The pentafluorosilicate anion has a slightly distorted trigonal bipyramidal configuration with C_2 symmetry (the second-order axis passes through the silicon atom and one of the equatorial ligands), and in complete conformity with the model of Musher[26] the axial Si–F bonds are longer (weaker) than the equatorial bonds:



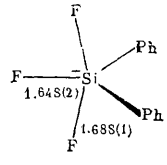
The axial F–Si–F fragment is virtually linear ($\angle F_aSiF_a$ = 179.4°). It is interesting that according to the results of an IR spectroscopic study, the pentafluorosilicate anion in matrix-isolated salts $MSiF_5$ (M = K^+ or Cs^+, which are comparable in size to the unsubstituted NH_4^+ cation) has an axially distorted geometry with C_{3v} symmetry.[23]

This observation can also have a natural explanation within the scope of the hypervalent bond model.[26] Since the scheme for three-centre bonding envisages a significant transfer of electron density within the axial F–Si–F group, the latter has high polarity and must have the maximum sensitivity towards the perturbing effect of small cations with high charge density and high polarising capacity.

The results of X-ray diffraction analysis of tetrapropylammonium phenyltetrafluorosilicate and 1,10-phenanthrolinium (benzoxymethyl)-tetrafluorosilicate are given in two reports.[33,34] The $[PhSiF_4]^-$ and $[PhCOOCH_2SiF_4]^-$ anions have a distorted trigonal bipyramidal structure with the phenyl or benzyloxymethyl group in an equatorial position:



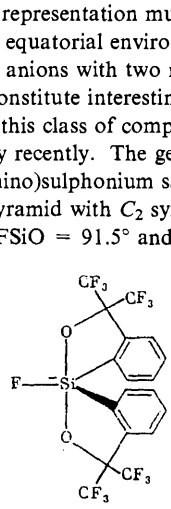
A similar structure was found for the isoelectronic phenyltetrafluorophosphorane.[35] The arrangement of electropositive ligands in the equatorial plane of the compounds and the nature of the angle deformations of the complexes when there is substitution are consistent with the concepts of hypervalency. The structure of the three-centre axial bonds is only stable in the case of highly electronegative ligands, whereby it follows from this model[26] that the axial and equatorial groups of bonds to a certain extent act independently in the transfer of electronic effects. It is logical to assume from this that the virtually identical angular distortion of the F_a-Si-F_a group in $[PhSiF_4]^-$ and the F_a-P-F_a group in $PhPF_4$ is due to the similar steric effect of the phenyl ligand in both complexes, whereas the differences in the equatorial angle deformations is caused by the steric and electronic effects acting in opposite directions. While the former compresses the angles in F_eSiF_e and F_ePF_e, the latter, on the other hand, increases them compared to the ideal angle for sp^2 hybrid atomic orbitals (120°) as a result of an increased *s* atomic orbital contribution in the Si–C and P–C bonds and a decreased *s* atomic orbital contribution in the Si–F and P–F bonds (Bent's rule[36]). For a complex of the more electropositive silicon ($EN_{Si} < EN_P$), the contribution of the 'electronic' component of the deformational forces proves to be greater than for the phosphorus derivative (the share of the *s* atomic orbital of Si in a Si–C bond is greater than the share of the *s* atomic orbital of P in a P–C bond), which, when the contribution of the steric effect from the phenyl group is deducted, results in the observed differences in the deformations of the equatorial angles ($\angle F_eSiF_e > \angle F_ePF_e$). An alternative interpretation of the nature of the angle deformations in the isoelectronic compounds $[PhSiF_4]^-$ and $PhPF_4$, based on the concepts of the Gillespie–Nyholm model,[37] is given by Schomburg.[33] According to the results of Schomburg and Krebs[32] a structural feature of the diphenyltrifluorosilicate anion in crystals of $(Me_4N)[Ph_2SiF_3]$ is the almost identical increase in length of the axial and equatorial Si–F bonds in comparision to the unsubstituted SiF_5^- anion. The angles of C_e-Si-C_e and F_a-Si-F_a are equal to 118.9 and 187.5° with ideal values of 120 and 180° respectively:



It should be noted that an equatorial configuration of the phenyl ligands in the trigonal bipyramidal structure of the $[Ph_2SiF_3]^-$ anion had previously been established in an analysis of the low-temperature ^{19}F NMR spectra of solutions of the salt $(Et_4N)[Ph_2SiF_3]$ in methylene chloride.[21] Similarly, the nature of the IR spectrum of the $[MeSiF_4]^-$ anion in the vibrational region for ν(SiF) (absorption bands at 712, 825, 837, and 862 cm^{-1}) and δ(SiF) (450 cm^{-1}) indicate that the anion has a symmetry which is of the type C_{2v} or lower, with the methyl group in the equatorial position.[24]

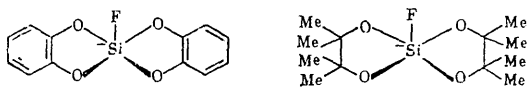
The structures of substituted anions of the type $[R_nSiF_{5-n}]^-$ (n = 1, 2) which have been examined above illustrate the validity of the well-known empirical rule of Muetterties,[38] which states that for a trigonal bipyramidal configuration of the complexes of non-transition elements, isomers with an axial orientation of the most electronegative substituents are stable. However, $SiF_4(L)$ complexes, L = Me_nNH_{3-n}, (n = 0–3) [39,40] or Py,[41] judging from the IR spectroscopy data, have a structure with the molecular ligands in the axial position, which is unexpected in relation to the models of Musher[26] and Gillespie.[37] This geometry, for the $SiF_4(NH_3)$ complex at least, has been accurately reproduced in *ab initio* calculations.[42,43] Out of the four alternative configurations of the coordination polyhedron of SiF_4N with C_{3v}, C_{2v}, C_{4v}, and C_s symmetry, the C_{3v} structure has the minimum energy, and according to the data of Mulliken population analysis the magnitude of the effective negative charge on the nitrogen atom (–1.15) is higher than the charges on the fluorine atoms [–0.49 (*a*), –0.48 (*e*)]. Subsequent to the study by Marsden,[42] if an attempt is made to correlate the electronegativities (Pauling) with the effective charges of the atoms (Mulliken), the axial position of the formally less electronegative nitrogen atom of the ammonia molecule in the trigonal bipyramidal structure of $SiF_4(NH_3)$ becomes clear. The results of quantum-chemical analysis show[44,45] (semiempirical MNDO method) that formation of the hypothetical anions $[XSiH_4]^-$ (X = H^-, F^-, Cl^-) and the molecular complex $FSiH_3(O=CH-OH)$ by the reaction $XSiH_3$ + Y (Y = H^-, O=CH–OH) is accompanied by a more substantial change (increase) in the interatomic distance of X_a-Si compared to the distance in H_e-Si. The latter is an indication of the *trans*-weakening effect on the axial bonds with a strengthening of coordination and is a logical consequence of the hypothetical models of Musher and Voronkov.[26,27] Frolov et al.[44,45] recorded significant contributions from the atomic orbitals of the equatorial ligands in the highest occupied molecular orbital (HOMO) representing the X_a-Si-H fragment in $[XSiH_4]^-$ anions. It was thus stressed that a complete hypervalent representation must take into account the atomic orbitals of the equatorial environment of the silicon atom.

Monofluorosilicate anions with two ring-forming *O*-donor ligands (λ^5-Si-spirosilicates) constitute interesting stereochemical compounds. The first examples of this class of compounds underwent structural analysis comparatively recently. The geometry of the anion (A) in the tris(dimethylamino)sulphonium salt is that of a slightly distorted trigonal bipyramid with C_2 symmetry: $\angle SiO$ = 176.6°, $\angle CSiC$ = 132.2°, $\angle FSiO$ = 91.5° and 91.9°, bond length of $Si-F_e$ 1.632(3) Å:[46]

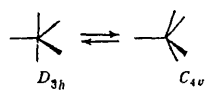


(A)

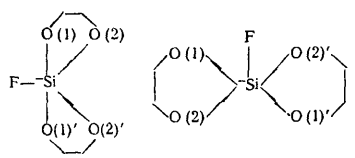
The structures of the spirobicyclic anions $[(OC_6H_4O)_2SiF]^-$ and $[(OCMe_2CMe_2O)_2SiF]^-$ have a different form of coordination polyhedron for silicon(IV):[47,48]



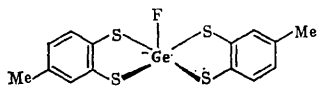
The immediate environment of the silicon atom in these complexes has a distorted tetragonal pyramidal (TP) structure. It was shown[49,50] that the structures of all known pentacoordinate complexes can be arranged in a series that exhibits a smooth transition from an ideal trigonal bipyramidal (TBP) geometry (D_{3h} symmetry) via an intermediate configuration with C_{2v} symmetry to a limiting TP geometry (C_{4v}). The observed deviations of the real structures of MX_5 complexes from the ideal D_{3h} and C_{4v} configurations corresponds to the C_{2v} coordinate in Berry pseudorotation:[51]



By using the formal procedures suggested by Porai-Koshits and Aslanov,[52] it is possible to make a quantitative comparison between the real structure of the pentacoordinate complex with C_{2v} symmetry and the D_{3h} and C_{4v} limiting configurations. The TBP limit is built up by arranging the O(1) and O(1)′ atoms of the spirobicyclic anion in axial positions and the O(2) and O(2)′ atoms in equatorial positions, while the TP limit is developed with an axial orientation of the fluorine atom:



In the Berry process the fluorine atom is a pivotal ligand. According to the results of two studies,[47,48] each of the $[(OC_6H_4O)_2SiF]^-$ and $[(OCMe_2CMe_2O)_2SiF]^-$ anions in tetraalkylammonium salts forms two crystallographically independent forms, which are distorted towards the TP limit by 68.7 and 52.8% or 69.1 and 52.3% respectively. It is interesting that distortion of the structure of the isoelectronic anion $[(OC_6H_4O)_2SiF]^-$ towards the TP limit even reaches 81%,[53] while similar deformations in the structure of the phosphorus analogue $(OC_6H_4O)_2PF$ amount to 65%.[54] Evidently the degrees of distortion of the coordination polyhedra of silicon(IV) and phosphorus(V) are fairly similar, while for a complex of the most electropositive of the three elements, germanium(IV), the deformation towards the C_{4v} limit are the greatest. The features of the structural deformations in pentacoordinate complexes of *p*-elements have been discussed in a review,[55] which includes the ideas of Gillespie and Nyholm. According to the hypervalent bond model, the TP structure of spirobicyclic monofluorosilicate anions and their isoelectronic analogues can be represented in terms of two hypervalent O–Si–O groups involving the $3p_x$ and $3p_y$ atomic orbitals of silicon, forming the equatorial plane of the complexes, and the sp_z hybrid for the Si–F bond. The increased stability of the TP configuration in the $[(OC_6H_4O)_2GeF]^-$ anion compared to the corresponding silicon(IV) and phosphorus(V) derivatives is completely natural since it is for the most electropositive germanium that the maximum stabilisation of the hypervalent three-centre groups is achieved. The importance of the condition $EN_A \ll EN_L$ being fulfilled for ensuring the stability of hypervalent L–A–L bonds becomes evident when the structures of $[(OC_6H_4O)_2CHF]^-$ and $[(SC_7H_6S)_2GeF]^-$ anions are compared.[53] Despite the structural similarity of the chelate ligands in these complexes, the thio analogue



is distorted towards the ideal TP configuration by only 40%.

The similarity noted above between the quantitative characteristics of structural deformations in pentacoordinate isoelectronic fluorocomplexes of silicon(IV) and phosphorus(V) may be related to the ideas of Bartlett[5] on the characteristic separation energy of *ns* and *np* orbitals for non-transition elements of a given *n*th Period. His hypothesis[56] was based on the known fact that the bond angles have an approximately equal value in each of the series of isoelectronic compounds of *p*-elements in an incomplete valency state: $PF_3-SF_3^+$, $AsF_3-SeF_3^+$, $SbF_5^{2-}-TeF_5^-$, $IF-XeF_5^+$. Subsequently, Bartlett's ideas[56] were used to account for the similarity in the values of isomerisation constants of isoelectronic hexacoordinate tetrafluoro-complexes of *p*-elements of Groups IV–VI in the third to fifth Periods.[57] We can show that the automatic extension of Bartlett's ideas[56] to complexes with central atoms in higher oxidation states is not absolutely correct. While for TP complexes of the type AF_5E (E = UEP) the equatorial F–A–F bonds have a pure *p* character (hypervalent-I bonds in the terminology of Musher[26]), in TBP and TP structures of complexes of Group IV–V elements the axial and equatorial bonding based on three-centre L–A–L groups requires a given contribution from the *ns* atomic orbital of atom A (hypervalent-II bond). For symmetry considerations this contribution is usually neglected,[27] but it is very probable that the observed differences in the structural deformations of pentacoordinate silicon(IV) and phosphorus(V) fluoro-complexes are due to the varying degree of disproportionation of the hypervalent bonding system[58] of these elements with unequal contributions from the 3*s* atomic orbitals of the central atoms.

IV. Properties

Tetraalkylammonium pentafluorosilicates as solutions in nitromethane behave as 1:1 electrolytes.[7] In aqueous solution pentafluorosilicates are hydrolysed to a considerable degree.[7] According to the studies of Harris and Rudner[11] the hydrolysis of trimethylammonium pentafluorosilicate in moist air is given by the equation:

$$2SiF_5^- + 2H_2O \rightarrow SiF_6^{2-} + SiO_2 + 4HF.$$

Judging by the IR spectroscopic data, the SiF_5^- anion undergoes a similar conversion when the double salt $(Et_2NH_2)_2SiF_6(Et_2NH_2)SiF_5$ is dissolved in water.[13] The ^{19}F NMR spectra of a 19.1% aqueous solution of $(Pr_3NH)SiF_5$ indicate that a more complex equilibrium occurs:[59]

$$3SiF_5^- + 3H_2O \rightarrow SiF_6^{2-} + [SiF_5(H_2O)]^- + SiO_2 + 4HF.$$

Heating of an aqueous solution of $(Ph_4As)SiF_5$ leads to rapid and quantitative hydrolysis[8] in accordance with the equation:

$$SiF_5^- + 2H_2O \rightarrow F^- + SiO_2 + 4HF.$$

At the same time Kleboth[60] made a satisfactory interpretation of the IR and Raman spectra of an aqueous solution of tetraethylammonium

pentafluorosilicate by proposing C_{4v} symmetry for the coordination polyhedron of silicon, in other words, the formation of an aqueous pentafluoroaquo-complex is not accompanied by disproportionation of fluorine [sic] in solution:

$$SiF_5^- + H_2O \rightarrow [SiF_5(H_2O)]^-.$$

The stability of dialkyl-, trialkyl- and tetraalkyl-ammonium pentafluorosilicates regularly increases with the size of the cation,[7,12,13] which is due to the decrease in its polarising effect. For example, diisopropylethylamine forms a stable pentafluorosilicate. Triethylammonium pentafluorosilicate is stable in benzene and acetonitrile solutions but when the solvent is removed SiF_4 is lost and there is formation of the compound $(Et_3NH)_4Si_3F_{16}$, which is the double salt $(Et_3NH)_2SiF_6.2(Et_3NH)SiF_5$.[20] The salt $(Me_3NH)SiF_5$, with a smaller cation, is stable in acetonitrile but not in benzene solutions. However, all attempts to isolate trimethylammonium pentafluorosilicate by crystallisation at low temperatures have led to a product of composition $(Me_3NH)_3Si_2F_{11}$.[12] Similarly, diethyl- and dibutylammonium pentafluorosilicates are stable in a solvating acetone medium; removal of the solvent is accompanied by the formation of the double salt $(R_2NH_2)_2SiF_6.(R_2NH_2)SiF_5$.[13] According to Durkin and Schram,[9] the compound $(Pr_4N)SiF_5$ is stable on heating to 230 °C in a vacuum whereas tetramethylammonium pentafluorosilicate disproportionates at 100 °C according to the equation

$$2(Me_4N)SiF_5 \rightarrow SiF_4 + (Me_4N)_2SiF_6.$$

This was confirmed by the IR spectrum of the solid residue.[61] According to the results of thermogravimetric analysis,[25] tripropylammonium pentafluorosilicate dissociates over the temperature range 207–273 °C with the components passing complete into the gas phase:

$$(Pr_3NH)SiF_5 \rightarrow SiF_4 + HF + Pr_3N.$$

In two studies[13,62] it is proposed that the act of dissociation of pentafluorosilicates should be regarded as the vibrational movement of an anion of the type A_2'' smoothly converting the SiF_5^- complex of D_{3h} symmetry to an SiF_4 molecule (T_d). The intermediate distorted structures of the SiF_5^- anion, which link the initial geometry of the complex with the tetrahedral reaction product, should have C_{3v} symmetry:

$$SiF_5^-(D_{3h}) \rightleftarrows SiF_5^-(C_{3v}) \rightleftarrows SiF_4(T_d) + F^-.$$

According to the method of structural correlations,[63] the A_2'' route for the SiF_5^- anion may be reconstructed by analysing the geometric deformation of the anion in crystalline structures of pentafluorosilicates with cations of varying polarising effect. As was mentioned above, the geometry of the SiF_5^- anion in salts with large cations only slightly differs from an ideal TBP, while in $MSiF_5$ ($M = K^+$, Cs^+) salts that were isolated in a low-temperature matrix an axially distorted structure of the anion with C_{3v} symmetry was found as expected.

Having marked acceptor properties, tetraalkylammonium pentafluorosilicates react with ammonia[7,61,64] and methylamines[61] to form complex salts $(R_4N)[SiF_5(Me_nNH_{3-n})]$ ($n = 0$–3) which are isolated in a pure state. By using spectroscopic methods it was possible to study the donor-acceptor interaction between the SiF_5^- anion and a number of bases in non-aqueous media. Clark et al.[7] used IR spectroscopy to study complex formation in the system $SiF_5^- - L - MeCN$, having previously established that the process of dissolving pentafluorosilicate in acetonitrile is not accompanied by coordination of solvent molecules. An increase in concentration of the molecular ligand L produced a decrease in the intensity of the $\nu(Si-F)$ absorption band at ~ 874 cm^{-1} that is characteristic for the SiF_5^- anion. On the basis of this the following order of change in ligand donor capacity relative to SiF_5^- was established:

$$Et_2NH > Et_3N > n\text{-}Pr_3N > Py \sim Et_3P.$$

The basicity of these ligands decreases in the same series. According to the results of Gibson et al.,[65] introduction of ammonia or diethylamine into a solution of $(Pr_4N)SiF_5$ in methylene chloride results in the equilibrium

$$SiF_5^- + L \rightleftarrows [SiF_5(L)]^-,$$

which can be monitored by ^{19}F NMR spectroscopy. When the temperature is lowered, there is a shift in the equilibrium towards the formation of the pseudooctahedral anion.

It is interesting that by studying the interaction of $(Pr_4N)[PhSiF_4]$ and Pr_4NF in methylene chloride it was possible to resolve the problem concerning the structure of complex anions $[RSiF_5]^{2-}$ which had remained the subject of controversy for a considerable length of time. The opinion was held[21,66] that in the absence of structural data compounds with the empirical formula $M_2[RSiF_5]$ (M is an alkali metal, ammonium, or alkylammonium cation) should be regarded as double salts $M_2[RSiF_4]F$ containing pentacoordinate anions $[RSiF_4]^-$ rather than substituted derivatives of the corresponding hexafluorosilicates. However, Marat and Janzen[66] established that the $[PhSiF_4]^-$ anion accepts a fluoride ion to give a hexacoordinate complex $[PhSiF_5]^{2-}$, which has a structure that can be clearly demonstrated by low-temperature ^{19}F NMR spectroscopy.

The pentafluorosilicate anion may be regarded as the product of partial compensation of the acceptor capacity of silicon tetrafluoride by coordination of a single fluoride ion with the latter. Consequently the SiF_5^- anion should have a lower Lewis acidity than the initial SiF_4 molecule. This fairly obvious conclusion has been confirmed from quantitative data on the enthalpy of dissociation of the complexes $(R_4N)[SiF_4(L)]$ and $SiF_4(L)_2$:

$$(R_4N)[SiF_5(L)](s) \rightarrow (R_4N)SiF_5(s) + L(g),$$
$$SiF_4(L)_2(s) \rightarrow SiF_4(g) + 2L(g).$$

The determination was made using the results of tensiometric measurements (Table 1).

The noticeable difference in the values of the enthalpy of dissociation that were obtained by different research workers attracts attention. According to Wharf and Onyszchuk[64] the value $\Delta H = 7.9$ kcal mol^{-1} is not the true enthalpy of dissociation of the complex but is an average enthalpy for two processes—the adsorption of ammonia on the surface of solid pentafluorosilicate and the actual dissociation of the complex. It follows from the data of Table 1 that the enthalpies of dissociation of complexes $(R_4N)[SiF_5(NH_3)]$ depend on the size of the cation, increasing in the series $Et_4N^+ < Pr_4N^+ < Bu_4N^+ \sim Pent_4N^+$. The following thermodynamic cycle was examined in one report:[61]

$$\begin{array}{ccc} (R_4N)[SiF_5(NH_3)](s) & \xrightarrow{\Delta H_1} & NH_3(g) + (R_4N)SiF_5(s) \\ \downarrow & & \downarrow \\ R_4N^+(g) + [SiF_5(NH_3)]^-(g) & \xrightarrow{\Delta H_2} & NH_3(g) + R_4N^+(g) + SiF_5^-(g), \end{array}$$

From which

$$\Delta H_1 = \Delta H_2 + (U_1 - U_2).$$

It was proposed[61] that for complexes $(R_4N)SiF_5$ and $(R_4N)[SiF_5(NH_3)]$ with cations that are greater in size than the anions SiF_5^- and

$[SiF_5(NH_3)]^-$ the structure of the crystal lattice is mainly determined by the packing of the cation and the crystal lattice energies of the complexes are very similar. When this approximation is used ($U_1 = U_2$), the experimentally determined enthalpy of dissociation (ΔH_1) and the corresponding value (ΔH_2) for the process in the gas phase which is not dependent on the nature of the cation become equal. Wharf and Onyszchuk[61] assumed that the condition $U_1 = U_2$ was met for the tetrabutyl- and tetrapentyl-ammonium complexes and the slight difference in enthalpy of dissociation for these compounds could occur because the term $(U_1 - U_2)$ was the difference between two large quantities. A value of $\Delta H^0 = 16.8 \pm 0.6$ kcal mol^{-1} was taken by Wharf and Onyszchuk[61] to be the lower limit of the enthalpy of dissociation of the complex anion $[SiF_5(NH_3)]^-$ in the gas phase. If the crystal lattice energies of the complexes $(R_4N)[SiF_5(L)]$ and $SiF_4(L)_2$ are assumed to have similar values,[64] the thermochemical data given in Table 1 indicate that the SiF_5^- anion has a lower acceptor capacity than silicon tetrafluoride relative to this group of donors.

Table 1. Enthalpies of dissociation of silicon fluoro-complexes with nitrogen-donor ligands.

Complex	ΔH^0, kcal mol^{-1}	Refs.
$(Et_4N)[SiF_5(NH_3)]$	6.0±0.4	[61]
$(Pr_4N)[SiF_5(NH_3)]$	12.0±0.5	[61, 64]
»	7.9	[7]
$(Bu_4N)[SiF_5(NH_3)]$	16.8±0.6	[61]
$(Pent_4N)[SiF_5(NH_3)]$ *	14.5±0.7	[61]
$(Pent_4N)[SiF_5(MeNH_2)]$	14.3±0.3	[61]
$(Pent_4N)[SiF_5(Me_2NH)]$	12.3±0.3	[61]
$(Pent_4N)[SiF_5(Me_3N)]$	12.4±0.7	[61]
$SiF_4(NH_3)_2$	52.7±1.9	[67]
»	54.6	[68]
$SiF_4(MeNH_2)_2$	58.1±1.9	[67]
$SiF_4(Me_2NH)_2$	55.2±0.7	[67]
$SiF_4(Me_3N)_2$	40.5±0.4	[67]
»	41.5	[69]

*Pent = C_5H_{11}.

V. Mechanisms of intra- and inter-molecular ligand exchange in solution

IR and Raman spectroscopic studies indicate[7] that the SiF_5^- anion in the solid state and in non-aqueous solution exists in the TBP configuration with non-equivalent axial and equatorial Si–F bonds. At the same time ^{19}F NMR spectra of pentafluorosilicates show that all the fluorine atoms are equivalent.[16,21,65] This apparent contradiction may be due to the difference in time-scale characteristics of these methods and to the rapid (on the time-scale of NMR) exchange of axial and equatorial fluorine atoms. It can be seen from the data given in Table 2 that spectroscopic equivalence of the fluorine atom is also exhibited in the monosubstituted anions $[RSiF_4]^-$ and $[XSiF_4]^-$ but the low-temperature ^{19}F NMR spectra of the disubstituted anions $[Ph_2SiF_3]^-$ and $[PhMeSiF_3]^-$ contain separate signals from the non-equivalent F_a and F_e.

The fact that $^{29}Si-^{19}F$ spin-spin coupling is preserved in the ^{19}F NMR spectra of solutions of pentafluorosilicates at temperatures below –60 °C has been related[21] to the intramolecular nature of ligand exchange, which most probably occurs by the pseudorotation mechanism proposed by Berry.[51] It may be recalled that exchange results in the transposition of two axial and two equatorial ligands in the TBP anion structure. The TP configuration acts as an intermediate state in this polytopic rearrangement.[71] The temperature dependence of the shape of the lines in the NMR spectra[46,70,72,73] is consistent with the pseudorotation mechanism of Berry for pentacoordinate fluorosilicate anions, although alternative mechanisms cannot be entirely excluded.[61,64] Damrauer and Danahey[70] calculated the activation parameters for intramolecular fluorine exchange in $[Ph_2SiF_3]^-$ and $[PhMeSiF_3]^-$ anions. The results obtained are given in Table 3 together with data for related pentacoordinate trifluorosilyl molecular complexes.

Table 2. ^{19}F NMR spectroscopic parameters of pentacoordinate fluorosilicate anions in non-aqueous solution.[21,22,70]

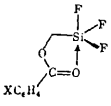
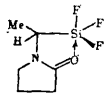
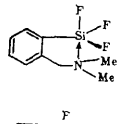
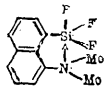
Compound	Solvent	^{19}F Chemical shift, rel. to $CFCl_3$, p.p.m.	$J(^{29}Si-^{19}F)$, Hz	t, °C
$(Pr_4N)SiF_5$	CH_2Cl_2	136.0	148±2	–66
$(Pr_4N)[MeSiF_4]$	CH_2Cl_2	110.9	218±1	–60
$(Bu_4N)[MeSiF_4]$	CH_2Cl_2	110.5	218	–60
$(Pr_4N)[BuSiF_4]$	CH_2Cl_2	116.6	223±2	–62
$(Me_4N)[PhSiF_4]$	Me_2SO	116.8	205	25
$(Pr_4N)[PhSiF_4]$	$CHCl_3$	119.2	206±2	35
$(Et_4N)[Ph_2SiF_3]$	CH_2Cl_2	98.0 (F_a); 134.0 (F_e)	254±4 212±2	–62
(18-crown-6.K)$[Ph_2SiF_3]$	acetone-d_6/vinyl chloride	100.5 (F_a); 133.9 (F_e)	252.7 204.6	–62
(18-crown-6.K)$[PhMeSiF_3]$	acetone-d_6/vinyl chloride	83.5 (F_a); 133.3 (F_e)	251 210	–62
$(Me_4N)[CF_3COOSiF_4]$	SO_2	124.9	92	–75
$(Me_4N)[MeCOOSiF_4]$	SO_2	120.8	155	–75
$(Me_4N)[PhSSiF_4]$	SO_2	125.5	—	–75
$(Me_4N)[ClO_3SiF_4]$	CH_2Cl_2	135.7	—	–75
$(Me_4N)[HCOOSiF_4]$	SO_2	117.8	—	–75
$(Me_4N)[NO_2SiF_4]$	CH_2Cl_2	136.5	150	–75
$(Me_4N)[NO_3SiF_4]$	CH_2Cl_2	142.3	—	–75
$(Me_4N)[N_3SiF_4]$	CH_2Cl_2	136.0	132	–75
$(Me_4N)[CNSiF_4]$	SO_2	130.1	105	–75
$(Me_4N)[SCNSiF_4]$	SO_2	148.7	—	–75

It is evident from the data of Table 3 that the energy barriers for intramolecular exchange of fluorine in pentacoordinate anionic and molecular SiF_3 derivative forms are very similar. It should be noted that the results from temperature-dependent ^{19}F NMR spectroscopic studies on 2-{(methyltrifluorosilylamino)methyl}pyridine[79] and 1-(trifluorosilyl)-1,2,3,4-tetrahydro-1,10-phenanthroline [80] (energy barriers for fluorine exchange are 13.2 and 7.5 kcal mol^{-1} respectively) were interpreted by the authors of these studies in terms of an exchange model which incorporated the cleavage of an intramolecular Si ← N coordinate bond followed by rotation of the SiF_3 group in the tetrahedral intermediate. It was suggested[80] that this type of scheme for fluorine exchange is to be preferred to the alternative mechanisms for compounds with relatively weak intramolecular Si ← N coordinate bonds.

Wilhite and Spialter[81] carried out non-empirical calculations on the mechanism of the Berry pseudorotation for the hypothetical anions SiH_5^- and $[SiH_{5-n}X_n]^-$ (n = 1–5), where introduction of a more electronegative substituent X (EN_X = 2.9 on the Pauling scale) was formally effected by increasing the charge of the hydrogen atomic nucleus to +1.1. It was found that the pseudorotation barriers for SiH_5^- and SiX_5^- complexes were small (2.87 and

2.94 kcal mol^{-1} respectively) and that rearrangement took place almost freely whereas pseudorotation in the mixed anion $[SiH_2X_3]^-$ occurred via several alternative configurations and required a greater consumption of energy (about 7.03 kcal mol^{-1}). According to similar *ab initio* calculations on the rearrangements of PF_5 and PF_3H_2 molecules,[82,83] the change to trifluorophosphorane, as in the case of the substituted anion $[SiH_2X_3]^-$, is accompanied by an increase in the pseudorotation barrier and a greater complexity of rearrangement mechanism, the calculated values of the energy barriers being similar to the experimental values. If it is assumed that SiX_5^- and $[SiH_2X_3]^-$ complexes to a given approximation simulate the behaviour of the real anions SiF_5^-, $[Ph_2SiF_3]^-$, and $[PhMeSiF_3]^-$, the decrease in rate of axial-equatorial exchange of fluorine atoms on going from SiF_5^- to $[Ph_2SiF_3]^-$ and $[PhMeSiF_3]^-$ becomes clear.[21,70] Calculations[81-83] confirm the empirical rule of Muetterties and Schunn,[38] according to which isomers with an axial orientation of the electronegative substituents are the most stable for the TBP configuration of complexes of non-transition elements.

Table 3. Activation parameters for intramolecular exchange of fluorine in pentacoordinate trifluorosilyl complexes.

Compound	$\Delta G^{\neq}$, kcal mol^{-1}	$\Delta H^{\neq}$, kcal mol^{-1}	$\Delta S^{\neq}$, cal deg^{-1} mol	Refs.
$[Ph_2SiF_3]^-$	11.7	11.2	2.5	[70]
$[PhMeSiF_3]^-$	9.9	9.4	−4.4	[70]
	7.4—9.0	—	—	[75]
	9.5	—	—	[76]
	13.1	—	—	[77]
	12.0	—	—	[78]

A discussion of the probable mechanisms for intermolecular exchange of fluorine in pentacoordinate fluorosilicate anions first appeared in a study of Klanberg and Muetterties.[21] These authors proposed that the broadening of the ^{19}F NMR resonance signal from the SiF_5^- anion for a solution of tetrapropylammonium pentafluorosilicate in methylene chloride with a loss of the fine structure from $^{29}Si-^{19}F$ at temperatures above −60 °C could be due to either the dissociation:

$$SiF_5^- \rightleftarrows SiF_4 + F^-,$$

or association with formation of polymeric anions with fluoride bridges:

$$nSiF_5^- \rightleftarrows (nSiF_5)^-,$$

with both equilibria accompanied by cleavage of Si−F bonds. When the Lewis acidity of the pentafluorosilicate anion was taken into consideration, an associative mechanism was considered[21] to be the most favourable. On the other hand, alkyl- and aryl-substituted $[R_nSiF_{5-n}]^-$ anions have a much lower acceptor capacity than SiF_5^- and so dissociation is more probable for such compounds:

$$[Ph_2SiF_3]^- \rightleftarrows Ph_2SiF_2 + F^-.$$

This conclusion is indirectly confirmed by the results of a non-empirical calculation on the energy of the intermolecular ligand exchange in hypothetical $[SiH_{5-n}X_n]^-$ anions[81] (Table 4). However, the results of Damrauer and Danahey,[70] which demonstrate the absence of dissociative exchange of fluorine in solutions of $[Ph_2SiF_3]^-$ over a wide temperature range (^{19}F and ^{29}Si NMR data), should be noted. An important factor in this case is the relatively high dielectric constant of the solvent used[70] (acetone-d_6/vinyl chloride), which should favour this particular dissociative process involving the $[Ph_2SiF_3]^-$ anion.

Table 4. Calculated values of ΔH for intermolecular exchange in the hypothetical systems $[SiH_{5-n}X_n]^-$.

n	Reaction	ΔH, kcal mol^{-1}*
0	$SiH_4 + H^- \rightleftarrows SiH_5^-$	16.97 (16.97)
1	$SiH_4 + X^- \rightleftarrows [SiH_4X]^-$	12.59 (35.77)
2	$SiH_3X + X^- \rightleftarrows [SiH_3X_2]^-$	30.16 (55.08)
3	$SiH_2X_2 + X^- \rightleftarrows [SiH_2X_3]^-$	44.05 (70.72)
4	$SiHX_3 + X^- \rightleftarrows [SiHX_4]^-$	58.27 (86.73)
5	$SiX_4 + X^- \rightleftarrows SiX_5^-$	72.79

*Values in brackets refer to a reaction with hydride ion as the leaving group.

It cannot be ruled out that the occurrence of a given mechanism for fluorine exchange in the diphenyltrifluorosilicate anion—intermolecular dissociative exchange for a solution of $(Et_4N)[Ph_2SiF_3]$ in methylene chloride[21] and the intramolecular Berry process for a solution of (18-crown-6.K)$[Ph_2SiF_3]$ in an acetone-d_6/vinyl chloride mixture[70]—is due to the differences in polarising effects of the external cations. When the higher charge density on the Et_4N^+ cation compared to $(18\text{-crown-6.K})^+$ is taken into account, these difference in the mechanism for fluorine exchange in diphenyltrifluorosilicates then become completely consistent. In this connection there are some interesting results[84] which indicate that in non-aqueous solutions of trialkyl- and dialkyl-ammonium pentafluorosilicates dissociative intermolecular exchange of fluorine is occurring:

$$2SiF_5^- \rightleftarrows SiF_4 + SiF_6^{2-}.$$

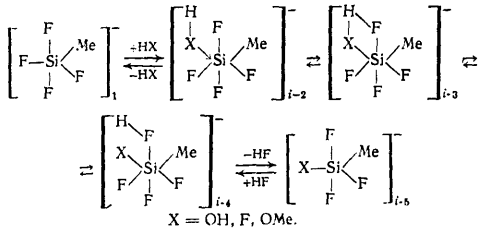
It was indicated[21] that intermolecular exchange processes with cleavage of Si–F bonds in pentacoordinate fluorosilicate anions may be caused by the presence of impurities in the samples studied. This question has been the subject of special studies.[65,85] The connection between exchange and hydrolysis processes is the most obvious. For example, the reversible loss of fine structure in ^{19}F NMR spectra of non-aqueous solutions of tetraalkylammonium pentafluorosilicate and methyltetrafluorosilicate when water is added to the samples followed by treatment with hexamethyldisilazane is consistent[65,85] with a hydrolysis mechanism of intermolecular fluorine exchange:

$$SiF_5^- + H_2O \rightleftarrows [SiF_4OH]^- + HF,$$
$$[MeSiF_4]^- + H_2O \rightleftarrows [MeSiF_3OH]^- + HF.$$

The action of $(Me_3Si)_2NH$ leads to HF, which is a fluorine carrier in the exchange process, being removed from the system by the reaction:

$$(Me_3Si)_2NH + 2HF \rightarrow 2Me_3SiF + NH_3.$$

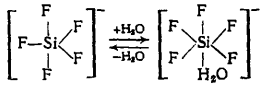
By using the concept of the change in coordination numbers of elements during the reaction, namely, Si(5) ⇆ Si(6), H(1) ⇆ H(2), F(1) ⇆ F(2), O(2) ⇆ O(3), Marat and Janzen[85] proposed the following generalised mechanism for intermolecular exchange of fluorine in the $[MeSiF_4]^-$ anion in the presence of H_2O, HF, or MeOH:



X = OH, F, OMe.

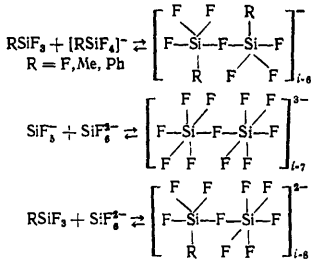
At the first stage the formation of the hexacoordinate intermediate *i*-2 is postulated, which is converted by a four-centre mechanism to *i*-3. The subsequent cleavage of the X–H bond and elimination of an HF molecule leads to the substitution product *i*-5.

It was demonstated[16,65] that the Lewis acid-base interaction in the system $SiF_5 - H_2O$ and the rapid exchange between penta- and hexacoordinate complexes can be taken as the basis for the mechanism of low-temperature intramolecular axial-equatorial ligand exchange in the SiF_5^- anion:



Exchange leads to 'averaging out' of the position of the fluorine atoms in the coordination polyhedron, but their bond with the silicon atom is preserved.

In conclusion, mention should be made of the results of the study by Marat and Janzen[16] on the intermolecular exchange of fluorine in the systems $SiF_4^- - SiF_5^-$, $MeSiF_3 - [MeSiF_4]^-$, $PhSiF_3 - [PhSiF_4]^-$, $SiF_5^- - SiF_6^{2-}$, $SiF_4 - SiF_6^{2-}$, and $MeSiF_3 - SiF_6^{2-}$ (external cation Pr_4N^+). The ^{19}F, ^1H, and ^{13}C NMR spectroscopic data obtained[16] were interpreted on the basis of the coordination model of the reaction mechanism[85] involving a change in coordination numbers Si(4) ⇆ Si(5), Si(5) ⇆ Si(6), Si(4) ⇆ Si(5) ⇆ Si(6), F(1) ⇆ F(2) in formation of the intermediates *i*-6, *i*-7, and *i*-8:



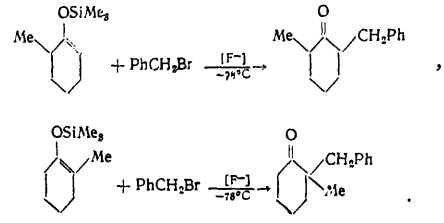
According to the results of this study[16] intermolecular exchange of fluorine is rapid (on the time-scale of NMR) if the fluoro-complexes participating in exchange have different coordination numbers. For example, introduction of excess ammonia into the system $SiF_5^- - SiF_6^{2-}$ inhibits exchange because of the formation of the hexacoordinate complex $[SiF_5(NH_3)]^-$. On the other hand, addition of diethylamine to a sample of $MeSiF_3$ is accompanied by a loss of fine structure from $^{19}F-Si-C-^1H$ spin-spin coupling in its ^{19}F and ^1H NMR spectra since $MeSiF_3$ is involved in exchange with penta- and hexacoordinate products of donor-acceptor interaction.

VI. Use in preparative synthesis

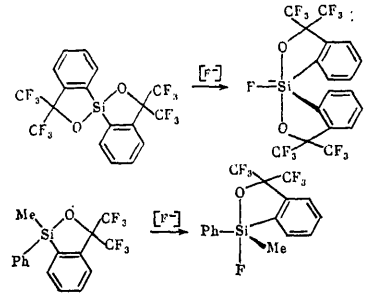
The known examples where salts of pentacoordinate fluorosilicate anions have been used in preparative synthesis are few in number but they serve as a good illustration of the synthetic possibilities of this class of compounds. Thus, tris(dialkylamino)sulphonium trimethyldifluorosilicates, which are fairly readily available and stable, serve as useful sources of the unhydrated fluoride ion:[86]

$$[(R_2N)_3S][Me_3SiF_2] \rightleftarrows (R_2N)_3S^+ + F^- + Me_3SiF.$$

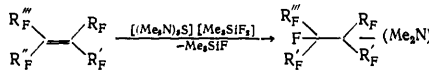
In the presence of $[(Et_2N)_3S][Me_3SiF_2]$, silyl enol ethers readily react under very mild conditions with primary alkyl bromides and alkyl iodides to form products from regiospecific *C*-monoalkylation (yield 60–95%):[87]



The analogous derivative, $[(Me_2N)_3S][Me_3SiF_2]$, was used in the synthesis of pentacoordinate monofluorosilicates:[46]



It was recently shown[88] that tris(dimethylamino)sulphonium trimethyldifluorosilicate reacts with perfluoroolefins in THF or acetonitrile to form stable fluorocarbanion salts:



Reactions of $(Me_2N)_3S^+CF_3(CF_2)_2C^-(CF_3)_2$ with a number of organic compounds have been reported, demonstrating the synthetic value of the salts obtained.

In two studies Gel'mbol'dt[89,90] has proposed a method for the synthesis of hexacoordinate silicon tetrafluoride complexes with molecular nitrogen-donor ligands by reaction of tripropylammonium pentafluorosilicate or the double fluorosilicates $(R_3NH)_2SiF_6.2(R_3NH)SiF_5$ (R = Et, Bu) with the respective bases in methylene chloride or acetonitrile, for example:

$$2SiF_5^- + \alpha,\alpha'\text{-Bipy} \rightarrow SiF_4(\alpha,\alpha'\text{-Bipy}) + SiF_6^{2-}.$$

This method of synthesis does not require operations involving gaseous silicon tetrafluoride; $SiF_4(L)$ complexes are virtually insoluble in the solvents used and are readily separated from a solution of trialkylammonium hexafluorosilicate. The use of alcohol solutions of silicon tetrafluoride[91] to obtain such compounds is unacceptable since even a base of medium strength such as aniline and especially highly basic amines bring about the alcoholysis of SiF_4.[92]

Finally, we should mention a simple and effective variant of the synthesis of graphite intercalation compounds by reaction of the readily available salt $C_{24}SiF_5$ [93,94] with strong Lewis acids such as PF_5, BF_3, or $C_6F_5PF_4$:

$$C_{24}SiF_5 + 2PF_5 \rightarrow C_{24}PF_6 \cdot PF_5 + SiF_4,$$
$$C_{24}PF_6 \cdot PF_5 \xrightarrow{20\ ^\circ C,\ \text{vacuum}} C_{24}PF_6 + PF_5,$$
$$C_{24}SiF_5 + C_6F_5PF_4 \rightarrow C_{24}C_6F_5PF_5 + SiF_4.$$

This method compares favourably with the traditional scheme for the synthesis of salts of graphite with fluorine-containing anions because of the possibility of using Lewis acids such as $C_6F_5PF_4$ which are unstable towards elemental fluorine.

References

1. L Sommer *Stereochemistry and Reaction Mechanisms of Organosilicon Compounds* (Translated into Russian), Izd. Mir, Moscow, 1966
2. A A Ennan, L A Gavrilova, V O Gel'mbol'dt *Usp. Khim.*, 1986, **55**(9) 1480 [English translation in *Russ. Chem. Rev.*, 1986(9)]
3. V O Gel'mbol'dt, A A Ennan *Koord. Khim.*, 1982, **8** 1176
4. M I Kabachnik, N N Bubnov, S P Solodovnikov, A I Prokof'ev *Usp. Khim.*, 1978, **53**(3) 487 [English translation in *Russ. Chem. Rev.*, 1984(3)]
5. H C Clark, P W R Corfield, K R Dixon, J A Ibers *J. Am. Chem. Soc.*, 1967, **89** 3360
6. H C Clark, K R Dixon, *J Chem. Soc., Chem. Comm.*, 1967, 717
7. H C Clark, K R Dixon, L G Nicolson *Inorg. Chem.*, 1969 **8** 450
8. K Behrends, G Kiel *Naturwissenschaften*, 1967, **54** 537
9. T R Durkin, E P Schram *Inorg. Chem.*, 1972, **11** 1948
10. P Bird, J F Harrod, K A Than *J. Am. Chem. Soc.*, 1974, **96** 1222
11. J J Harris, B Rudner *J. Am. Chem. Soc.*, 1968, **90** 515
12. J J Harris, B Rudner *J. Inorg. Nucl. Chem.*, 1972, **34** 75
13. V O Gel'mbol'dt, L A Gavrilova, P N Yurkevich, A A Ennan *Zh. Neorg. Khim.*, 1986, **31**(9) 2423 [English translation in *Russ. J. Inorg. Chem.*, 1986(9)]
14. L A Gavrilova, V O Gel'mbol'dt, P N Yurkevich, A A Ennan *Tezisy Dokladov IX Ukrainskoi Respublikanskoi Konferentsii po Neorganicheskoi Khimii* (Abstracts of Reports at the IXth Ukrainian Republic Conference on Inorganic Chemistry), Izd. KGU, Kiev, 1986, p. 37
15. V O Gel'mbol'dt, P N Yurkevich, L A Gavrilova, et al. *Tezisy Dokladov VIII Vsesoyuznogo Simpoziuma po Khimii Neorganicheskikh Ftoridov* (Abstracts of Reports at the VIIIth All-Union Symposium on the Chemistry of Inorganic Fluorides), Izd. Nauka, Moscow, 1987, p. 102
16. R K Marat, A F Janzen, *Can. J. Chem.*, 1977, **55** 3845
17. A A Ennan, L A Gavrilova, V O Gel'mbol'dt, S P Petrosyants *Zh. Neorg. Khim.*, 1981, **26**(11) 2964 [English translation in *Russ. J. Inorg. Chem.*, 1981(11)]
18. V O Gel'mbol'dt, L A Gavrilova, A A Ennan, S P Petrosyants *Zh. Neorg. Khim.*, 1983, **28**(10) 2693 [English translation in *Russ. J. Inorg. Chem.*, 1983(10)]
19. V O Gel'mbol'dt, L A Gavrilova, A A Ennan, S P Petrosyants *Zh. Neorg. Khim.*, 1985, **30**(5) 1173 [English translation in *Russ. J. Inorg. Chem.*, 1985(5)]
20. V O Gel'mbol'dt, L A Gavrilova, S P Petrosyants, A A Ennan *Koord. Khim.*, 1985, **11** 1077
21. F Klanberg, E L Muetterties *Inorg. Chem.*, 1968, **7** 155
22. S Brownstein *Can. J. Chem.*, 1980, **58** 1407
23. B S Ault *Inorg. Chem.*, 1979, **18** 3339
24. B S Ault, U Tandoc *Inorg. Chem.*, 1981, **20** 1937
25. V O Gel'mbol'dt, L A Gavrilova, P N Yurkevich, A A Ennan *Zh. Neorg. Khim.*, 1985, **30**(6) 1597 [English translation in *Russ. J. Inorg. Chem.*, 1985(6)]
26. J J Musher *Angew. Chem., Int. Ed. Engl.*, 1969, **8** 54
27. V F Sidorkin, V A Pestunovich, M G Voronkov *Dokl. Akad. Nauk SSSR*, 1977, **235** 1363
28. V F Sidorkin, V A Pestunovich, M G Voronkov *Usp. Khim.*, 1980, **49**(5) 789 [English translation in *Russ. Chem. Rev.*, 1980(5)]
29. M G Voronkov, A A Kashaev, E A Zel'bst, et al. *Dokl. Akad. Nauk SSSR*, 1979, **247** 1147
30. E A Zel'bst, V S Fundamenskii, A A Kashaev, et al. *Dokl. Akad. Nauk SSSR*, 1985, **287** 342
31. P W R Corfield, J A Ibers *Abstracts, Annual Meeting of the American Crystallographic Association*, 1968, p. 52
32. D Schomburg, R Krebs *Inorg. Chem.*, 1984, **23** 1378
33. D Schomburg *J. Organomet. Chem.*, 1981, **221** 137
34. V E Shklover, Yu T Struchkov, L I Gubanova, M G Voronkov *Zh. Strukt. Khim.*, 1987, **28** 118
35. C Dittebrandt, H Oberhammer *J. Mol. Struct.*, 1980, **63** 227
36. J E Huheey *Inorg. Chem.*, 1981, **20** 4033
37. R Gillespie *Molecular Geometry* (Translated into Russian), Izd. Mir, Moscow, 1975
38. E L Muetterties, R A Schunn *Quart. Revs.*, 1966, **20** 245
39. B S Ault *Inorg. Chem.*, 1981, **20** 2817
40. T J Lorenz, B S Ault *Inorg. Chem.*, 1982, **21** 1758
41. B S Ault *J. Mol. Struct.*, 1985, **129** 287
42. C Marsden *Inorg. Chem.*, 1983, **22** 3178

43. J M Chebayber, S T Nagy, C S Lin *Can. J. Chem.*, 1984, **62** 27
44. Yu L Frolov, S G Shevchenko, M G Voronkov *J. Organomet. Chem.*, 1985, **292** 159
45. Yu L Frolov, S G Shevchenko, M G Voronkov *Teor. Eksp. Khim.*, 1986, **22** 70
46. W B Farnham, R L Harlow *J. Am. Chem. Soc.*, 1981, **103** 4608
47. J J Harland, R O Day, J F Vollano, et al. *J. Am. Chem. Soc.*, 1981, **103** 5269
48. D Schomburg *Z. Naturforsch. B*, 1983, **38** 938
49. E L Muettertes, L J Guggenberger *J. Am. Chem. Soc.*, 1974, **96** 1748
50. E L Muetterties *Tetrahedron*, 1974, **30** 1595
51. R S Berry, *J. Chem. Phys.*, 1960, **32** 933
52. M A Porai-Koshits, L A Aslanov *Zh. Strukt. Khim.*, 1972, **13** 266
53. R O Day, J M Holmes, A C Sau, R R Holmes *Inorg. Chem.*, 1982, **21** 281
54. H Wunderlich, D Mootz *Acta Crystallogr., Sect. B*, 1974, **30** 935
55. V O Gel'mbol'dt *Koord. Khim.*, 1984, **10** 1299
56. N Bartlett *Z. Vses.Khim. Obshch. im D I Mendeleeva*, 1983, **28** 28
57. V O Gel'mbol'dt *Zh. Neorg. Khim.*, 1985, **30**(8) 2159 [English translation in *Russ. J. Inorg. Chem.*, 1985(8)]
58. M A Porai-Koshits *Koord. Khim.*, 1978, **4** 842
59. V O Gel'mbol'dt, S P Petrosyants, L A Gavrilova, A A Ennan *Koord. Khim.*, 1988, **14** 1615
60. K Kleboth *Monatsh. Chem.*, 1970, **101** 357
61. I Wharf, M Onyszchuk *Can. J. Chem.*, 1972, **50** 3450
62. V O Gel'mbol'dt *Tezisy Dokladov VIII Vsesoyuznogo Simpoziuma po Khimii Neorganicheskikh Ftoridov* (Abstracts of Reports at the VIIIth All-Union Symposium on Inorganic Fluorides), Izd. Nauka, Moscow, 1987, p. 101
63. L Salem *Electrons in Chemical Reactions: First Principles*, Wiley, New York, 1982 (Translated into Russian), Izd. Mir, Moscow, 1985, p. 202
64. I Wharf, M Onyszchuk *Can. J. Chem.*, 1970, **48** 2250
65. J A Gibson, D G Ibbott, A F Janzen *Can. J. Chem.*, 1973, **51** 3203
66. R K Marat, A F Janzen *J. Chem. Soc., Chem. Comm.*, 1977, 671
67. B J Aylett, I A Ellis, C J Porritt *J. Chem. Soc., Dalton Trans.*, 1972, 1953
68. D B Miller, H H Sisier *J. Am. Chem. Soc.*, 1955, **77** 4998
69. C J Wilkins, D K Grant *J. Chem. Soc.*, 1953, 927
70. R Damrauer, S E Danahey *Organometallics*, 1986, **5** 1490
71. E L Muetterties *J. Am. Chem. Soc.*, 1969, **91** 1636
72. W H Stevenson, S Wilson, J C Martin, W B Farnham *J. Amer. Chem. Soc.*, 1985, **107** 6340
73. W H Stevenson, J C Martin *J. Amer. Chem. Soc.*, 1985, **107** 6352
74. I Ugi, D Marguarding, H Klusacek, et al. *Accounts Chem. Res.*, 1971, **4** 288
75. A I Albanov, L I Gubanova, M F Larin, et al. *J. Organomet. Chem.*, 1983, **244** 5
76. V A Pestunovich, M F Larin, A I Albanov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 1931
77. R J P Corriu, A Kpoton, M Poirier, G Royo *J. Organomet. Chem.*, 1984, **277** C25
78. R J P Corriu, M Mazhar, M Poirier, G Royo *J. Organomet. Chem.*, 1986, **306** C5
79. G Klebe, M Nix, K Hensen *Chem. Ber.*, 1984, **117** 797
80. G Klebe, K Hansen *J. Chem. Soc., Dalton Trans.*, 1985, 5
81. D L Wilhite, L Spialter *J. Am. Chem. Soc.*, 1973, **95** 2100
82. A Strich, A Viellard *J. Am. Chem. Soc.*, 1973, **95** 5547
83. A Strich *Inorg. Chem.*, 1978, **17** 942
84. V O Gel'mbol'dt *Tezisy Dokladov IX Vsesoyuznogo Soveshchaniya "Fizicheskie i Matematicheskie Metody v Koordinatsionnoi Khimii"* (Abstract of Reports at the IXth All-Union Conference "Physical and Mathematical Methods in Coordination Chemistry"), Vol. 2, Izd. Instituta Kataliza SO AN SSSR, Novosibirsk, 1987, p. 148
85. R K Marat, A F Janzen *Can. J. Chem.*, 1977, **55** 1167
86. G G Yakobson, V V Bardin *Ftorid-ion v Organicheskoi Khimii* (The Fluoride Ion in Organic Chemistry), Izd. Nauka, Novosibirsk, 1986, p. 27
87. R Noyori, I Nishida, J. Sakata *Tetrahedron Lett.*, 1980, **21** 2085
88. B E Smart, W J Middleton, W B Farnham *J. Am. Chem. Soc.*, 1986, **108** 4905
89. V O Gel'mbol'dt *Zh. Obshch. Khim.*, 1987, **57** 709
90. V O Gel'mbol'dt *Zh. Neorg. Khim.*, 1989, **34**(1) 231 [English translation in *Russ. J. Inorg. Chem.*, 1989(1)]
91. Yu A Buslaev, V O Gel'mbol'dt, S P Petrosyants, A A Ennan *Koord. Khim.*, 1978, **4** 555
92. L V Ostapchuk, L A Gavrilova, V O Gel'mbol'dt, A A Ennan *Zh. Neorg. Khim.*, 1987, **32**(4) 918 [English translation in *Russ. J. Inorg. Chem.*, 1987(4)]
93. G L Rosenthal, F Okino, T E Mallouk, N Bartlett *J. Fluorine Chem.*, 1982, **21** 26
94. G L Rosenthal, T E Mallouk, N Bartlett *Synth. React. Inorg.Metal-Org. Chem.*, 1984, **9** 433

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Mechanodegradation of polymers. The method of molecular dynamics

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ABSTRACT. The experimental results in the field of the mechanodegradation of polymers, indicating significant differences between this process and thermal degradation, are discussed; the mechanism of both processes have been subjected to a comparative analysis. The principal results obtained by the method of molecular dynamics in the study of related processes such as mechanodegradation and the effect of shock waves are examined. Attention is concentrated on the mechanisms of ruptures, the formation of excited low-molecular-weight products, and the process energetics. The prospects for further research are discussed.

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I. Introduction

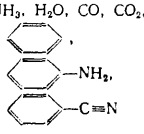
Mechanodegradation is one of the main chemical processes occurring in polymers both during their processing and during their use under load. The most effective physical method for the investigation of molecular mechanodegradation products is mass spectrometry.[1-5]

In the field of the mechanodegradation of polymers, it is now possible to distinguish two groups of experimental facts on the explanation of which the understanding of the mechanism of this process depends to a large extent. The first group includes results indicating a significant difference between the compositions of the molecular thermal degradation and mechanodegradation products (Table 1). For a number of polymers investigated by different workers[1-3] by mass spectrometry, it has been established that heavy fragments characteristic of thermal degradation are completely absent from the mechanodegradation products. The formation of only light products in mechanodegradation apparently shows that the vibrational energy is distributed significantly non-uniformly in mechanodegradation and is localised in regions whose size does not exceed 10 Å. This result is difficult to understand within the framework of the generally accepted thermofluctuation concept.[6]

The second group of experimental facts, which does not fit within the framework of the thermofluctuation concept, is the discovery of high-energy molecular products of the mechanodegradation of a series of polymeric materials (Table 2).[5] A linear polymer—poly(methyl methacrylate) (PMMA), a network epoxide polymer based on the diglycidyl ether of resorcinol and *m*-phenylenediamine (DGER–MPDA), and a composite material (ebonite) have been investigated. Table 2 shows that the molecular mechanodegradation products—both the main products (MMA, acetaldehyde) and the occluded water—have extremely high kinetic energies of translational motion ranging from 0.25 to 0.70 eV, which corresponds to translational temperatures ranging from 2000 to 5400 K.

The impossibility of explaining the results described above within the framework of the thermofluctuation concept necessitates a theoretical study of the mechanodegradation of polymers by a method which would be free from *a priori* postulates similar to those

Table 1. The molecular products of the thermal degradation and mechanodegradation of polymers.

Polymer	Volatile thermal degradation products	Volatile mechanodegradation products	Agreement between product compositions	Refs.
Poly(methylmethacrylate) (PMMA)	monomer	monomer	ec	[1]
Polystyrene (PS)	monomer, oligomers	monomer, dimer	no	[1]
Poly-α-methyl-styrene-(isotactic) (P-α-MS)	monomer	monomer	yes	[1]
Polyformaldehyde (PFA)	monomer	monomer, unidentified products	no	[1]
Polyethylene (PE)	low-molecular-weight saturated and unsaturated hydrocarbons	low-molecular-weight saturated and unsaturated hydrocarbons	?	[1]
Polypropylene (PP)	low-molecular-weight saturated and unsaturated hdyrocarbons	low-molecular-weight saturated and unsaturated hydrocarbons	?	[1]
Polyacrylonitrile (PAN)	HC ≡ N, monomer	unidentified products	no	[1]
Nitrocellulose (NC)	CO, CO_2, H_2O, NO, NO_2, CH_2O	CO, CO_2, H_2O, CH_2O	no	[1]
Polycapramide (PCA)[1]	H_2O, CO_2, NH_3, hydrocarbons	CO_2, NH_3, hydrocarbons	no	[1]
Polyepoxide	H_2, CO, CH_4, C_2H_4, C_2H_6, C_6H_6, C_8H_8	H_2, CO, CH_4, C_2H_6	no	[1]
DGER-MPDA	CH_3CHO, H_2O, resorcinol, decomposed aromatic compounds	CH_3CHO, H_2O, H, CH_4, HC≡N, CH≡CH	no	[2]
Poly-*m*-phenylene-isophthalamide (PMPIA) (nomex, phenylon); poly-*p*-phenylene-terephthalamide (PPTA) (kevlar, arenka); poly-*p*-benzamide; polyamidebenzimidazole (PABI)	NH_3, H_2O, CO, CO_2, 	NH_3, H_2O, CO, CO_2	no	[3]

underlying the thermofluctuation concept. If the treatment is restricted to the investigation of the mechanodegradation of a macromolecule only within the framework of classical mechanics, then one can expect that the method of molecular dynamics (MD) will prove most compatible with the significantly non-linear character of the mechanodegradation process and will be most effective in the given instance.

At the present time, this method has been developing vigorously on the basis of modern computer techniques. With the aid of the MD method, it is possible to investigate in detail the molecular dynamics of various processes in the time range 10^{-14}–10^{-11} s.

Table 2. High-energy molecular products of the mechanodegradation of polymeric materials.[5]

Polymer	Products	V, m s^{-1}	E_{trans}, eV	T_{tr}, K
PMMA	MMA	1160^{+160}	$0.70^{+0.21}$	5410^{+1530}
	H_2O	1580^{+338}	$0.23^{+0.11}$	2190^{+460}
DGER–MPDA	CH_3CHO	1210^{+100}	$0.33^{+0.08}$	2570^{+450}
	H_2O	1680^{+305}_{-100}	$0.26^{+0.11}_{-0.03}$	2040^{+810}_{-280}
Ebonite	H_2O	1690	27	2065

Note. V is the velocity of the translational motion of the moelcules, $E_{trans} = mV^2/2$ the kinetic energy of the translational motion of the molecules, T_{tr} the translational temperature [the experimental errors ($\pm$), determined by the accuracy of the method, are indicated for V, E_{trans}, and T_{tr}].

II. The application of the method of molecular dynamics

1. Mechanodegradation

The decomposition of an extended chain of atoms was investigated by the MD method for the first time by Toda et al.[7] on a one-dimensional model. The interaction between neighbouring atoms was specified by a potential of a special type:

$$\Phi(r) = \begin{cases} e^{-r} + r + \text{const}, & r < r_{cr} \\ \text{const}, & r > r_{cr}, \end{cases}$$

since simple analytical solutions of the equations of motion $f_n = \Omega^2 \operatorname{sech}^2(kn \pm \Omega t)$, where f_n is the force of the compression of the nth bond, $\Omega = m^{-1/2} \sin nk$, r is the deviation of the position of the atom from equilibrium (bond deformation), m the mass of the atom, k a constant, and t the time, are known for a chain with such a potential. These solutions represent unified compression waves (solitons) propagated along the chain of atoms.

The following sequence of events after the rupture of a uniformly extended chain has been noted:[7] (1) immediately after rupture, a wave of stresses is generated and is propagated in the direction towards the fixed end; (2) after reflection from the latter, the wave is transformed into a sequence of compression pulses (solitons); (3) each soliton reaching the free end of the chain leads to the extension of the extreme bond, which exceeds by several per cent the initial extension r_{init}. However, since the critical stretching deformation of the bond r_{cr} was always specified by the authors[7] in the range $(1.015–1.07)r_{init}$, then such extension always leads to the abstraction of the extreme atom of the chain. Thus, in the initial degradation stage consecutive removal of atoms from the free end takes place and is followed by random breaks of the chain in different places. The above degradation sequence holds for a wide range of initial extensions of the chain.

The fragmentation of a uniformly extended one-dimensional chain of atoms has also been studied by the MD method in other investigations.[8,9] In contrast to Toda, Mel'ker et al.[8] and Grigoryan et al.[9] used the Morse potential for the description of the interaction between neighbouring atoms of the chain. The generation of large-amplitude compression pulses on reflection of the relaxation wave from the fixed end, analogous to those observed by Toda,[7] was noted. However, in contrast to Toda's work,[7] the rupture of the extreme bond was not observed on reflection of the compression pulses from the free end despite the fact that the stretching deformation exceeded ε_{cr}.† The kinetic energy of the motion of the centres of mass of the fragments was considerable and amounted to 25% of the total energy of the system. The deformation of the individual bonds in the fragments reached $2.2\varepsilon_{cr}$ although further fragmentation was not observed.

The occurrence of low-frequency vibrations in the extended chain has been noted by Mel'ker and Kuznetsova,[10] which the authors attribute to the "two-well nature" of the potential for any internal chain atom.[11] The two-well form of the potential is responsible for the existence of stable lengthened bonds capable of migrating. It has been suggested[10] that they be referred to as quasi-particles—dilatons, and the dissociation of an extended chain has been interpreted[12] as a result of the merging of dilatons.

A series of studies by Mel'ker and co-workers has been devoted to the mechanism of the dissociation of an interatomic bond in an extended chain of atoms.[13–15] Two types of ruptures are distinguished. The first type of rupture—the single-step rupture—is associated with the generation of a dissociative energy fluctuation embracing approximately 10 atoms. In the region of the fluctuation, the deformation of the interatomic bonds exceeds the average value and the motion of the atoms is correlated.[13] In rupture, the energy of the fluctuation is concentrated on one bond, which is rapidly and monotonically lengthened up to dissociation. This type of rupture is characteristic of a relatively high energy density in the deformed chain of atoms, when its lifetime does not exceed 10^3 periods of the atomic vibrations. The second type of rupture of the interatomic bond—the two-step rupture, whose probability increases with decrease in the energy density in the chain, has been noted by Mikhailin and Mel'ker.[14,15] The interatomic bond is rapidly lengthened up to values in the range $\varepsilon = (2–4)\varepsilon_{cr}$ and oscillates about the level attained over a period $(2–7)\tau_0$. The bond dissociation is then rapidly completed.

The longevity of the polymer chain under load at a specified temperature has been investigated by Zaitsev and Razumovskaya.[16] A one-dimensional chain of atoms, whose interaction is described by the Morse potential, was used as the model. The appearance of two compression regions (lattice solitons), diverging from the site of chain rupture at ultrasonic velocities, was noted.

†The bond deformation $\varepsilon \equiv (r - r_0)/r_0$, where r is the distance between the atoms and r_0 its equilibrium value. The critical bond formation $\varepsilon_{cr} = \ln 2/\alpha r_0$ corresponds to the ultimate strength of the interatomic bond $F_m = \alpha U_0/2$, where α and U_0 are parameters of the Morse potential.

Taking into account the fact that the principal characteristics of the mechanodegradation of the polymer chain are determined by the strong anharmonicity of the vibrational-wave excitations, arising during the different stages, it is useful to analyse the instances of intense shock interaction of polyatomic systems in which anharmonicity plays a decisive role.

2. Shock waves

A study by Bettech and Powell was devoted to the numerical modelling of the propagation of a shock wave in a one-dimensional chain.[17] The investigation established that the development of the process involving the oscillation of particles behind the shock wave front is determined in the early stage by the dispersion, after which non-linear effects become increasingly more significant. During the propagation of a shock wave, decaying oscillations are converted into a sequence of distinct pulses—solitons (Fig.1*a*). The stability of solitons (*A*, *B*, *C*) in relation to collisions and the thermal background (Fig.1*b*) leads to the absence of a tendency towards the "disordering" of the energy, i.e. towards the attainment of thermal equilibrium. The energy is not thermalised behind the shock wave front and hence the temperature does not increase.

The propagation of a shock wave in an iron crystal has been investigated by Walker et al.[18] The behaviour of impurity diatomic molecular H_2 and C–H species (probes) in the three-dimensional iron lattice during the passage of the shock wave front was investigated by the MD method. Figs.2 and 3 illustrate the time variation of the translational (*a*), rotational (*b*) and vibrational (*c*) energies of the H_2 and C–H probe molecules respectively as well as the disposition of the iron atoms and probe molecules in the system before the impacts (*d*) of the plate against the block and at the instant corresponding to 40 time units (1 time unit = 10^{-14} s) (*e*) corresponding to the attainment of the end of the block by the shock wave. The iron

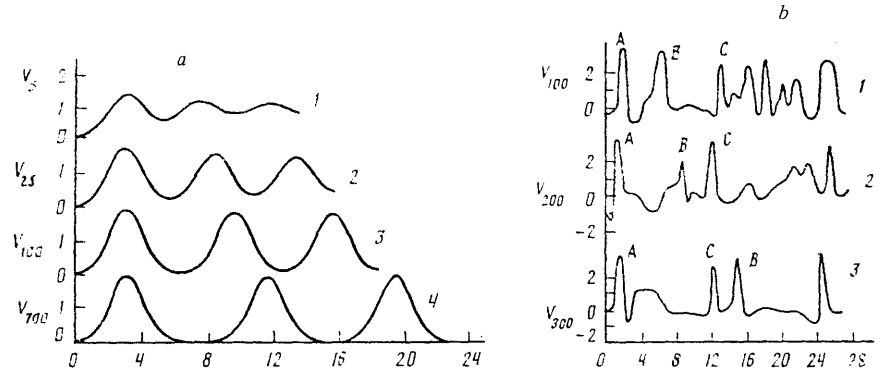


Figure 1. Variation with time τ of the velocities V of different particles (5th, 25th, 100th, and 700th) in the chain:[17] *a*) initially unperturbed; *b*) at a non-zero initial temperature; τ_0 (arbitrary units)—the instant when each particle is acted upon by the shock wave: *a*: *1*) τ_0 = 5.6; *2*) τ_0 = 36.5; *3*) τ_0 = 148.9; *4*) τ_0 = 1041.0; *b*: *1*) τ_0 = 73; *2*) τ_0 = 140; *3*) τ_0 = 209.

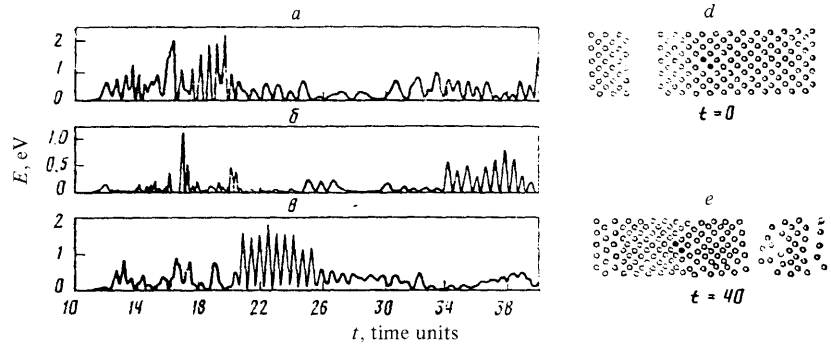


Figure 2. Time variation of the energy E [*a*) translational; *b*) rotational; *c*) vibrational] of the H_2 probe molecule in the Fe lattice during the passage of the shock wave front; *d*) disposition of atoms in the system before impact; *e*) instantaneous disposition of atoms in the system after 40 time units have elapsed (1 unit = 10^{-14} s) corresponding to the shock wave reaching the end of the block; Fe atoms are represented by open circles and the atoms of the H_2 probe molecule by filled circles.[18]

atoms are represented by circles and the atoms of the probe molecules are represented by points. Figs.2 and 3 show that the variation of the kinetic energy of the translational motion of the diatomic probe molecules reaches 6 eV and has the form of a sequence of unified brief ($\sim 10^{-14}$ s) pulses resembling solitons. The changes in the energies of rotational and vibrational motions (b) and (c), reaching several eV, have a similar form. Such large energies of the vibrational motion lead to the dissociation of molecules: for a short period if the molecule is in a 'cage' and irreversibly if the molecule is at the boundary of the free volume.

3. Elementary thermal excitations

In his analysis by means of the procedure described by Battech and Powell[17] of the thermal vibrations in a one-dimensional chain of 500 atoms, whose interaction is described by the Morse potential, Zhukov[19] showed that two types of lattice excitations coexist in the thermalised chain: solitons and phonons. The solitons are in fact the high energy carriers and their contribution to the overall thermal energy of the thermalised lattice amounts to tens per cent and increases with increase in temperature. Fig.4 illustrates the instantaneous velocities of the atoms in the middle part of a 500-atom chain. In the initial instant (*a*), only a small zone in the centre of the chain comprising 20 atoms (from the 250th to the 270th) is heated and the rest of the chain is "cold". The migration of energy from "hot" to the "cold" zone is effected both by phonons and solitons. However, since the velocity of the soliton is greater than the velocity of sound, the solitons emerge from the heated zone, overtaking the phonons. Figs.4*b* and 4*c* illustrate the instantaneous velocities of atoms after 2000 and 4000 time steps respectively and the solitons which have emerged are designated by vertical arrows.

The occurrence of stable elementary excitations of the soliton type in a chain of atoms fixed at the edges, whose interaction is described by the Morse potential, has been demonstrated analytically by Collins[20] and numerically by Rolfe et al.[21] Rolfe et al.[21] not only demonstrated the possibility of the existence of solitons in one-dimensional chains with different interatomic interaction potentials (Morse, Lennard-Jones 6–12 and 16–32) but also established that the reflection of the solitons from the fixed and free ends as well as the collision of the solitons with one another are similar to the behaviour of solitons in a Toda chain for all the potentials examined.

The appearance of such excitations in the mechanodegradation of a uniformly extended one-dimensional chain of Morse oscillators and the interaction of solitons having different energies with the extended chain have been described.[22,23] In addition, a study has been made[22] of the dependence of the mass spectrum of the mechanodegradation products on the length and degree of extension of the chain.

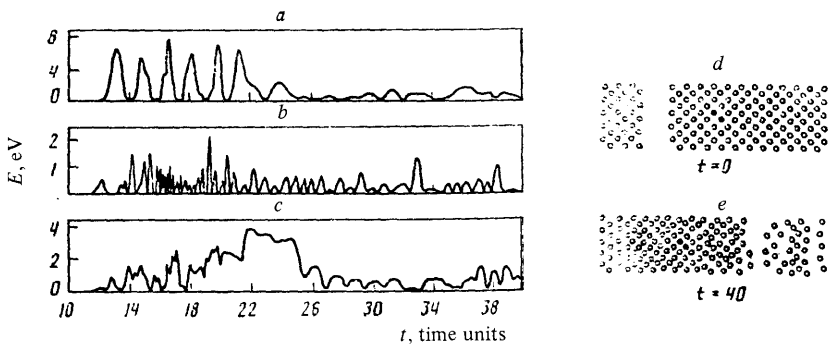


Figure 3. See the caption to Fig. 2; C–H molecular probe in the Fe lattice.[18]

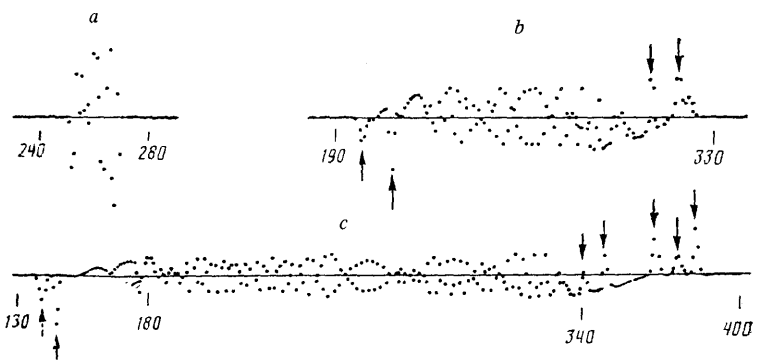


Figure 4. Instantaneous velocities of the atoms in the chain: *a*) in the initial instant; *b*) after 2000 time steps; *c*) after 4000 time steps;[19] the numerals denote the numbering of the atoms.

In his study of the properties of the elementary thermal excitations in a strongly heated chain of atoms, whose interaction is described by the Lennard-Jones potential, Lagunov[24] established that, as in the case of the Morse potential, they are equivalent to the lattice solitons existing in the Toda chain.[25] On the basis of this conclusion, he examined[24] the thermal fluctuation-induced dissociation of a uniformly extended chain either as a result of the interaction of countercurrent streams of solitons and antisolitons or as a result of the interaction of dilatons with antidilatons. It is suggested that the large-scale regions between the centres of solitons, migrating together with them, rather than the highly extended chain as in the study of Mel'ker et al.,[12] be regarded as dilatons functioning as elementary carriers of the stretching deformation. Lagunov[24] analysed the dissociation step solely in "dilaton" and "antidilaton" terms, referring, however, to the dissociation mechanism itself as a "soliton" mechanism. Furthermore, he noted[24] that a pair comprising a kink and an antikink (i.e. a pair of solitions of the topological type) diverge from the rupture site, which leads to a gradual relaxation of the chain.

Unfortunately, on the basis of the individual experimental[1-5] and theoretical[7-24] results available at present in the field of the mechanodegradation of polymers, it is impossible to achieve a clear understanding of the mechanism of this process. The theoretical results of different workers are contradictory and unrelated to the available experimental data. However, one should note that the intense anharmonic excitations resembling solitons observed by different workers undoubtedly play an important role. This complex situation in the mechanodegradation of polymers, which has a great practical importance, has led the present authors to carry out a more detailed investigation of this process.[26,27]

The stretching (as far as rupture) and subsequent mechanodegradation of a continuous polymer chain in an amorphous layer of a linearly oriented polymer with a fibrillar structure was investigated by the method of molecular dynamics. One-dimensional chains made up of 50 and 100 atoms were chosen as the object of study. The masses of all the atoms were the same and equal to that of the carbon atom (2×10^{-23} g). The interatomic interaction was described by the Morse potential with the parameters characteristic of the C–C bond in polyethylene. Account was taken only of the interaction between nearest neighbour atoms. For the numerical solution of the system of differential equations of motion of the chain atoms, the RKF 45 program[28] was used with the automatic selection of the integration step, based on the modified fourth–fifth order Runge-Kutta method. In order to avoid the unjustified decrease in the step after the sharp cut-off of the potential, a "smooth" cut-off was achieved with the aid of a cubic polynomial. Thus the potential employed had the form

$$U(r) = \begin{cases} D\left[e^{-2b(r-r_0)} - 2e^{-b(r-r_0)}\right], & r \leqslant r_1, \\ C_1(r-r_2)^2 + C_2(r-r_2)^3, & r_1 \leqslant r \leqslant r_2, \\ 0, & r_2 \leqslant r. \end{cases}$$

The parameters of the Morse potential were $D = 3.5$ eV, $b = 2$ Å^{-1}, and $r_0 = 1.54$ Å.

The constants C_1 and C_2 were selected on the basis of the condition of the continuity of the potential and of its first derivative at the point r_1.

At the initial instant, the distances between neighbouring atoms are r_0 and the velocities of all the atoms are zero (the chain is at the temperature 0 K). The first atom is fixed so that it is immobile. The extension of the chain was specified by the movement of the last atom in the positive direction at a constant velocity V. The calculations were performed for two rates of stretching: $V = 0.1V_{so}$ and $V = 0.05V_{so}$, where $V_{so} = r_0 b(2D/m)^{1/2} = 23.08 \times 10^3$ m s$^{-1} \simeq$ 231 Å ps^{-1} is the velocity of sound. The stretching of chains at such high rates takes place at the apex of a major crack at the concluding stage of its growth at a rate close to the velocity of sound. In an experimental study of precisely this stage of the rupture process,[5] it was possible to detect high-energy molecular products of the mechanodegradation of polymers (Table 2).

The time used to observe the trajectories of the motion of atoms was 3.5–7 ps.

III. Characteristic features of the mechanodegradation of polymer chains

1. The mechanisms of the ruptures

We shall consider the principal characteristics of the mechanodegradation in relation to a 50-atom chain stretched at a rate of 23 Å ps^{-1} $\simeq 0.1V_{so}$. In the initial instant, the velocities of all the atoms are zero, i.e. the chain is at the temperature 0 K.

Fig.5 presents the trajectories of the motion of all the 50 chain atoms. The coordinates $X_i(t)$ (i = 1–50) of all the atoms (in Å) are plotted along the left-hand ordinate axis and the time t [in time units (1 time unit = 10^{-14} s)] is plotted on the abscissa axis. Scale divisions, in steps of 1 Å are indicated on the right-hand ordinate axis to facilitate analysis of the process. The upper straight line represents the trajectory of the motion of the last (51st) atom at a constant velocity $V_{51} = 23$ Å ps^{-1}. The figure clearly shows the sites and instants of all the ruptures. Certain ruptures are "healed", i.e. recombination takes place, which is associated with the presence of two boundaries, one stationary and one moving at a constant velocity, which prevent the free movement of the degradation products by virtue of the one-dimensional nature of the model. It can be assumed that the first four breaks, indicated in the figure by filled circles, occurred without being influenced by the boundaries (if one disregards the reflection from the stationary boundary of the extension wave, which initiates the first chain rupture, as will be shown below). The first stage of the chain extension process is fully determined by the propagation of the extension wave (Fig.6). Each curve represents the distribution of the bond deformations along the chain at a fixed instant. The numbers of the bonds are plotted along the abscissa axis and the number of the curve is plotted on the left-hand side ordinate axis (the position of the number on the ordinate axis specifies the zero deformation level for the corresponding curve). On the left, the time (in time units) elapsed from the instant of the start of the extension is indicated above each curve and the deformation scale (in 10^{-1} Å) is indicated on the right-hand ordinate axis. The extension wave is propagated along the chain from right to left, i.e. from the extreme (51st) atom, moving at a constant velocity, to the fixed end. The velocity of the potential wave front is 245 Å ps^{-1}, which is close to the velocity of sound calculated from the formula $V_{so} = r_0 b(2D/m)^{1/2} \simeq 231$ Å ps^{-1}.

By virtue of the dispersion of the system considered, decaying atomic vibrations, also propagated along the chain in the form of a wave, are observed behind the wave front. However, the vibration wave is propagated along a chain which has already been stretched (whose effective force constants are smaller than those of the unstretched chain) and its velocity is therefore lower than that of sound. This factor leads to the "spreading" of the extension wave front. At the instant corresponding to 31 time units, the front

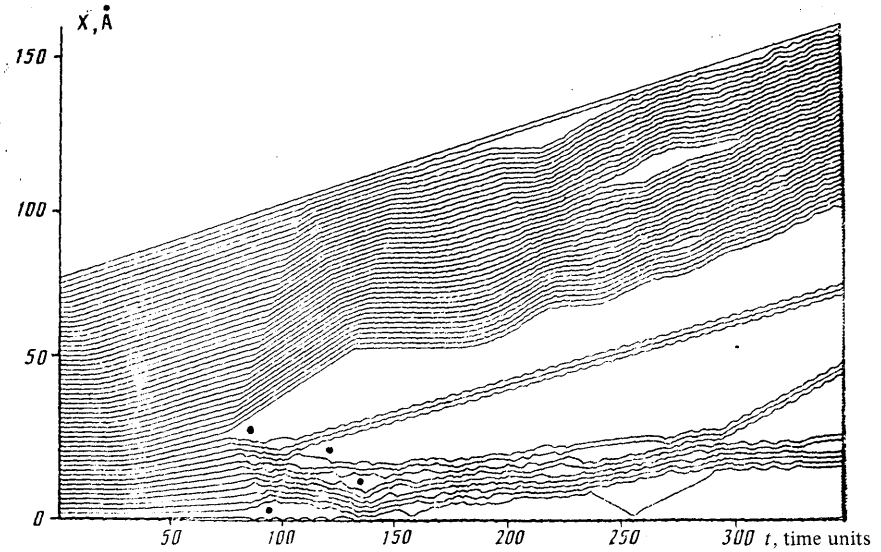


Figure 5. Time variation of the coordinates of the atoms of a 50-atom chain stretched at the rate $V_{str} = 0.1V_{so}$;[27] in the initial instant, the chain temperature is 0 K.

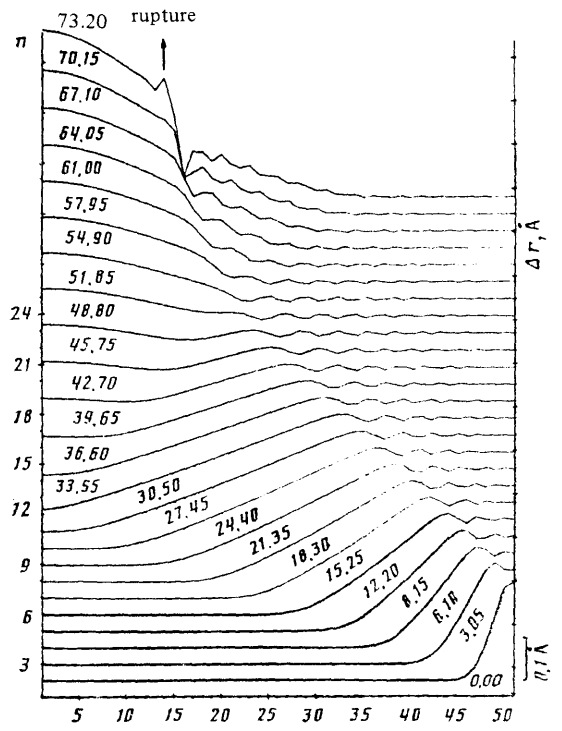


Figure 6. Time variation of the distribution of the bond deformations $\Delta r \equiv r - r_0$ along the chain from the initial instant up to the instant of the first rupture;[27] i = number of the bond; n = number of the atom.

reaches the fixed end and is reflected from it in the form of a high-amplitude wave. From this instant, the high-amplitude extension wave is propagated towards the vibration wave. Collision of these two waves occurs at time $t \simeq 50$ time units in the 22nd bond. The velocity of the vibration wave then diminishes as it passes to the increasingly stretched regions of the extension wave front. When the vibration wave front reaches the region with the deformation $\varepsilon > \varepsilon_{cr} = 0.224$, the chain ruptures (in the given instance, the 14th bond is ruptured).

Thus the mechanism of the first rupture of the "cold" chain stretched at a rate $V = 0.1V_{so}$ is due to the collision of the dispersion vibration wave with the extension wave moving in opposition to it, the rupture step itself occurring at the site where the following two conditions are satisfied simultaneously at the instant of the arrival of the first vibration: $\varepsilon > \varepsilon_{cr}$ and $\dot{\varepsilon} > 0$.

At the instant of rupture (73 time units), the propagation of the deformation along the chain is significantly non-uniform: $\varepsilon > \varepsilon_{cr}$ for bonds 1–14 and $\varepsilon < \varepsilon_{cr}$ for bonds 15–50. The forms of the relaxation waves propagated from the rupture site are therefore different in the chain fragments 1–13 and 14–51 (Fig.7). The relaxation wave front in the fragment 1–13 ($\varepsilon > \varepsilon_{cr}$) represents a kink (a topological soliton) and that in the fragment 14–51 is a lattice soliton. The propagation of kinks from the rupture site has also been noted by Grigoryan et al.[23]

For a slower ($V_{ext} = 0.05V_{so}$) extension of the cold chain, a different rupture mechanism, associated with a structural transition in the most stretched part of the chain, is observed. When the stretching deformation reaches $\varepsilon_{cr} = 0.224$, there is an abrupt transition of the chain atoms to a new state of equilibrium. The chain structure then changes in such a way that, instead of uniformly extended bonds, a sequence of long (L) and normal (N) bonds alternating along the chain arises: ...LNLNLNLN...

The length of the L-bond is $l_L \simeq r_0 + 2\varepsilon_{cr}r_0 = (1 + 2\varepsilon_{cr})r_0$, where $\varepsilon_{cr} \simeq 0.224$, while the length of the N-bond is $l_N \simeq r_0$. This structural transition is associated with the fact that, when the stretching deformation reaches the critical value ε_{cr}, there is a qualitative change in the form of the effective potential for each internal chain atom: the potential changes from the one-well type to the two-well type. A similar change in the form of the potential for an internal atom of the chain when the latter was stretched was investigated previously by Mel'ker and Kusnetsova.[11] Fig.8 shows how the form of the potential for an internal atom in a three-atom one-dimensional system changes when the extreme atoms move apart by 0.3, 0.5, and 0.7 Å. Evidently the transition from the one-well to the two-well potential takes place for stretching deformations in the range 0.3 to 0.5 Å.

Figs.9 and 10 illustrate the slow extension of a 50-atom chain in which a structural transition, terminating in two chain ruptures, takes place over a long segment. Fig.9 illustrates the trajectories of the motion of all the 50 atoms. The numbers of the atoms are

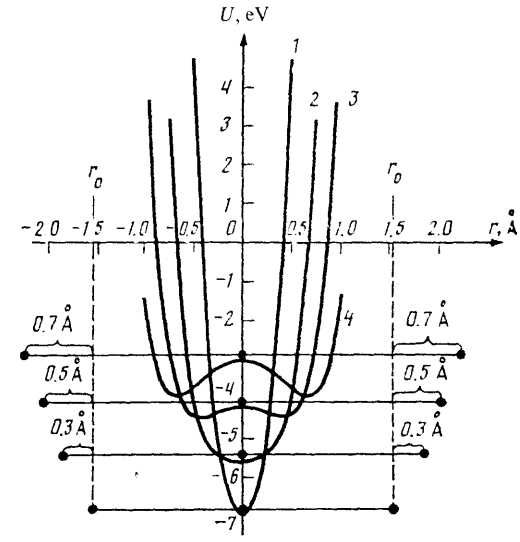


Figure 8. The change in the form of the potential for an internal atom of the chain on extension of the latter; $\Delta r \equiv r - r_0$ (Å): *1*) 0; *2*) 0.3; *3*) 0.5; *4*) 0.7.[27]

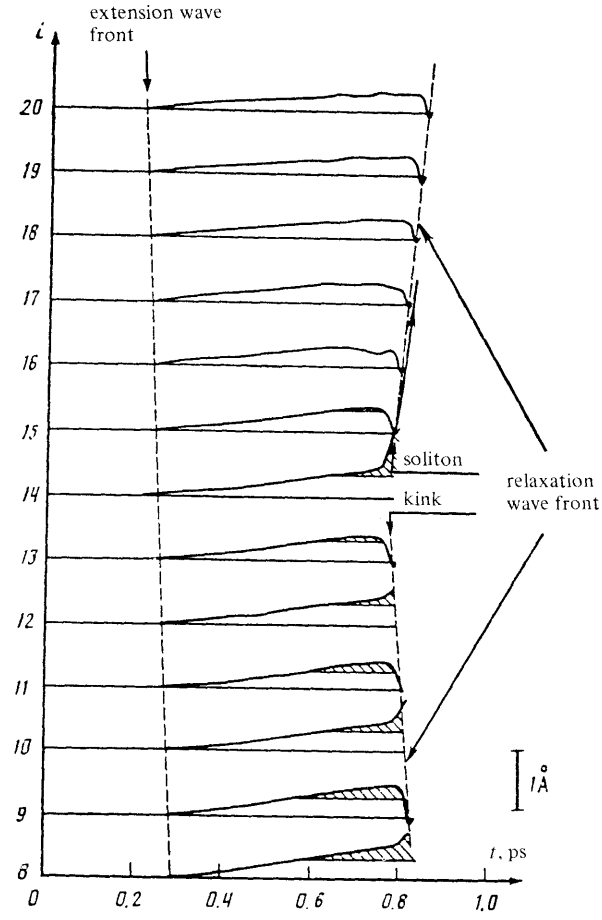


Figure 7. Time variation of the bond deformations in the vicinity of the first rupture; qualitative difference between the relaxation waves propagated at the site of the first rupture in the highly stretched ($\varepsilon > \varepsilon_{cr}$) fragment 1–13 and in the slightly stretched ($\varepsilon < \varepsilon_{cr}$) fragment 14–51;[27] *i* = number of the bond.

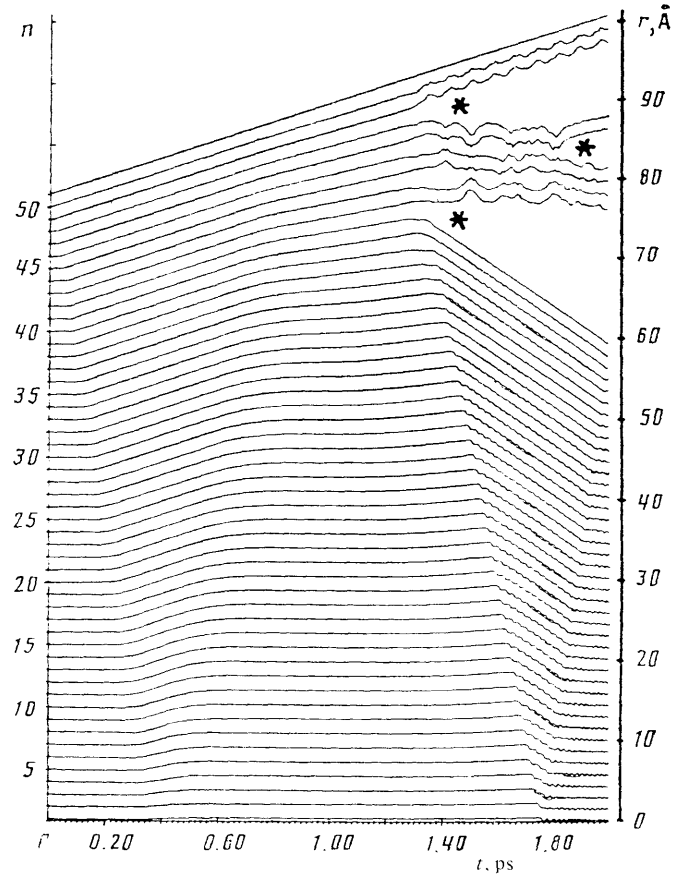


Figure 9. The trajectories of the motion of the atoms of a 50-atom chain stretched at the rate $V_{str} = 0.05V_{so}$. The ruptures are designated by an asterisk (*);[27] *n* = the number of the atom; *t* = time; *r* = atomic coordinate.

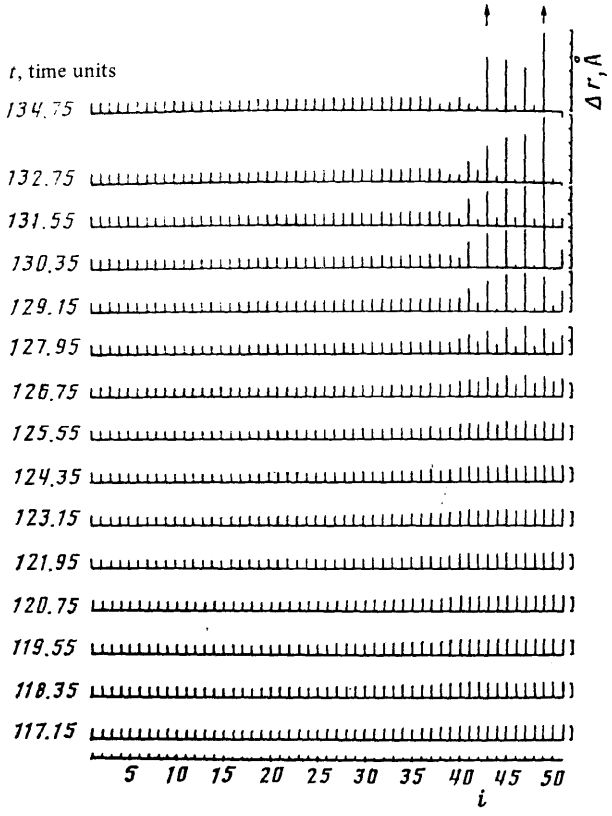


Figure 10. The structural transition in a 50-atom chain stretched at the rate $V_{str} = 0.05V_{so}$ in the pre-rupture stage:[27] i = the number of the bond in the chain; $\Delta r \equiv r - r_0$ the stretching deformation in Å; 1 division = 0.3 Å; t = time expressed in time units (1 time unit = 10^{-14} s).

plotted on the left-hand ordinate axis, the atomic coordinates (r) (in Å) are plotted on the right-hand ordinate axis, and the times (in ps) are plotted on the abscissa. In the time interval 1.20–1.35 ps in the section between the 40th and 50th atom, the critical stretching deformation $\varepsilon_{cr} = 0.224$ is attained and leads to a structural transition with subsequent ruptures of the 43rd and 49th bonds and the formation of a free 6-atom fragment 43–48. This structural transition in the pre-rupture stage is illustrated in greater detail in Fig.10. The time variation of the deformations of all the chain bonds is illustrated here at intervals of 1.2 time units.

We shall consider the characteristic features of the rapid extension of a polymer chain ($V_{ext} = 0.1V_{so}$). The wave process arising on rapid chain extension leads to a significantly non-uniform distribution of the deformation and energy along the chain. This fact has been disregarded in studies,[7–9,22] devoted to the degradation of "cold" stretched one-dimensional chains. It has been assumed that, at the instant of the first rupture, all the bonds of the chain, except that which is ruptured, are equally stretched. Fig.11 presents the distribution of the potential (curve *1*) and kinetic (curve *2*) energies along the chain at the instant 0.73 ps, i.e. immediately before the first rupture of the 50-atom chain illustrated in Fig.5. The non-uniformity of the energy distribution at the pre-rupture instant is in this case so considerable that significantly different excitation levels are characteristic of the chain fragment formed after the first rupture: thus the energy densities are 1.66 and 0.83 eV/bond in the fragments 1–13 and 14–50 respectively. This fact is responsible not only for the different character of the wave processes in the two fragments (Fig.7) but also leads to more rapid and vigorous degradation of the fragment 1–13 (three ruptures after ~0.5 ps) compared with the slow degradation of the fragment 14–50 (two ruptures after ~3 ps).

We shall now consider the wave processes developing after the first rupture of the chain stretched at a rate $0.1V_{so}$. Fig.12 illustrates the time variation for the kinetic energy of all the chain atoms (see also Fig.5). The numbers of the chain atoms (on the left) and the

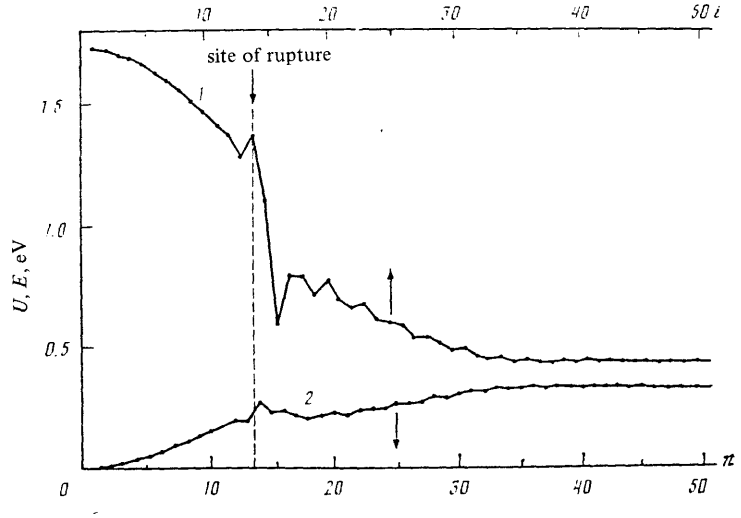


Figure 11. Distribution of the potential energy U (curve *1*) and the kinetic energy E (curve *2*) along the chain at the instant of the first rupture (t = 0.73 ps) of a 50-atom chain stretched at the rate $V_{str} = 0.1V_{so}$;[27] n = number of the atom; i = number of the bond.

kinetic energy scale with 1 division = 1 eV (on the right) are plotted along the ordinate axes and the time (in time units) is plotted along the abscissa axis. As before, the fixed end of the chain is at the lower end of the figure and the end moving at a constant velocity corresponds to the upper part of the figure.

After the first chain rupture (t_1 = 76 time units), individual irregular high-energy (more than 3 eV) localised waves of the type of solitons arise in the fragment 1–13, while a regular sequence of primary solitons, propagated from the site of the first rupture at the upper end of the chain moving at a constant velocity, is formed in the fragment 14–50. On reaching the upper end of the chain, the solitons are reflected and move towards the arriving stream of primary solitons. Interference then occurs between the incoming and reflected streams of solitons, which leads to the amplitude modulation of the soliton sequence. Thus we see that the process developed after the first rupture in both sections of the ruptured chain is quite different from what might have been expected on the basis of the existing ideas about the thermofluctuation character of the degradation process.[6] Instead of the expected conversion of elastic energy into thermal energy and the subsequent appearance of large thermofluctuations under the conditions of random motion, in the initial stages of the degradation process highly ordered modes are observed in the form of localised running waves—solitons. The size of the soliton depends only slightly on the degree of extension (compression) of the part of the chain in which it is located in the given instant and amounts to two–three units. At the instant when the soliton reaches the free end of the chain, its entire energy is converted into the potential energy of the extension of the extreme bond. The energy of the soliton can be determined accurately in this way.

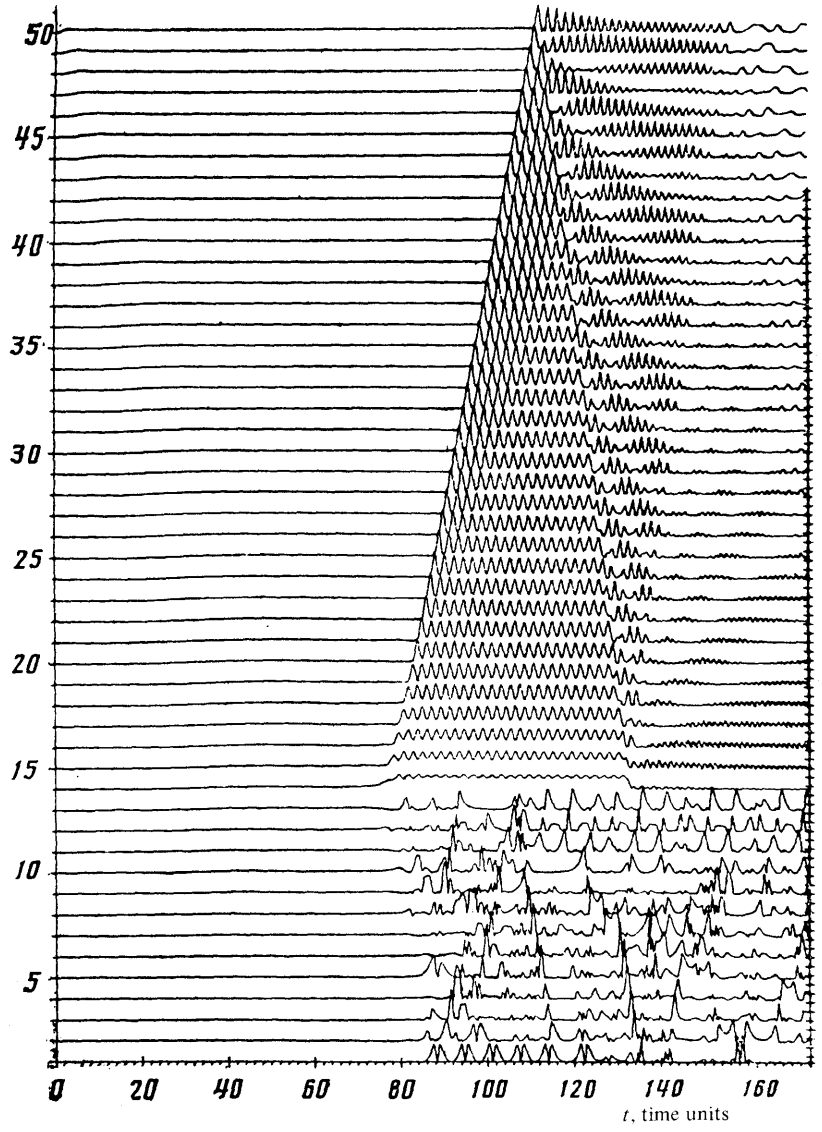


Figure 12. Time variation of the kinetic energy of the atoms of a 50-atom chain stretched at the rate $V_{str} = 0.1V_{so}$; on the right—1 division = 1 eV; n = the number of the atom; t = time expressed in time units (1 time unit = 10^{-14} s).

By analysing the observed secondary ruptures and then comparing them, it has been possible to identify two most characteristic mechanisms of the rupture processes. The first mechanism, characteristic of the rupture of short fragments (starting from the free ends of larger fragments) is determined by the arrival at the given free end of a packet of solitons moving in one direction. The following feature then holds: the packet, containing N solitons, breaks off a fragment containing N atoms. This mechanism can be briefly formulated as follows: N_{sol} + free end → $N_{atom.fragm.}$. For example, consider the abstraction of the three-atom fragment 20–22 from the 14-atom freely moving fragment 9–22 (Fig.13)—one of the intermediate products of the mechanodegradation of a 100-atom chain. The trajectories of the motion of all the atoms of the freely moving fragment 9–22 are illustrated in Fig.13*a*. At the instant $t \simeq 469$ time units, the 20th bond is ruptured and the three-atom fragment 20–22 is broken off. Fig.13*b* illustrates the time variation of the velocities of all the atoms of the fragment 9–22. The packet of three solitons (numbers *1*, *2*, and *3* in Fig.13*b*), moving from the 9th to the 22nd atom, is clearly seen. Having reached the free end, the first soliton alters sharply the trajectory of the motion of the extreme (22nd) atom. The second soliton, which immediately follows the first, also alters sharply the trajectory of the 21st atom. As a result of this, the diatomic fragment 21–22 begins to separate and the 21st bond is lengthened. Having reached the 20th atom, the somewhat lagging third soliton transfers to this atom its momentum and "throws it over" to the fragment 21–22 being eliminated. As a result the 21st bond is restored and the 20th is lengthened until rupture. In the pre-rupture state ($t \simeq 469$ time units) in the region of the future break, a correlated motion of the atoms in the opposite directions from the site of the future break is observed. The occurrence of the correlated motion of atoms in the pre-rupture instant has been pointed out by Mel'ker and co-workers.[13–15] However, the causes of such correlated motion of atoms were not considered. We suggested that such a cause is the movement of the packets of solitons *1–3* and *4–6* towards each other (Fig.3*b*), resulting in rupture. The size of the packet of solitons determines the size of the region of the correlated motion of atoms.

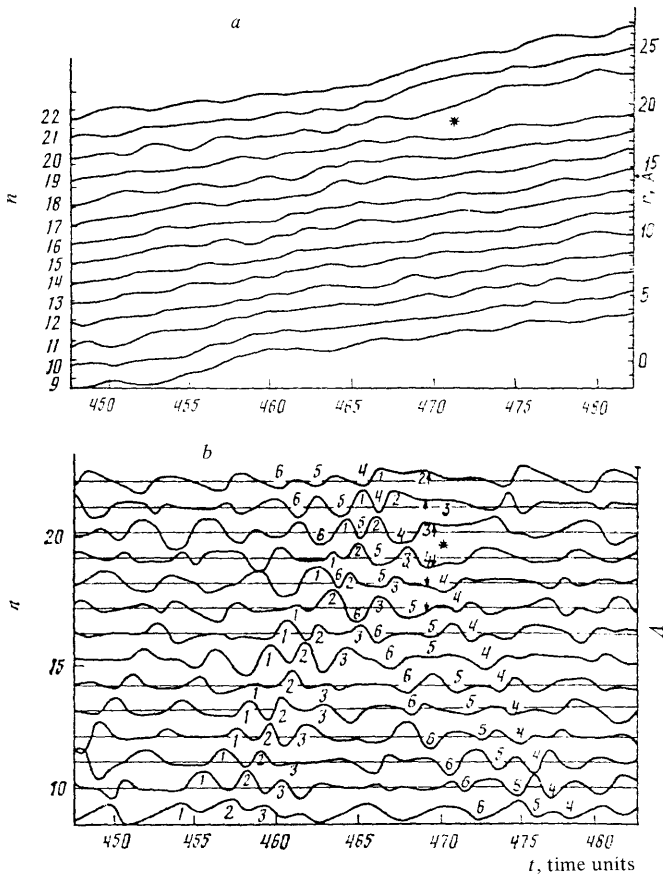


Figure 13. The abstraction of a three-atom fragment by a three-solition packet: *a*) trajectories of the motion of the atoms in the dissociating fragment 9–22; *b*) time variation of the velocities of the atoms in the dissociating fragment 9–22;[27] n = number of the atom; r = atomic coordinate in Å (1 division = 1 Å); V = velocity of the atom (arbitrary units); t = time expressed in time units.

The second rupture mechanism involves the entry of a soliton into the stretching region of the chain, i.e. into the zone for which the following two conditions are fulfilled simultaneously: $\varepsilon > \varepsilon_{cr}$ and $\varepsilon > 0$. This mechanism is similar to the mechanism of the first rupture considered above (Fig.6) and therefore does not require special illustrations.

2. The formation of C = C double bonds and excited products

In the intense excitation of the chain observed after its first rupture, there is a possibility of the formation of multiple bonds (C = C double bonds and even C ≡ C triple bonds) together with degradation. Since a soliton is a zone of compressed bonds and at the same time a zone with a high kinetic energy (momentum), the movement of high-energy (1–3 eV) solitons entails the compression of bonds to lengths equal to and even smaller than the length of the C = C double bond and the simultaneous transfer of momentum to the lateral atoms sufficient to break them off. The time variation of only those compressive deformations which exceed 0.2 Å, which correspond to the formation of a C = C double bond, is illustrated in Fig.14 for the first molecular product (2–13) of the mechanodegradation of a 50-atom chain (the stretching and degradation are illustrated in Fig.5). It is seen from Fig.14 that, even after the very short lifetime of the free fragment, all its bonds undergo repeatedly strong compressions under the influence of the high-energy solitons. Thus one may expect that the propagation of high-energy solitons in a real macromolecule leads to the formation of C = C double bonds and the "shedding" of side groups. A similar result was obtained in a quantum-mechanical study[29] of the behaviour of terminal alkyl radicals following intense compression of the $C_\alpha - C_\beta$ bond.

Another important result is the formation in the course of the mechanodegradation of the chain of excited low-molecular-weight products with an excess vibrational energy (up to 1.0–1.5 eV/bond) and translational energy E_{trans} (a few eV) (Table 3) which are hence capable of initiating the decomposition of the surrounding polymer chains on collision with the latter. The fact that several "hot", highly excited molecular products, each of which is capable of transmitting excitation and initiating the rupture of one of the neighbouring stressed chains, are formed on rupture and subsequent decomposition of one polymer chain is especially important. Thus there is a possibility of the branching of the mechanodegradation process. Similar considerations have been put forward by Mel'ker and Kuznetsova.[8]

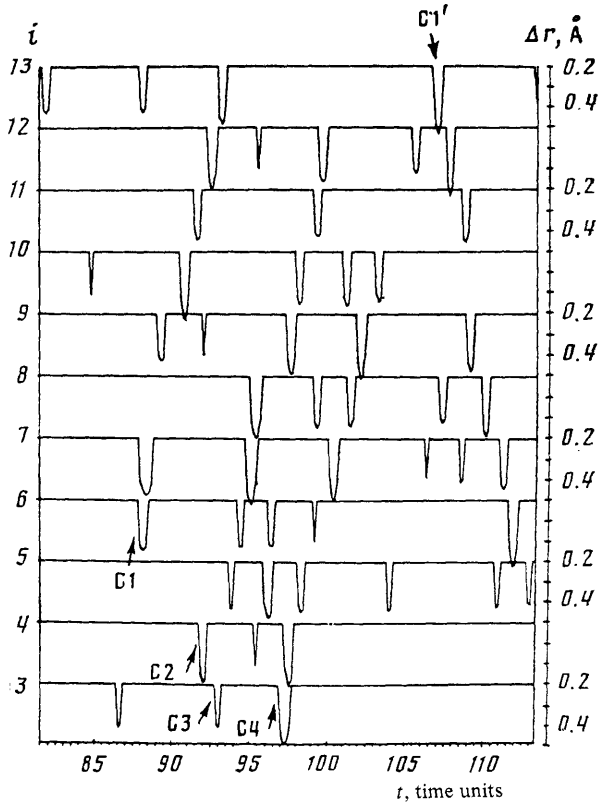


Figure 14. Compression of the C–C bonds by high-energy solitons (~3 eV) to lengths less than the length of the C = C double bond;[27] Δr = compressive deformation (in Å) exceeding 0.2 Å (1 division = 1 Å); C1, C2, C3, C4, and C1′ = high-energy solitons; i = number of the bond; t = time expressed in time units (1 time unit = 10^{-14} s).

Table 3. Information about the molecular products of the mechanodegradation of chains at 0 K.

N	V_{str}	Initial position of fragment in chain	τ, time units	n'	E_{trans}, eV	E_{vibr}, eV	$E_{vibr}/(n'-1)$, eV
50	$0.1V_{so}$	2—13	93.977	12	0.001	17.364	1.58
		11—13	119.25	3	**0.764**	2.024	1.01
		8—10	136.971	3	0.001	3.261	1.63
50	$0.05V_{so}$	43—48	148.881	6	0.516	5.20	1.04
		43—46	201.026	4	**0.656**	1.438	0.48
		47—48	201.026	2	0.028	0.096	0.096
100	$0.1V_{so}$	10—27	157.741	18	0.016	21.40	1.26
		5—27	180.691	23	0.040	20.97	0.95
		5—22	182.579	18	0.312	13.52	0.80
		23—27	182.579	5	**2.22**	1.07	0.27
		15—22	217.149	8	0.295	7.49	1.07
		19—22	307.930	4	0.259	2.20	0.73

Note. N is the number of atoms in the chain, V_{str} the rate of stretching of the chain, τ the instant of the formation of the product, n' the number of atoms in the product, E_{trans} the kinetic energy of the translational motion of the product, E_{vibr} the vibrational energy of the product, $n' - 1$ the number of bonds in the product, and $E_{vibr}/(n' - 1)$ the density of the vibrational energy in the product.

The proposed branched chain mechanism of the breakdown of polymer chains can explain the known explosive character of the formation of submicrocracks and microcracks.

3. The energetics of the mechanodegradation process

In order to determine the mechanodegradation yields, we shall consider the energetics of the entire process. The energy balance will be expressed by the equation

$$U_0 = nD + \sum_{i=2}^{n-1} E_i + E_1 + E_n,$$

where U_0 is the elastic (potential) energy stored in the initial polymer chain at the instant of the first rupture, n the number of ruptures, D the C–C bond dissociation energy, E_i the total energy of the ith molecular product ($E_i = E_{vibr} + E_{trans}$), and E_1 and E_n are the total energies of the two ends of the chain remaining after mechanodegradation and linked to the polymer matrix.

The first term (nD) on the right-hand side of the equation represents the "pure" energy expenditure on the mechanodegradation. We shall call the ratio nD/U_0 the energy yield of the mechanodegradation and shall designate it by the letter Y. We also introduce the following quantities: the yield of mechanodegradation in terms of ruptures Y', defined as the number of ruptures per 10 eV of the stored elastic energy, and the yield of the mechanodegradation in terms of molecular products Y'', defined as the amount of molecular products formed as a result of the mechanodegradation per 10 eV of the stored elastic energy.

The quantities Y' and Y'' were introduced because they can be determined in a physical experiment, for example, by EPR, IR spectroscopy, and mass spectrometry, and can be compared with the results of numerical modelling. Table 4 presents the yields Y, Y', and Y'' for the case investigated.

Table 4. The mechanodegradation yields.

N	V_{str}, Å ps^{-1}	U_0, eV	n	Y	Y', $n/(10$ eV)	$n-1$	Y'', $(n-1)/(10$ eV)
50	23	42.5	3	0.247	0.7	2	0.47
50	11.5	30.0	3	0.350	1.0	2	0.66
100	23	76.0	4	0.184	0.5	3	0.40

Note. T = 0 K, U_0 is the potential energy stored in the chain at the instant of the first rupture, and $n - 1$ is the number of products.

The energy of the molecular mechanodegradation products

$$\left(\text{the sum } E_1 + \sum_{i=2}^{n-1} E_i + E_n\right)$$

over a period of ~10^{-12} s is transmitted to the macromolecules nearest to the rupture site and then spreads into the bulk of the polymer already in the form of waves of the type of solitons. The high stability of solitons suggests that the scattering of their energy requires an appreciable number of scattering centres, as a result of which the energy of the relaxation wave is thermalised over a large ensemble of atoms and the heating of the polymer in the vicinity of the rupture is therefore insufficient for the occurrence of secondary thermal degradation reactions. This factor is apparently the cause of

the difference between the compositions of the molecular products of thermal degradation of mechanodegradation, established experimentally by different investigators for different polymers (Table 1).

IV. Principal results and prospects

The study of the mechanodegradation of a one-dimensional model of a polymer chain by the method of molecular dynamics and analysis of the results in terms of the theory of non-linear waves have shown that unified non-linear waves of the type of solitons, which are the only high-energy agents in the process, play a decisive role in mechanodegradation. For a long time ($\sim$10 ps) after the rupture of the stretched chain, there is no significant thermalisation of the elastic energy stored in it and no thermofluctuations are observed in the generally accepted sense.[6] The high-energy molecular mechanodegradation products observed experimentally by Enikolopian et al.[5] are formed only in the initial stage of the degradation of the polymer chain over a time range 10^{-2}–1 ps after its first rupture.

Comparative analysis of all the observed ruptures established that the ruptures occur via three main mechanisms. The first mechanism, characteristic solely of primary ruptures, involves a structural transition in the most stretched section of the polymer chain. The second mechanism, characteristic solely of secondary ruptures in the initial stage of the mechanodegradation in those sections of the polymer chain where the energy density is very high ($\sim$1 eV/unit), is determined by the arrival at the free end of the chain (or a large fragment) of a packet of N solitons moving in one direction. The following feature has been established: a packet of N solitons breaks off a fragment containing N atoms. The third mechanism, characteristic of both primary and secondary ruptures in sections of the polymer chain with a low energy density ($\sim$0.1 eV/unit), involves the entry of a soliton into the stretching region of the chain, i.e. into the zone for which the following two conditions are fulfilled simultaneously: $\varepsilon > \varepsilon_{cr}$ and $\varepsilon > 0$.

It has been shown that high-energy solitons, which are localised compression waves with a high kinetic energy (momentum), can lead to conditions under which there is a possibility of the formation of C = C double bonds and the shedding of lateral atoms. It has been observed that, on rupture of a single chain, there is a possibility of the formation of several high-energy molecular products, each of which is capable of 'damaging' the surrounding polymer chains. Thus the rupture of one chain can be the cause of the branching of the chain process, leading to the explosive formation of submicrocracks and microcracks.

It has been established that an appreciable proportion (tens per cent) of the elastic energy stored in the chain is expended on its degradation.

Despite the satisfactory agreement of the results of MD calculations of the kinetic energy of the translational motion of the moelcular mechanodegradation products (Table 3) and the experimental data (Table 2), further theoretical studies are necessary for the following reasons.

Firstly, the one-dimensional nature of the model precludes the determination of the contribution to the intramolecular dynamics of the deformation of the valence angles and of conformational rearrangements by the motion of lateral atoms and groups and by intermolecular interactions.

Secondly, the "rigid" fixation of the chain at the boundaries leads to its unrealistic isolation. The complete (100%) reflection of the compression and relaxation waves as well as solitons from the boundaries makes the energy level of the entire mechanodegradation process unduly high. A decrease in the influence of the boundaries may be expected in the rupture of "hot" and longer chains.

Thirdly, the consideration of the macromolecules solely in terms of classical mechanics does not permit a direct observation of the quantum-mechanical pathway leading to changes in its structure (for example, hybridisation) under the conditions of high deformations.

In a more complete consideration of the macromolecule as a quantum-mechanical object, it is necessary to take into account the possible conversion of part of the stored energy on extension into the electronic excitation and ionisation energy, which may be observed, as shown by Zarkhin et al.,[30] for considerable deformations of the macromolecule both in the stage involving its extension and after rupture—in the stage of intense intramolecular dynamics.

References

1. V R Regel', O F Pozdynakov, A V Amelin, et al. *Materialy I Vsesoyuznoi Konferentsii po Mass-Spektrometrii* (Proceedings of the Ist All-Union Conference on Mass Spectrometry), Izd. LIYaF, Leningrad, 1972, p. 198
2. L S Zarkhin Abstract of Candidate's Thesis in Chemical Sciences, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1979
3. A E Gal', K E Perepelkin, O F Pozdnyakov, et al. *Preprinty 3-go Mezhdunarodnogo Simpoziuma po Khimicheskim Voloknam* (Preprints of the 3rd International Symposium on Chemical Fibres), Izd. VNIISV, Kalinin, 1981, Vol. 5, p. 69
4. M A Grayson, C J Wolf *Latest Instrumental Methods for the Investigation of the Structure of Polymers* (Edited by J L Koenig) (Translated into Russian), Izd. Mir, Moscow, 1982, pp. 55–88
5. N S Enikolopian, L S Zarkhin, E V Prut *J. Appl. Polyum. Sci.*, 1985, **30** 2291
6. V R Regel', A I Slutsker, E E Tomashevskii *Kineticheskaya Priroda Prochnosti Tverdykh Tel* (Kinetic Nature of the Strength of Solids), Izd. Nauka, Moscow, 1974, p. 540
7. M Toda, R Hirota, J Satsuma *Supplement of the Progress of Theoretical Physics*, 1976(59), 148–162
8. A I Mel'ker, A I Mikhailin, T E Kuznetsova *Mekh. Kompoz. Mater.*, 1979(4), 720
9. G A Grigoryan, L S Zarkhin, L I Manevich *Tesizy Dokladov VIII Vsesoyuznogo Simpoziuma po Mekhanoemissii i Mekhanokhimii Tverdykh Tel. Tallin* (Abstract of Reports at the VIIIth All-Union Symposium on Mechanoemission and the Mechanochemistry of Solids, Tallin), Izd. Moskov. Lesotekh. Inst., 1981, p. 80
10. A I Mel'ker, T E Kuznetsova *Fiz. Tverd. Tela*, 1980, **22**(4) 1039
11. A I Mel'ker, T E Kuznetsova *Fiz. Tverd. Tela*, 1977, **19**(8) 1531
12. A I Mel'ker, T E Kuznetsova, A E Vladimirov *Mekh. Kompoz. Mater.*, 1980(3), 387
13. A I Mel'ker, A I Mikhailin *Fiz. Tverd. Tela*, 1981, **23**(6) 1746
14. A I Mikhailin, A I Mel'ker *Fiz. Tverd. Tela*, 1980, **22**(8) 2518
15. A I Mikhailin, A I Mel'ker *Khim. Fiz.*, 1985, **4**(1) 15
16. M G Zaitsev, I V Razumovskaya, *Vysokomol. Soedin.*, 1979, **21B**(6) 461
17. J H Batech, J D Powell *Solitons in Action* (Edited by K Longren, E Scott) (Translated into Russian), Izd. Mir, Moscow, 1981, p. 269

18. F E Walker, A M Karo, J R Hardy *Non-equilibrium Cooperative Phenomena in Physics and Related Fields* (Edited by M G Velarde), Elsinor, Madrid, 1983, p. 363
19. V S Zhukov *Pis'ma v Zh. Eksp. Teor. Fiz.*, 1983, **38**(11) 523
20. M A Collins *Adv. Chem. Phys.*, 1983, **53** 225
21. T J Rolfe, S A Rice, J Dancz *J. Chem. Phys.*, 1979, **70**(1) 26
22. G A Grigoryan, L S Zarkhin, L I Manevich *Doklady VIII Vsesoyuznogo Simpoziuma po Mekhanoemissii i Mekhanokhimii Tverdykh Tel* (Reports at the VIIIth All-Union Symposium on Mechanoemission and the Mechanochemistry of Solids), Valgus, Tallin, 1986, Part II, p. 63
23. G A Grigoryan, L S Zarkhin, L I Manevich *Dokladdy VIII Vsesoyuznogo Simpoziuma po Mekhanoemissii i Mekhanokhimii Tverdykh Tel* (Rreports at the VIIIth All-Union Symposium on Mechanoemission and the Mechanochemistry of Solids), Valgus, Tallin, 1986, Part II, p. 69
24. V A Lagunov *Fiz. Tverd. Tela*, 1985, **27**(7) 2175
25. M Toda *Phys. Lett.*, 1975, **18**C(1) 1
26. L S Zarkhin, S V Sheberstov, N V Panfilovich, L I Manevich *Tezisy Dokladov X Yubileinogo Vsesoyuznogo Simposiuma po Mekhanoemissi i Mekhanokhimii Tverdykh Tel* (Abstracts of Reports of the Xth Jubilee All-Union Symposium on Mechanoemission and the Mechanochemistry of Solids), Izd. Moskov. Lesotekh. Inst., Moscow, 1986, p. 88
27. L S Zarin, L I Manevich, N S Enikolopian *Makromol. Chem.* (in press)
28. J Forsyth, M Malcolm, K Mowler *Machine Methods for Mathematical Computations* (Russian Translation from English edited by Kh D Ikramov), Izd. Mir, Moscow, 1980, p. 280
29. L S Zarkhin, K Ya Burshtein *Vysokomol. Soedin.*, 1982, **24**B(9) 695
30. L S Zarkhin, K Ya Burshtein, N S Enikolopian *Dokl. Akad.'. Nauk SSSR*, 1987, **293**(1) 133

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The formation of polymers on the surfaces of disperse carbon materials

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ABSTRACT. The characteristic features of the synthesis of polymers (radical and ionic polymerisation, polyaddition, polycondensation) on the surfaces of disperse carbon materials (graphite, carbon black, and diamond) are examined. The processes involving the formation of polymers, their structures, and their properties are analysed taking into account the chemistry of the surfaces of disperse carbon fillers, which plays an important role in the preparation of filled polymeric materials by the method of polymerisation filling.
The bibliography includes 106 references.

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I. Introduction

The introduction of solid disperse or fibrous substances into the polymer phase makes it possible in a number of instances to improve significantly the physicochemical, mechanical, thermal, electrical, frictional, and other properties of the polymers. The chemical properties of the solid surfaces of fillers influence the efficacy of their use in compositions with high molecular weight compounds. The surfaces of fillers frequently contain functional groups, which can participate in various chemical reactions and determine to a large extent the character of the solid–polymer interaction. By altering specifically the chemical properties of the surface, it is possible to influence the nature of the interaction of the polymer with the filler surface and ultimately to improve significantly the operating properties of the polymeric material.

The graft polymerisation of monomers initiated by complex catalysts, organometallic compounds, free radicals, or ions fixed on the surface is a promising method, from the theoretical and applied points of view, of obtaining filled polymeric materials.

Among the fillers used to obtain filled polymeric materials, disperse carbon materials (carbon black, graphite) are widely used. In connection with the wide-scale development of the manufacture of synthetic diamond powders in our country, there has been a sharp increase in the interest of investigators in the creation on their basis of filled polymeric materials having many interesting and even unique properties.

However, the results of numerous novel investigations of the corresponding polymerisation processes have not so far been subjected to a due analysis, especially from the standpoint of the influence of the chemistry of the surfaces of carbon fillers and the formation processes and structures of the polymers. The aim of the present review is to fill this gap.

II. The chemistry of the surfaces of disperse carbon materials and the structure and morphology of their particles

Since carbon atoms are capable of forming chemical bonds of different types as a result of the different degrees of hybridisation of the orbitals of their valence electrons, there exist a wide variety of structures of solid carbon compounds. Among them three principal forms can be distinguished—diamond, graphite, and carbyne and in addition carbon fibres and carbon black. We shall consider briefly the chemical structure and the properties of the surfaces of these materials.

Diamond. The surface of diamond, like that of any other solid, can be regarded as one of the main defects of the three-dimensional structure of the crystal.[1] The edge of the structure of the diamond skeleton, where the coordination sphere of the surface carbon atoms is altered, as well as the high enthalpy of formation of the ideal surface promote the spontaneous occurrence of processes lowering the energy of the system. One of such processes may be the formation of surface functional groups.[2]

The existence of unsaturated bonds on the diamond surface ensures the possibility of the formation of various surface compounds. The interaction of the atomically clean diamond surface with low-molecular-weight compounds leads to the appearance of surface functional groups. Using chemical analytical, spectroscopic, and resonance methods,[2] the existence on the surface of diamond of carboxy-, hydroxy-, carbonyl, lactone, ether, $=CH_2$, $=CF_2$, and $-CH_3$ groups has been established.

Studies have been published recently concerning the fixation on the surfaces of carbon materials, including diamond powders, of functional groups having a definite chemical nature.[3–7] In order to remove various impurities (non-recrystallised graphite, metals, metal carbides, and organic substances) from their surface, diamond powders are first etched with $HClO_4$.[6] Concentrated HNO_3 and the chromic acid mixture (conc. H_2SO_4 + $K_2Cr_2O_7$) are also used to obtain a chemically clean diamond surface.[6]

As a result of the action of oxidants and the subsequent vacuum heat treatment, the surface of diamond powders is freed from the majority of oxygen-containing groups and can be used for the

fixation on it of various functional groups, for example, halide and hydride groups.

Experimental data have established that, when the diamond surface is halogenated, the following chemical reactions take place:[5]

$$2[C]+Hal_2 \rightarrow 2[C-]-Hal,$$
$$[C-]-H+Hal_2 \rightarrow [C-]-Hal+HHal.$$

The maximum amount of chloride groups (~ 11 μmol m^{-2}) add to the diamond surface at 523–673 K which corresponds to a monolayer surface coverage.[5] When the surface of diamond which is modified with Cl groups is hydrogenated and treated with methane, the following reactions take place:[4]

$$[C-]-Cl+H_2 \rightarrow [C-]-H+HCl,$$
$$[C-]_m-Cl_n+nCH_4 \rightarrow [C-]_{m+n}-H_{3n}+nHCl.$$

An increase in temperature promotes a gradual increase in the degree of surface coverage by hydride and methyl groups (the maximum chemical monolayer coverage is attained at 823 K).

The formation of highly polar reactive functional groups of the type OH, COOH, and NH_2 on the surface of carbon, including diamond, powders, is of special interest. Thus the substitution of chlorine atoms on the surfaces of carbon substances on treatment with steam at 373–733 K results in the formation of an equivalent amount of surface OH groups:[4,8]

$$[C-]-Cl + H_2O(steam) \rightarrow [C-]-OH + HCl.$$

The fixation of COOH groups is observed when specimens of carbon materials are heated with concentrated HNO_3 for 5 h.[9]

Apart from nitric acid, the chromic acid mixture and perchloric acid are also used to oxidise carbon-graphite materials.[5] When carbon substances are boiled for 3 h in the oxidants indicated, acid groups and activated hydrogen are produced on the surfaces of the carbon-graphite materials. The number of these groups increases in the sequence initial powder < HNO_3-treated powder < chromic acid mixture-treated powder < $HClO_4$-treated powder.[5]

The NH_2 functional groups are fixed on the carbon surface when its chlorine atoms are treated with gaseous ammonia at 623–673 K:[4–6]

$$[C-]-Cl+NH_3 \rightarrow [C-]-NH_2+HCl.$$

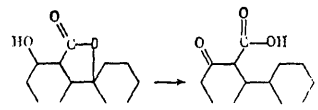
Graphite. One of the crystalline forms of carbon, widely used in various branches of industry and technology, is graphite.[10] The prospects for the intensive utilisation of graphite are associated, in particular, with the creation on its basis of anti-friction materials and filled materials with optimum properties.[11]

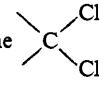
The interaction of graphite with polymers is known to be influenced significantly by the nature and concentration of its surface functional groups. Various oxygen-containing functional groups, both acid and basic, are present on the surface of graphite stored in air,[12,13] their ratio depending on the method of preparation, the subsequent treatment, and the conditions of storage of the specimens. Sub-groups include the carbonyl, phenolic, hydroxy-, and lactone groups.

The results of chemical analysis[16] indicate a relatively high concentration of COOH groups and also the presence of hydroxy- and hydroperoxy-groups, which arise on hydration of the oxidised graphite surface by water vapour. Apparently, unidentified oxygen partly enters into the composition of heterocyclic compounds, radicals, and internal oxygen bridges.[14]

It is notable that the names employed above for the oxygen-containing groups are rather conventional in character, since neighbouring groups interact in solid carbon compounds, especially in conjugated systems, which results in the formation of oxygen-containing groups with a more complex polyfunctional composition.[14]

Analysis of the real surfaces of graphites with the aid of physico-chemical (mass spectrometric and IR and EPR spectroscopic) and chemical (reactions with CH_3Mg and CH_2N_2) methods established the structures of the acid oxygen-containing groups, which were identified as cyclic esters (lactones) existing as tautomeric forms:[13,15]



Important information about the chemical nature of the graphite surface can be obtained by investigating the adsorption interaction with it by substances of different types. Only prismatic faces of graphite are known[16] to be reactive, since all the bonds in the basal plane are saturated. The sorption of hydrogen on an atomically clean graphite surface at 300 K is fully irreversible and the amount of hydrogen adsorbed on the prismatic faces is $N_H = 1.1 \times 10^{14}$ atoms cm^{-2}, which is almost 13 times smaller than the corresponding value for oxygen. The chemisorption of oxygen on a graphite specimen after it had been kept in a hydrogen atmosphere followed by desorption differs little from the adsorption of oxygen on the atomically clean surface. The number of adsorbed H and O atoms is the same as the number of carbon atoms forming the prismatic graphite faces.[16] The adsorption of molecular chlorine on an atomically clean graphite surface proceeds similarly to the adsorption of hydrogen and leads to the formation of the  groups.

Analysis of data on the surface chemistry of graphite confirms the reactivity of its prismatic faces and the possibility of the formation of surface groups of the same type as on diamond. The presence of functional groups creates the possibility for the chemical grafting of polymers on the graphite surface and for increasing its reinforcing effect in polymer compositions.

Carbon black. The wide scale and great variety of the applications of carbon blacks in the national economy makes the study of their structure, methods of preparation, and modification of current interest. The existing views on the structure of carbon black particles, as a molecular and supermolecular organisation of condensed carbon, cannot be regarded as fully established. Fairly contradictory views are frequently expressed in the literature on this question.[17] Apart from the generally accepted models of the structure of carbon black—the 'graphite' and condensed carbon models—others have also been suggested on the basis of all the forms of the organisation of carbon known at the present time. Furthermore, there exist views in conflict with traditional ideas about the structure of carbon materials and especially carbon black.[18]

Transitional forms of carbon, including carbon black and carbon fibre, have a more complex structure, in contrast to the principal crystalline forms (diamond and graphite) owing to the different nature of the surface carbon atoms on the carbon black particles, existing in different hybrid states (sp^3, sp^2, sp). The edge atoms in carbon black crystallites, like those in the graphite crystal, have less than three neighbours, i.e. their valences are not fully saturated. They are saturated by hydrogen or hydrocarbon radicals formed in the carbon black formation process.

Apart from carbon, carbon black also contains hydrogen, sulphur, oxygen, and minerals. Hydrogen and oxygen enter into the composition of various chemical groups of the surface layer, determining its chemical properties. The existence on the surface of carbon blacks of both acid and basic groups, whose ratio depends on the method of preparation and the subsequent treatment of the carbon blacks, has been established by physicochemical and chemical methods.[14] Carboxy-, carbonyl, phenolic, and lactone groups[19,20] as well as the groups formed by nitrogen and sulphur atoms[19] have been detected on the surfaces of carbon black and graphite.

The functional groups are bound mainly to edge carbon atoms in the basal planes. These carbon atoms influence strongly the properties of the groups linked to them. Thus the COOH groups retain their acidity, which may even increase: they are in fact responsible for the low pH of aqueous suspensions of certain carbon blacks and also for their ability to absorb bases. The carboxy-groups bound to aromatic rings enter into the composition of quinones. The quinone oxidation and reduction processes can occur on the surfaces of carbon blacks, which determines certain properties of the surface layer.[13,15]

The presence of oxygen on the surface of the carbon black predetermines to a large extent its physical, physicochemical, and operating properties.[21] The enhancement of the polar character of the surfaces of carbon blacks when they are partly coated by oxygen has a significant influence on the adsorption properties: the degree of adsorption of polar substances increases in this case[22,23] but the ability of carbon blacks to absorb non-polar substances never fully disappears under these conditions.[20]

The oxygen-containing groups formed on the surfaces of graphite and carbon black are in principle identical. However, it has been demonstrated by enthalpymetric titration that the acidity of the oxygen-containing groups on graphite is greater than on carbon black.[15] Consequently, the nature of the substrate undoubtedly influences the properties of the surface compounds (the degree of conjugation of the chemical bonds in graphite is greater and the proton participating in the reaction is therefore more mobile).[16]

Carbon blacks contain (mainly in the bulk of the particles) paramagnetic centres which do not interact with free radicals under the usual conditions. The complexity of the EPR spectra of carbon black[24,25] is explained by the presence of at least two types of paramagnetic centres and several types of unpaired electrons weakly interacting with one another. Furthermore, the form of the EPR spectrum may become complicated as a result of the appearance of lines corresponding to the radical oxidation products.

The interaction of free radicals, including growing polymer radicals, with radicals present on the surface of the carbon black leads to the firm fixation of the macromolecules or to grafting. The fixation of free radicals on carbon black can also be due to the presence of surface quinonoid groups, since the number of radicals bound to the surface is greatly diminished when such groups are reduced.[26]

The surface of carbon black particles is physically and chemically inhomogeneous. In many instances, this makes it impossible to obtain sufficiently reliable results in the study of chemical processes with its participation. In order to impart to the surface of the carbon black specific properties and to improve the adhesion interaction in carbon black compositions, specific modification of the chemical composition of the surface is carried out.[24,27-29] The methods used to obtain functional groups on the surface of the carbon black are analogous to those already described for diamond and graphite.

The specific features of carbon fillers of different types are determined by two principal factors: the structure of the skeleton of the particles and the chemistry of the surface which depends on it. In particular, the presence in the structure of graphite (and partly also carbon black) of aromatic rings increases the reactivity of the surface groups bound to the carbon atoms in these rings. The identical chemical reactivities of the functional groups on the surface of diamond is due to the equivalence of all the carbon atoms in its crystal structure.

III. The formation of polymers on the surfaces of disperse carbon materials

Much attention has been devoted in recent years to the preparation of composite polymeric materials by synthesising polymers in the presence of fillers.[30,31] Carbon materials with a fairly high reactivity in polymerisation initiation processes, which in many cases makes it possible to obtain graft polymers even without any preliminary treatment of the filler surface, are therefore of considerable interest. The nature of the interaction of polymer molecules with the carbon black surface has been investigated fairly thoroughly, while the monomer polymerisation processes on the surfaces of carbon black and graphite have been inadequately studied. Very few studies have been devoted to the nature of the active polymerisation centres on the newly formed surfaces of carbon blacks and graphite and for diamond such data have until recently been virtually lacking.

1. Free-radical polymerisation in the presence of carbon substances

Vibromilling of carbon blacks and graphite without access of air in vinyl monomers results in the graft polymerisation of the latter.[16] The ground carbon substances retain for a long time their ability to initiate polymerisation after dispersion. It has been suggested[16] that polymerisation is initiated by the free radicals formed on rupture of the C–C bonds and also by carbon atoms in the singlet state.

In the presence of graphite, the rate of polymerisation of methyl methacrylate under the influence of $NaHSO_3$ in an aqueous medium increases while the activation energy falls compared with the unfilled monomer.[32,33]

The molecular weight of poly(methyl methacrylate) diminishes with increase in the amount of filler, which is apparently due to processes involving the transfer of the growing chain to graphite. It has been suggested that polymerisation is initiated by the radicals $H\dot{S}O_3$ formed on interaction of $NaHSO_3$ with methyl methacrylate and water in accordance with the following scheme:

$$2HSO_3^{\ominus} + CH_2{=}\underset{\displaystyle COOCH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}} + 2H_2O \rightarrow 2H\dot{S}O_3 + 2OH^{\ominus} + CH_3{-}\underset{\displaystyle COOCH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{CH}}}}\ .$$

In general, much attention has been devoted to the thermal graft polymerisation of vinyl monomers on the surface of carbon black. It has been established that, when a carbon black is introduced into the monomer during the thermal polymerisation of styrene, the yield of the polymer diminishes.[34] The inhibiting effect of carbon black has been explained[16] by the interaction of the growing polymer radicals with the free radicals on the carbon black surface. It has been pointed out that the carbon black free radicals are incapable of initiating the polymerisation of monomers under the usual conditions

but they readily interact with the radicals of the growing macromolecular chain. The duration of the inhibition period is a function of the amount of carbon black introduced into the monomer.[35]

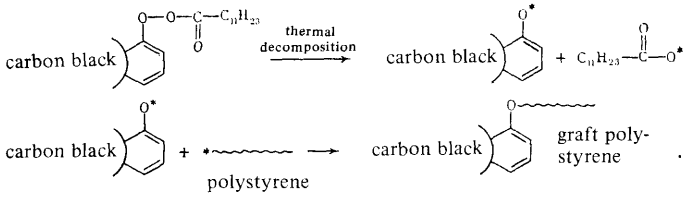
The inhibiting effect of carbon black has been attributed[34–36] to the presence on its surface of quinone groups which are reduced to hydroquinones groups in the course of polymerisation. The hydrogen atoms in the hydroxy-groups of the latter are mobile and capable of adding to the double bond of styrene, initiating its polymerisation. At the end of the inhibition period, the polymerisation of styrene is greatly accelerated in the presence of the carbon black. Both the inhibition stage and the acceleration stage are attributed to the presence on the surface of the carbon black of oxygen, which influences the duration of the inhibition period.[37–39]

The usual but accelerated thermal polymerisation takes place in the concluding stage of the reaction, which is explained by the fact that the chain termination rate constant is smaller in the presence of the carbon black than in the pure solution.[35,40]

It has been established[40] that part of the polymer formed in the presence of the carbon black is strongly bound to its surface, which indicates the grafting of the polymer chains. The amount of the grafted polymer can reach in many instances 15–20%. Since there are many radical centres on the surface of the carbon black capable of reacting with peroxy- and cyanoisopropyl radicals,[16,34] one can assume that the polystyrene radicals can also react with these centres, forming grafted chains.

In order to diminish the inhibiting effect of the carbon black and to increase the yield of the graft polymer, its surface is treated by peroxides. The surfaces of carbon substances promote in most cases the decomposition of peroxides, whose mechanism depends on the composition of the surface functional groups.[34,41–43] The fixation of peroxide initiators, especially 4,4-peroxobis(4-oxo)butanoic acid, on PM-100 carbon black[42] increases considerably their decomposition rate constant compared with the process occurring in the absence of the carbon black.

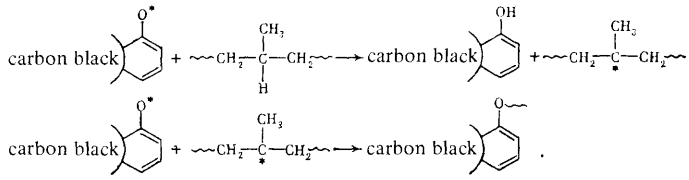
The rate of polymerisation in the presence of initiators fixed on the surface of the carbon black increases.[34] This effect can be accounted for by assuming that the growing chains are adsorbed on the surface of the carbon black and that such adsorption obeys the Langmuir–Hinshelwood law.[16] The mechanism of the formation of the graft polymer can be represented schematically as follows



As a result of the treatment of the carbon black by peroxides, the polymerisation interaction period can vanish (for example, on treatment with lauryl peroxide[16]), which indicates the blocking of the surface quinone groups or their reduction to hydroquinone groups, or it may increase (for example, on treatment with benzoyl peroxide[44]).

The efficacy of the grafting of polymers on the surfaces of carbon materials depends both on the nature of the initiator and on the chemistry of the surface. Measurements have been made[45] of the constants for chain transfer to the surfaces of oxidised carbon fibres during polymerisation carried out in the presence of lauroyl peroxide, benzoyl peroxide, and azobisisobutyronitrile. In the system with lauroyl peroxide, the chain transfer rate constant exceeds by a factor greater than 2 the corresponding value in the system with azobisisobutyronitrile. A highly oxidised surface with an increased content of carboxy-groups is the most reactive in the reaction with primary radicals.[34]

The quinone and aryloxy-groups present on the carbon black surface are capable of abstracting a hydrogen atom from a tertiary carbon atom. The radical derived from the polymer or an organic compound, formed under these conditions, can add to the surface of the carbon black:[40]



Despite the large number of studies on the polymerisation of monomers on carbon black, the influence of the chemistry of the filler surface on the characteristics of the formation of polymers was not studied in most of them, since the nature and number of surface functional groups on carbon black were as a rule unknown. In connection with the recent appearance of data on the chemical homogenisation of the surfaces of disperse carbon substances,[4–7] we investigated the influence of the chemistry of the surfaces of carbon fillers on the kinetics and characteristic features of the radical polymerisation and copolymerisation of vinyl monomers.[49,50]

One of the ways of modifying the surfaces of fillers by polymers is known to be[47,48] radical polymerisation which is initiated in this instance by the radicals fixed on the filler surface and formed as a result of the thermal decomposition of the initiators.[39] In particular azoisobutyronitrile (AIBN) and 4,4′-azobis-4-cyanovaleric acid (ACVA) have been used as initiators.[49] The latter initiator is of special interest in view of its ability to be chemisorbed in a number of instances on the substrate surface. A study of the adsorption of AIBN and ACVA from solutions on powdered ASM 1/0 diamond, ARV graphite, and GG-10 carbon black with specific surfaces of 10 000, 5000, and 10 000 $m^2\ kg^{-1}$ respectively and containing surface groups of a specific type (H, Cl, COOH, or NH_2 [2–6]) made it possible to establish that the equilibrium degree of adsorption of AIBN and ACVA depends both on the nature of the surface functional groups and on the nature of the filler skeleton. In all the instances investigated, the degree of adsorption of AIBN and ACVA on carbon substances containing different surface groups increased in the sequence H < Cl < COOH < NH_2. The degrees of the equilibrium adsorption of AIBN and ACVA on fillers with identical functional groups, referred to their concentration, differ significantly and increase as a function of the nature of the filler in the sequence carbon black < diamond < graphite, which is probably associated with the different structures of the carbon skeletons of the fillers and their influence on the reactivity of the surface groups. At the same time, the degree of equilibrium adsorption calculated per unit surface of the test powders is significantly higher for ACVA than for AIBN (by a factor of 1.5 on carbon black, 3–4 on graphite, and 10 on diamond). This demonstrates a significant influence of the polarity of the COOH functional groups in the initiator molecules on its sorption interaction with the surfaces of disperse carbon substances.

In order to elucidate the characteristics of the modification of the surfaces of disperse carbon fillers by polymers, a study was made of the influence of the nature of the adsorption on the kinetic parameters of the thermal decomposition of the sorbed azo-initiators.[50] With increase in the polarity of the surface

functional groups of the carbon materials in the sequence H < Cl < COOH < NH_2, the decomposition constants of the adsorbed AIBN and ACVA increased, while their activation energy for the thermal decomposition fell. It has been suggested[50,51] that the significant influence of the adsorption of initiators on their thermal stability may be due to the following causes:

(1) the decrease in the number of degrees of freedom of the initiator molecules as a result of their fixation on the surfaces of the carbon materials;

(2) the possibility of the addition of ACVA molecules via both end groups to the surfaces of disperse carbon materials and the formation of strained rings, which are apparently less stable than the linear molecule.[52]

The fixation of initiators on a solid surface is known[35,53] to entail in many instances a sharp decrease in the rate of polymerisation. This effect has been explained by the limitation of the diffusional mobility of the primary radicals bound to the solid phase, which leads to their rapid recombination, and also by topochemical factors determined by the localisation of the chain initiation, propagation, and termination processes at the surface of the filler particles.[53]

Table 1. The influence of the chemistry of the surfaces of disperse carbon materials on the amount (wt.%) of polystyrene not extractable from their surfaces.[46,49,50]

Initiator	Surface groups	Amount* of polystyrene not extractable from the surface		
		graphite	diamond	carbon black
AIBN	—H	1.2/0.8	0.30/—	1.4/1.0
	—Cl	1.3/0.7	0.58/—	1.6/1.2
	Initial specimen	3.2/2.2	2.0/0.6	4.0/2.4
	—COOH	3.4/2.5	3.5/2.1	5.6/2.6
	—NH_2	6.1/2.9	7.3/2.4	7.8/2.6
ACVA	—H	2.1	0.71	2.2
	—Cl	2.4	0.84	2.4
	Initial specimen	6.2	6.5	7.3
	—COOH	10.5	12.4	14.5
	—NH_2	13.5	13.8	16.1

Note. The polystyrene was obtained by radical polymerisation in suspension in the presence of the adsorbed initiators AIBN and ACVA.

*The numerator and denominator indicate respectively data obtained in the presence and absence of the initiator.

The polystyrene formed on polymerisation of styrene in the presence of an initiator sorbed on the filler surface and introduced into the monomer (0.5% relative to the monomer) is a mixture of a non-extractable polymer grafted to the surfaces of the disperse carbon materials and a homopolymer extractable by hot toluene and benzene.[46,49,50] Table 1 shows that the nature of the functional groups on the surfaces of disperse carbon materials influences significantly the amount of polystyrene non-extractable from the surfaces, which is especially notable in the polymerisation of styrene initiated by ACVA. A much greater amount of non-extractable polystyrene is formed on the surfaces of graphite and carbon black containing H groups than on the surface of diamond, which is apparently associated with the presence on the graphite and carbon black surfaces of free radicals capable of reacting with the growing polystyrene macroradicals. This leads to the termination of the polymer chain and the grafting of polystyrene to the surface. Such radicals have not been detected on the surface of diamond stored in air, which is apparently the reason for the smaller amount of polystyrene grafted to its surface.

The amount of polystyrene grafted on carbon substances containing different surface groups increases in all the systems investigated in the sequence H < Cl < initial specimen† < COOH < NH_2, which is correlated with the increase in the amount of adsorbed azo-initiators on these surfaces.[46]

As in the studies of Ivanchev and co-workers,[34,37] Bryk and Burban[46] observed a low efficacy of the initiation of the polymerisation of monomers by initiators (especially ACVA) fixed on the surfaces of carbon substances and a deviation of the kinetics of such a reaction from those characteristic of radical polymerisation. The latter is expressed by a decrease in the polymerisation reaction order with respect to the initiator from 1 to 0.3–0.7. According to Ivanchev and co-workers,[34,47] the observed phenomena can be attributed to the localisation of the initiator on the surface of the solid phase. The approach of the monomer molecules to a surface reaction centre 'shielded' by the polymer can be hindered in many instances and the rate of reaction is then controlled by diffusional factors.[34] The lower rates of formation of graft polystyrene compared with the homopolymer may be associated with the increase in the probability of the recombination of the primary radicals in the surface layer and their involvement in the termination of the growing chains.[47]

Analysis of the results of these studies carried out permit the conclusion that the grafting of the polymers onto the surfaces of carbon fillers can proceed via several mechanisms:

(1) as a result of the termination of the growing macroradicals on the radical centres present on the surfaces of the fillers.

(2) as a result of polymerisation initiated by the active centres on the surfaces of carbon black and graphite.

(3) in the interaction of the surface functional groups of the filler with the macroradicals.

(4) as a consequence of the transfer of the growing polymer chain to the surfaces of the carbon materials.

The molecular weight of the polystyrene obtained in the presence of disperse carbon materials with adsorbed AIBN and ACVA depends significantly on the chemistry of the surfaces of the fillers. The increase in the rate constant for the decomposition of the adsorbed initiators[50] leads to an increase in both the rate of initiation and in the rate of termination of the growing chains, which promote a decrease in the molecular weight of the polymer (Table 2).[34]

The presence in the polymer matrix of a solid and, what is most important, an active surface is known[54] to influence significantly the properties of the polymer. The change in the main characteristics of thermoplastics in the presence of fillers is associated with the alteration of the physical structure of the polymer at the polymer–solid interface. When disperse fillers are introduced into amorphous polymers, the adsorption interaction of the polymer molecules with the surface leads to the formation of a definite structure, inducing changes in the thermomechanical properties of the polymer.[54–56]

†The specimen of the carbon material which has not been treated in order to generate functional groups of a specific type and containing different surface functional groups.

Thus the introduction of carbon fillers diminishes the mobility of the polymer macromolecules as a consequence of their interaction with the surfaces of the particles.

Table 2. Dependence of the molecular weight of the polystyrene obtained at 353 K by ACVA-initiated polymerisation on the rate constant for the decomposition of ACVA.[46,49,50]

Carbon material	Surface groups	$10^{-5} k_d$, s^{-1}	Molecular weight of graft polystyrene
Diamond	—H	10.1	57000
	—Cl	10.9	52000
	—COOH	12.0	32000
	—NH_2	14.0	30000
Graphite	—H	12.0	55000
	—Cl	12.8	52000
	—COOH	13.3	30000
	—NH_2	16.0	28000
Carbon black	—H	8.97	56000
	—Cl	9.70	54000
	—COOH	10.30	36000
	—NH_2	11.70	34000

The glass point of the polymer increases in this instance in the sequence of the following functional groups present on the fillers: H < Cl < COOH.[46,57] Such variation is characteristic of polystyrene obtained in the presence of AIBN and ACVA adsorbed on the surfaces of carbon substances and is more pronounced for ACVA apparently due to the higher energy of the interaction of the ACVA molecules and of the radicals formed on their decomposition with the surface.[50]

It has been established[46,57] that the presence of a carbon filler (especially one containing the COOH and NH_2 surface groups) appreciably increases the resistance of the polymer to thermo-oxidative degradation. This can apparently be accounted for by the structure-forming effect of the filler, whose particles become the nodes of a structural network arising as a result of the interaction of the polymer molecules with the surface.[57] The stabilising effect of the filler on the thermal properties of the polymer is manifested to a greater extent the stronger the bond between the polymer and the surface.

The energy of the interaction of the polymer with the surface influences appreciably also the mechanical properties of the compositions obtained by the polymerisation of filled monomers. Thus the ultimate compressive strength of compositions of polystyrene with disperse carbon materials increases with increasing adsorption and chemical interactions of the macromolecules with the surface, which is in many respects determined by the chemistry of the surface of the solid phase.[54]

The effect involving the strengthening of the polymers depends greatly on the nature of the fillers and their structure. The number of surface functional groups and their reactivity are then of primary importance.[58] The geometry of the surfaces of the disperse materials is also very important.

Among the multiplicity of polymeric materials, filled three-dimensional polymers, in the preparation of which polymerisation and structure formation processes are carried out in the presence of a filler with an active surface, should be given special consideration.

Studies on the characteristic features of the radical copolymerisation of styrene with divinylbenzene (DVB) in the presence of disperse carbon materials with initiators (AIBN and ACVA) adsorbed on their surfaces have shown that the yield of the copolymer diminishes with increase in the polarity of the surface groups of the fillers in the sequence H < Cl < COOH < NH_2.[59] This is apparently associated with the decrease in the rate of polymerisation when the initiator is fixed on a solid surface.[34,52]

Table 3. Dependence of M_c of the styrene–divinylbenzene copolymer obtained in the presence of disperse carbon materials on the chemistry of their surfaces.[59]

Initiator	Surface groups	M_c^* of the copolymer on		
		diamond	graphite	carbon black
AIBN	—H	415	420	410
	—Cl	418	426	420
	Initial specimen	440	456	438
	—COOH	455	466	450
	—NH_2	458	470	456
ACVA	—H	418	416	415
	—Cl	422	420	425
	Initial specimen	480	490	475
	—COOH	506	517	502
	—NH_2	515	530	510

Note. Divinylbenzene content 10 wt.%; polymerisation temperature 343 K.
*M_c = 400 for the unfilled copolymer.

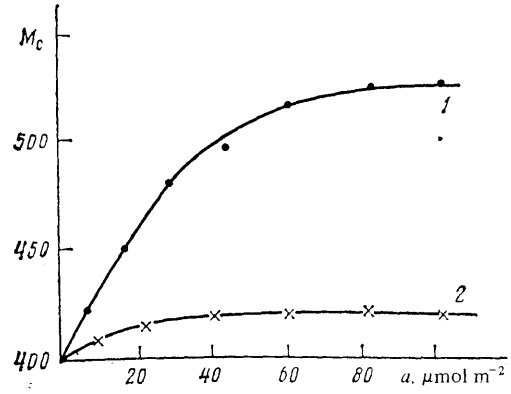


Figure 1. Dependence of M_c of the styrene–divinylbenzene (10 wt.%) copolymer, obtained in the presence of diamond containing surface NH_2 (curve *1*) and H (curve *2*) groups, on the concentration of the adsorbed ACVA initiator.[59]

Table 3 shows that the presence of fillers influences the density of the three-dimensional network [the molecular weight of the polymer between the nodes of the cross-linked structure (M_c)]: in all cases M_c for filled systems is greater than for the corresponding unfilled systems. This effect is manifested more strongly when fillers

containing the COOH and NH_2 surface groups are used. Furthermore, with increase in the amount of adsorbed initiator, the M_c of the copolymer formed increases only up to a specific initiator concentration (Fig. 1). Along the initial section of the curve, the dependence of M_c on the ACVA concentration is linear, which can apparently be explained by the dominant contribution of the surface to the termination of the polymer chain, which results in the formation of a defective three-dimensional network. On further increase in the amount of adsorbed initiator, a break in the curve is observed, which may be due to the initiation of the copolymerisation process by a much greater number of radicals, formed as a result of the thermal decomposition of the adsorbed initiators, and with their contribution to the formation of the polymer network of the copolymer. The final structure of the copolymer is determined by the overall effect of these factors acting in opposition.

2. Ionic polymerisation on the surfaces of disperse carbon substances

Studies have been published recently in which the ionic polymerisation of alkenes initiated by transition metal complexes fixed on the surfaces of fillers, including carbon fillers, was considered.[59-64] The presence on the carbon black surface of various oxygen-containing functional groups permits the fixation of $TiCl_4$ on the filler surfaces as a result of the formation of covalent bonds with the oxygen atoms:[60,61]

$$[C]_m(OH)_n \xrightarrow[-n\,HCl]{n\,TiCl_4} [C]_m(OTiCl_3)_n,$$

$$[C]_m(OH)_n \xrightarrow[-n\,HCl]{n/2\,TiCl_4} [C]_m(O_2{-}TiCl_2)_{n/2}.$$

Also possible is the addition of $TiCl_4$ to the carbonyl groups of the carbon black surface with formation of compounds having the composition (carbon black)—O.$TiCl_4$, which corresponds, according to Krasnobryzhii et al.,[61] to the "undissociated form of chemisorption" of $TiCl_4$. $TiCl_4$ adds to the graphite and diamond surfaces via a similar mechanism.[62-65]

Transition metal complexes fixed on the filler surface form the active centres for polymerisation. The characteristic features of the stereospecific polymerisation of ethylene initiated on the complexes of $TiCl_4$ with triethylaluminium have been determined.[62-65] In particular, the kinetics of this process under non-stationary conditions have been elucidated using graphite and diamond as fillers.[62] The much lower rate of polymerisation on graphite has been explained by the more pronounced reducing properties of its surface compared with the surface of diamond. In combination with the effect of alkyl groups, this gives rise to the possibility of the reduction of Ti(IV) ions to give a lower oxidation state, i.e. of their conversion into an inactive form.[66] The high rate of reaction on diamond is attributed to the formation of active complexes on interaction of the titanium chloride groups fixed on diamond with the triethylaluminium in the reaction medium.[62]

The study of the polymerisation of propene on stereospecific Ziegler–Natta catalysts, obtained by the alternate deposition of $TiCl_4$ and $(C_2H_5)AlCl_3$ on different carriers, established that the activity of the catalyst on graphite is several times greater than on perlite, talc, tuff, and other fillers.[67,68] The high activity and stereospecificity of the catalysts fixed on the graphite surface are determined both by the layered structure of graphite and by its electron-donating properties, which influence the structure of the polymerisation active centres.[67]

Further detailed studies on the kinetics and other features of the polymerisation of olefins on carbon fillers should give rise to the possibility of regulating the amount of the polymer formed on their surface in order to impart the required physicomechanical properties to the compositions.

Apart from the fixation of transition metal complexes, other methods for the modification of the surfaces of carbon black and graphite, used in the ionic polymerisation of monomers of different nature, are also known. It is known[69,70] that the inclusion compounds of alkali metals in graphite, having the general formula MC_n, are active catalysts of anionic polymerisation. It has been suggested that metal cations are inserted between the graphite layers, which then acquire a negative charge and ability to initiate polymerisation. The negative charge on the carbon network of graphite and hence the initiating activity depend significantly on the nature of the alkali metal and increase in the sequence Li < Na < K.[71,72] Polymerisation can occur both on the surfaces of the graphite layers and between the carbon networks. In the former case, chain propagation takes place following the adsorption of the monomer on the catalyst surface and in the latter after the insertion of the monomer between the graphite networks in the anion–graphite bonds.[72]

The possibility of using variable composition potassium–carbon black compounds as the catalyst of the anionic polymerisation of vinyl monomers has been studied.[77] It has been suggested that the polymerisation of monomers with strongly electro-negative groups may be initiated by radical-ions of the type R–$\dot{C}$H–$\overline{C}H_2$ arising as a result of electron transfer from the conductivity band of the catalyst to the monomer molecule adsorbed on its surface.

The direct propagation of ionic chains on the carbon black surface becomes possible as a result of a preliminary treatment which leads to the replacement of some of the hydrogen atoms, forming part of the polyaromatic structure, by lithium atoms.[16] Butyllithium, forming part of the composition of a complex with tetramethylenediamine, has been used for such "metallation" of the carbon black.[73-76]

An interesting way of obtaining graft polymers on the carbon black surface involves the initiation of the polymerisation by alkali metal and ammonium carboxylates.[78-80] It has been observed that, in the polymerisation of propiolactone, accompanied by ring opening and initiated by the COOM groups on the carbon black surface, the efficacy of the grafting diminishes with increase in the degree of conversion of the monomer.[78,79] This effect has been attributed to chain transfer to the monomer and the formation of the homopolymer. The reactivity of the COOM groups on carbon black depends on the nature of the alkali metal and increases in the sequence Li < Na < K < Rb < Cs.

Studies dealing with the modification of the carbon black surface by polymers formed via a cationic mechanism have been published recently.[81-85] A study has been made of the cationic polymerisation of α-methylstyrene, isobutyl vinyl ether, indene, and *N*-vinyl-2-pyrrolidinone on a carbon black surface.[83,84] It has been suggested that the polymerisation is initiated by the surface carboxy-groups of the carbon black.[81] In the polymerisation of *N*-vinylcarbazole on carbon black,[85] the polymerisation active centres are formed as a result of electron transfer from the monomer to the carbon black and the recombination of the radical-cation formed with the surface of the carbon black. The monomer cations fixed on the surface in this way function as the polymerisation active centres. The rate of polymerisation is directly proportional to the monomer concentration and the amount of the carbon black.

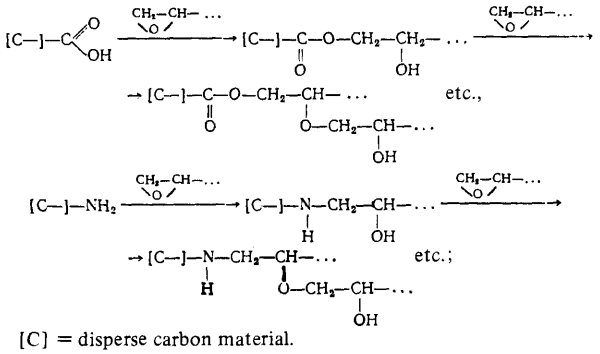
The cationic polymerisation of styrene on the surface of carbon black containing the $CO^+ClO_4^-$ functional groups has been studied.[86] The overall yield of the graft polymer increases linearly with increasing polymerisation time and reaches 85% at 313 K. The grafted $CO^+ClO_4^-$ groups are also capable of initiating the polymerisation of vinylpyridines and cyclic monomers.

3. Polyaddition and polycondensation on the surfaces of disperse carbon materials

The presence of reactive functional groups, especially COOH or NH_2, on the surfaces of carbon materials leads to the possibility of obtaining graft polymers by methods involving the polyaddition of oligomers and their polycondensation with the corresponding groups.

Modern ideas about the interaction of polymers with fillers are to a large extend based on the study of the adsorption of polymers and oligomers from solutions.[56] Thus, in the investigation of the adsorption interaction of the ED-20 epoxide resin on the phenol-formaldehyde Novolac resin with the surfaces of diamond, carbon black, and graphite powders, containing the H, Cl, COOH, or NH_2 groups, established that the degree of adsorption of the oligomers increases in the sequence H < Cl < COOH < NH_2.[87,88] This has been attributed to the differences between the energies of the sorption interactions of the oligomers with the surface. The hardening of the epoxide and phenolformaldehyde resins in the presence of disperse carbon materials without the introduction of a hardening agent into the system is induced by the participation of the surface groups of the carbon substances in this process.[9,89,90]

An IR spectroscopic study has led to the hypothesis[87,88] that the interaction of the epoxide resin with the COOH and NH_2 groups proceeds via the mechanisms



[C] = disperse carbon material.

There have been numerous studies in which the formation of three-dimensional polymer networks in the presence of disperse fillers was considered,[9,30,31] but at the present time the influence of the nature of the filler on the formation of network polymers and their structure still remains little investigated.[90]

The questions of the molecular interaction of the polymer–filler surface and of the mechanism of the influence of the filler on the polymer at comparatively large distances from its surface, greatly exceeding the radius of action of intermolecular forces (up to 150 to 200 μm), are also controversial.[91]

In order to ensure a strong adhesion bond between the polymer and the filler, both the chemistry of the surface of the filler[90,91] and the structure of the interfacial oligomeric adsorption layer[64,91,92] are very important. Depending on the nature of the oligomer and the filler, either rigid or elastic networks can be formed near the surface, which is also determined by the distance of the polymer layer formed from the surface.[90,91]

It is known[54,92] that the influence of the filler on the formation reactions of network polymers can be characterised by two opposed effects:

(1) By the chemisorption interaction between the macromolecules on the surface and also by the formation of strong physical adsorption bonds between them, which tends to reduce the degree of swelling of the compositions.

(2) By the termination of the reactions involving the growth of the macromolecules on the filler surface with formation of a defective network, which increases the degree of swelling of the filled network polymers.

In each specific case, the contributions of these processes acting in opposition are different and the final properties of the composition are determined by their overall effect.

Table 4. Dependence of the density of the polymer network (M_c) and the Huggins constant (χ) of the ED-20 epoxide resin, hardened in the presence of disperse diamond, graphite, and carbon black containing NH_2 groups, on the concentration of the filler.[88,89]

Filler	Filler concentration, wt.%	M_c^* at		χ at	
		298 K	333 K	298 K	333 K
Diamond	10	112	342	1.09	0.80
	30	103	—	1.10	—
	50	95	315	1.11	0.84
	90	82	300	1.14	0.84
Graphite	10	92	330	1.10	0.82
	30	88	—	1.10	—
	50	84	311	1.17	0.83
	90	71	292	1.26	0.85
Carbon black	10	216	424	0.85	0.44
	30	169	—	0.86	—
	50	146	391	0.92	0.46
	90	109	373	0.94	0.50

* M_c = 323 in the absence of the filler at 333 K.

The study of the structure of three-dimensional polymer networks has shown[88,89] that, with increase in the degree of filling of the resins, M_c diminishes (Table 4). This effect is associated with the increase in the total number of the surface COOH and NH_2 groups, functioning as centres for grafting and for the hardening of the resin on the surface, and leads to a diminution of M_c. The increase in the Huggins constant with the degree of filling can be explained, according to Burban et al.[93] and Lipatov et al.,[94] by the fact that the increase in the amount of filler diminishes the thermodynamic stability of the polymer–solvent system.

Fig. 2 shows that the degree of sorption of acetone vapour by the epoxide resin, hardening in the presence of carbon black (30% filling), depends significantly on the chemistry of its surface and increases in the sequence NH_2 < COOH < initial specimen < Cl < H.[88] The values of M_c for the corresponding compositions, amounting to 169, 182, 201, 221, and 254, increase in the same sequence. The phenomena indicated are apparently associated with the different kinds of interactions (chemical and physical with different energies)[93,95,96] of the epoxy-groups of the oligomers with the functional groups on the carbon black surface.

The values of M_c measured on the specimens swollen in solvent vapour at an elevated temperature (Table 5) characterise in the main the chemical nodes of the three-dimensional polymer network.[95,96]

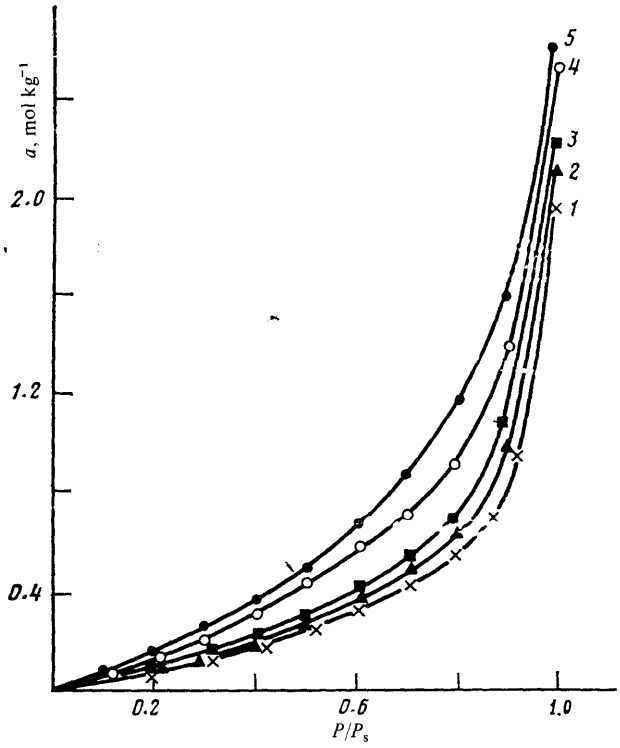


Figure 2. Isotherms of the sorption of acetone vapour by the ED-20 epoxide resin hardened in the presence of carbon black (30 wt.%) containing different surface groups at 298 K:[95] *1*, NH_2; *2*, COOH; *3*, initial carbon black; *4*, Cl; *5*, H.

Thus the structure of the polymer networks, formed when the epoxide and phenol formaldehyde resins are hardened on the surfaces of disperse carbon materials, depend significantly both on the chemistry of the surface and the structure of the fillers and on the total number of the chemical and physical cross links. Comprehensive investigation of the structure of three-dimensional polymers at different temperatures has made possible certain reliable conclusions about different interactions leading to the formation of the network structures.

The nature of the adsorption interaction of the oligomers and the structure of the polymer networks, formed when the epoxide and phenolformaldehyde resins are hardened on the surfaces of disperse carbon fillers, undoubtedly influence the properties of the polymeric materials obtained.

The increase in the glass point T_g of the network polymer in the presence of an active surface is due to the strong physical or chemical interaction of the polymer molecules with the solid phase, which limits the mobility of sections of the polymer chain, this being equivalent to the formation of an additional number of cross links.[91,92] In particular, the glass point of the composition is influenced by the state of the filler surface:[90,97-99] if the filler is subjected to the surface antiadhesion treatment, which eliminates the possibility of chemical interaction, then the T_g of the composition based on epoxide polymers does not increase and remains almost the same as for the unfilled resins.

It has been established[93] that the T_g of the epoxide and phenol-formaldehyde resins hardened in the presence of carbon materials increase significantly with increase in the content of the solid phase from 10 to 90% (Table 5). With increase in the polarity of the surface functional groups of the carbon materials, the glass point of the resin also increases.[88]

Table 5. Dependence of the glass points (T_g, K) of compositions based on epoxide and phenolformaldehyde resins on the degree of their filling by disperse carbon materials containing COOH and NH_2 surface groups.[93]

Resin	Degree of filling, wt.%	Diamond		Graphite		Carbon black	
		—COOH	—NH_2	—COOH	—NH_2	—COOH	—NH_2
ED-20*	10	435	434	435	436	433	434
	30	438	440	441	443	436	438
	50	443	447	446	449	441	445
	70	451	453	453	454	446	452
	90	454	458	458	459	452	456
FFS**	10	426	428	438	437	422	425
	30	433	436	445	446	428	430
	50	439	442	452	453	433	434
	70	446	447	458	459	443	442
	90	453	454	464	466	446	447

* T_g = 431 K in the absence of the filler.
** T_g = 460 K in the absence of the filler.

The improvement in the adhesion interaction at the polymer–solid interface and an increase in the strength of the material are important practical tasks in the creation of polymer compositions.

The question of the dependence of the mechanical properties of vitreous polymers on the concentration of chemical and physical nodes of polymer networks has been fairly adequately reflected in the literature.[100-103] The introduction of relatively small amounts of active fillers into polymers, including network polymers, increases the mechanical strength of the compositions as a consequence of the formation of additional cross links and the limitation of the mobility of segments of the macromolecules.[104]

For low and moderate degrees of filling of the epoxide and phenolformaldehyde resins, the ultimate compressive strength of the compositions increases with increase in the amount of carbon substances containing the COOH and NH_2 surface groups.[87,88,93] This phenomenon can evidently be attributed both to an increase in the density of the three-dimensional polymer network, formed in the presence of the filler, and to the formation on its surface of a more rigid boundary layer.[97] On the other hand, the decrease in the strength of the compositions in the region of high degrees of filling is apparently induced by the increase in the residual stresses at the polymer–solid surface interface and the increase in the defectiveness of the polymer network.[105,106]

The state of the filler surfaces also influences significantly the mechanical strength of the composition, since the adhesion bond between the polymer and the solid phase and the orientation and fixation of the oligomers on the surfaces of the particles depend on it.[91] The reinforcing effect of carbon fillers containing various surface groups increases in the sequence H < Cl < initial powder < COOH < NH_2. This is apparently associated with the increase in the same sequence in the density of the polymer networks formed as a result of the hardening of the epoxide and phenolformaldehyde resins on the surfaces of disperse carbon materials.

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The above analysis of the studies on the synthesis of polymers in the presence of disperse carbon materials shows that the chemistry of the filler surfaces influences significantly the process kinetics, the degree of grafting, and the molecular weight of the polymers formed and also the density of the three-dimensional networks of the polymers formed in the three-dimensional polymerisation and polycondensation of filled monomers and oligomers.

The physicochemical properties (glass points and degradation temperatures) and the mechanical properties (compressive strength) of the polymers obtained in the presence of carbon black, graphite, and diamond also depend on the chemistry of the filler surfaces. For the same type of surface functional groups, the polymerisation kinetics, the degree of grafting, and the structure and properties of the polymers formed on the graphite, carbon black, and diamond surfaces are influenced appreciably by the structure of the skeleton of the disperse carbon materials.

It is notable that ionic polymerisation and polycondensation processes on the surfaces of carbon materials with homofunctional groups have been inadequately investigated. Studies on the elementary stages of the free-radical polymerisation process on the surfaces of carbon materials containing surface groups of different kinds and having different structures of the skeleton require further development.

References

1. V P Kiselev, O V Krylov *Adsorbtsionnye Protsessy na Poverkhnosti Poluprovodnikov i Dielektrikov* (Adsorption Processes on the Surfaces of Semi-conductors and Dielectrics), Izd. Nauka, Moscow, 1978, 256 pp.
2. E P Smirnov, S K Gordeev *Almazy: Poluchenie, Svoistva, Primenenie* (Diamonds: Synthesis, Properties, and Applications), Izd. LTI im. Lensoveta, Leningrad, 1984, 73 pp.
3. A Ohira, K Komori, K Nakayama *Muki Jaisitsu Kenkyuse Kenkyu Hokokuse,* 1980(20), 49; *Ref. Zh. Khim.*, 1980, 8T162
4. E P Smirnov, S K Gordeev, S I Kol'tsov, V B Aleskovskii *Zh. Prikl. Khim.*, 1979, **52** 199
5. S K Gordeev, E P Smirnov, S I Kol'tsov, V B Aleskovskii *Zh. Prikl. Khim.*, 1980, **53** 94
6. E P Smirnov, S K Gordeev, S I Kol'tsov, V B Aleskovskii *Zh. Prikl. Khim.*, 1978, **51** 2572
7. S K Gordeev, E P Smirnov, S I Kol'tsov, Yu I Nikitin *Sverkhtverdye Materialy*, 1979(3) 27
8. V I Koval'kov, V P Smirnov, S I Kol'tsov, V B Aleskovskii *Zh. Obshch. Khim.*, 1976, **46** 2151
9. I N Ermolenko, V I Dubkova, I P Lyubiner *Vysokomol. Soedin., Ser. A*, 1978, **20** 2180
10. G A Sirenko *Antifriktsionnye Karboplastiki* (Antifriction Carboplastics), Izd. Tekhnika, Kiev, 1985, 196 pp
11. I A Gribova, O A Vinogradova *Usp. Khim.*, 1979, **48**(1) 177 [English translation in *Russ. Chem. Rev.*, 1979(1)]
12. O V Nikitina, N N Lezhnev, V S Kiselev *Nauch. Trudy VNII Sazhevoi Prom.*, 1972(1), 70
13. S S Barton, G L Boulton, B H Harrison *Carbon,* 1972, **10** 395
14. E P Smirnov, S K Gordeev *Tverdye Soedineniya Ugleroda* (Solid Carbon Compounds), Izd. LTI im. Lensoveta, Leningrad, 1983, 36 pp
15. S S Barton, B H Harrison *Carbon,* 1975, **13** 283
16. M T Bryk *Polimerizatsiya na Tverdoi Poverkhnosti Neorganicheskikh Veshchestv* (Polymerisation on the Solid Surfaces of Inorganic Substances), Izd. Naukova Dumka, Kiev, 1981, 288 pp
17. V M Mel'nichenko, A M Sladkov, Yu N Nikulin *Usp. Khim.*, 1982, **51**(5) 736 [English translation in *Russ. Chem. Rev.*, 1982(5)]
18. R K Arutyunyan *Kauch. Rezina* 1982(2), 29
19. H Fern *Ind. Vernice*, 1975, **29**(5) 20
20. M Jaycock, J Parfit *The Chemistry of Interfaces* (Translated into Russian), Izd. Mir, Moscow, 1984, 269 pp
21. T Van der Plas *The Structure and Properties of Adsorbents and Catalysts* (Translated into Russian), Izd. Mir, Moscow, 1973, p. 436
22. A V Kiselev, Yu V Malygin, V N Stroev, Yu A El'tekov *Kolloidn. Zh.*, 1982, **44** 1051
23. A V Kiselev, Yu V Malygin, V N Stroev, Yu A El'tekov *Kolloidn. Zh.*, 1983, **45** 63
24. A V Kiselev, N N Kovaleva, L S Kosheleva, T I Titova *Kolloidn. Zh.*, 1982, **49** 684
25. A A Merkulov, E I Shalukhanskaya, S V Orekhov *Zh. Fiz. Khim.*, 1981, **55**(1) 188 [English translation in *Russ. J. Phys. Chem.*, 1981(1)]
26. L I Ivashchenko, V Yu Glushchenko *Kolloidn. Zh.*, 1975, **37** 376
27. E P Smirnov, S I Kol'tsov, V B Aleskovskii *Zh. Obshch. Khim.*, 1974, **44** 961
28. V I Koval'kov, E P Smirnov, S I Kol'tsov, V B Aleskovskii *Zh. Obshch. Khim.*, 1986, **46** 2151
29. S I Kol'tsov, A A Malkov, E P Smirnov, V B Aleskovskii *Zh. Prikl. Khim.*, 1976, **49** 1242
30. J A Manson, L H Sperling *Polymer Blends and Composites* (Translated into Russian), Izd. Khimiya, Moscow, 1979, 438 pp
31. P G Babaevskii (Editor) *Promyshlennye Polimernye Kompozitsii* (Industrial Polymer Compositions), Izd. Khimiya, Moscow, 1980, 472 pp
32. T Yamaguchi, T Ono, Y Saito, S Ohara *Angew. Makromol. Chem.*, 1976, **53** 65
33. A B Moustafa, M Abd-Ei-Maboud Sakr *Angew. Makromol. Chem.*, 1976, **55** 11
34. S S Ivanchev *Radikal'naya Polimerizatsiya* (Radical Polymerisation), Izd. Khimiya, Leningrad, 1985, 280 pp
35. L P Vishnevetskaya, G V Shipina *Sbornik Trudov LTI im. Lensoveta* 1974, **4** 103
36. R Kroker, M Schneider, K Hamann *Usp. Khim.*, 1974, **43**(2) 349 [English translation in *Russ. Chem. Rev.*, 1974(2)]
37. K Ohkita, T Tsuita, M Maoda *Kobunshi Rombunsyu,* 1980, **37** 343; *Ref. Zh. Khim.*, 1980, 19S385
38. N Tsubokawa, H Matsumoto, Y Sone *J. Polym. Sci., Polym. Chem. Ed.*, 1982, **20** 1943

39. E N Zil'berman, V I Trachenko, T F Shatskaya, A I Kalinin *Vysokomol. Soedin., Ser. B.*, 1984, **26** 137
40. J B Donnet, E Papirer *Peint. Pigm. Vernis*, 1972, **48** 382
41. Z N Nudel'man, V I Myshkovskii, V L Antonovskii *XII Mendeleevskii S'ezd po Obshchei i Prikladnoi Khimii* (The XIIth Mendeleev Congress on General and Applied Chemistry), Izd. Nauka, Moscow, 1981, p. 113
42. S S Ivanchev, A M Krupnik, A M Mesh, et al., *Zh. Prikl. Khim.*, 1984, **57** 52
43. E Papirer *J. Polym. Sci., Polym. Chem. Ed.*, 1979, **17** 1843
44. K Ohkita, N Tsubokawa, E Saiton, et al., *J. Soc. Rubb. Ind. Japan*, 1976, **49** 900
45. A Tanaka, T Engisawa, R Josomiya *J. Polym. Sci., Polym. Chem. Ed.*, 1980, **18** 2267
46. M T Bryk, A F Burban *Polymer Composites*, Walter de Gruyter and Co., West Berlin, New York, 1986, p. 269
47. S S Ivanchev, A V Dmitrenko *Usp. Khim.*, 1982, **51**(7) 1178 [English translation in *Russ. Chem. Rev.*, 1982(7)]
48. V A Popov, V V Guzeev, Yu A Zvereva, et al. *Vysokomol. Soedin., Ser. A*, 1984, **26** 2489
49. M T Bryk, A F Burban, S K Gordeev, E P Smirnov *Kolloidn. Zh.*, 1986, **48** 131
50. M T Bryk, A F Burban, S K Gordeev, E P Smirnov *Kinet. Katal.*, 1985, **26** 583
51. N M Emanuel', D G Knorre *Kurs Khimicheskoi Kinetiki* (Textbook of Chemical Kinetics), Izd. Vys. Shkola, Moscow, 1974, p. 400
52. V A Popov, Yu A Zvereva, E S Klimov, et al. *Vysokomol. Soedin., Ser. A*, 1982, **24** 729
53. Yu A Zvereva, V A Popov, V V Guzeev, et al. *Dokl. Akad. Nauk SSSR*, 1980, **252** 1174
54. Yu S Lipatov *Kolloidnaya Khimiya Polimerov* (Colloid Chemistry of Polymers), Izd. Naukova Dumka, Kiev, 1984, 344 pp.
55. P A Rebinder *Izbrannye Trudy* (Selected Works), Vol. 2 *Poverkhnostnye Yavlenniya v Dispersnykh Sistemakh* (Surface Phenomena in Disperse Systems), Izd. Nauka, Moscow, 1978, 368 pp
56. Yu S Lipatov *Usp. Khim.*, 1981, **50**(3) 355 [English translation in *Russ. Chem. Rev.*, 1981(3)]
57. A F Burban, M T Bryk *Plast. Massy*, 1987(10), 26
58. V B Aleskovskii *Stekhiometriya i Sintez Tverdykh Soedinenii* (The Stoichiometry and Synthesis of Solid Compounds), Izd. Nauka, Leningrad, 1976, 142 pp
59. M T Bryk, A F Burban *Ukr. Khim. Zh.*, 1988, **54** 982
60. A A Baulin, A I Krasnoshchekov, A S Deyanova, Yu I Vasilenok *Zh. Prikl. Khim.*, 1982, **55** 2534
61. A V Krasnobryzhii, E P Smirnov, S I Kol'tsov *Zh. Prikl. Khim.*, 1981, **54** 1605
62. E P Smirnov, A O Mikheev, S K Gordeev, et al. *Dokl. Akad. Nauk SSSR*, 1985, **284** 911
63. A O Mikheev, E P Smirnov, S K Gordeev, V G Korsakov, Manuscript deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 26.11.84, No.7553-84D.
64. A O Mikheev, E P Smirnov, V G Korsakov, Manuscript deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 30.01.85, No.873-85D
65. A O Mikheev, Abstract of Candidate's Thesis in Chemical Sciences, Lensovet Leningrad Technological Institute, Leningrad, 1986
66. Yu I Ermakov, V A Zakharov, B I Kuznetsov *Zakreplennye Kompleksy na Okisnykh Nositelyakh v Katalize* (Immobilised Complexes on Oxide Carriers in Catalysis), Izd. Nauka, Novosibirsk, 1980. 248 pp
67. V S Skazka, A E Ruchin, V G Shevchenko, et al. *Vysokomol. Soedin., Ser. B*, 1984, **26** 596
68. N I Galashina, P M Nedorezova, V I Tsvetkova, et al. *Dokl. Akad. Nauk SSSR*, 1984, **278** 620
69. E Loria, J P Pascault, G Merle *New Develop. Ion. Polym. Ist. Eur. Discuss. Meet. Polym. Sci. Strasbourg*, 1978, 146
70. J Gole *Mater. Sci. Eng.*, 1977, **31** 309
71. Yu N Novikov, Ts V Kakuliya, L M Khananashvili, et al. *Dokl. Akad. Nauk SSSR*, 1979, **245** 848
72. Ts V Kakuliya, L M Khananashvili, L S Dneprovskaya, et al. *Vysokomol. Soedin., Ser. A*, 1980, **22**, 1690
73. K Ohkita, N Nakayama, A Funaki, M Simomura, *Kobunshi Rombunsyu*, 1980, **37** 595; *Ref. Zh. Khim.*, 1981, 2S435
74. M Shimomura, N Nakayama, K Ohkita *Am. Chem. Soc. Polym. Prepr.*, 1979, **20** 851
75. K Ohkita, N Nakayama, A Funaki *Sikidzai Kekaishi*, 1980, **53** 583; *Ref. Zh. Khim.*, 1982, 2T69
76. K Ohkita, N Nakayama, M Shimomura *Carbon*, 1980, **18** 277
77. V A Kargin, V A Kabanov, T K Metel'skaya *Vysokomol. Soedin.*, 1960, **2** 162
78. N Tsubokawa, A Funaki, Y Hada, Y Sone *J. Polym. Sci., Polym. Chem. Ed.*, 1982, **20** 3297
79. N Tsubokawa, A Funaki, Y Hada, Y Sone *Polym. Bull.*, 1982, **7** 589
80. N Tsubokawa, A Funaki, Y Sone *J. Appl. Polym. Sci.*, 1983, **28** 2381
81. N Tsubokawa, N Takeda, T Iwasa *Polym. J.*, 1981, **13** 1093
82. N Tsubokawa, N Takeda, K Kudoh *Carbon*, 1980, **18** 163
83. N Tsubokawa, N Takeda, A Kanamaru *J. Polym. Sci, Polym. Lett. Ed.*, 1980, **18** 625
84. N Tsubokawa, N Takeda, K Kudoh *J. Chem. Soc. Japan, Chem. and Ind. Chem.*, 1980, 1264
85. M Biswas, S A Haque *J. Polym. Sci., Polym. Chem. Ed.*, 1983, **21** 1861
86. N Tsubokawa *J. Polym. Sci., Polym. Lett. Ed.*, 1983, **21** 705
87. A F Burban, M T Bryk *Napolniteli Polimernykh Materialov* (Fillers for Polymeric Materials), Izd. MDNTP im. Dzerzhinskogo, Moscow, 1983, p. 69
88. M T Bryk, A F Burban, S K Gordeev, et al. *Ukr. Khim. Zh.*, 1984, **50** 1054
89. V I Dubkova, I N Ermolenko, I P Lyubliner *Vysokomol. Soedin., Ser. A*, 1984, **26** 1139
90. I Z Chernin, S M Smekhov, Yu V Zherdev *Epoksidnye Polimery i Kompozitsii* (Epoxide Polymers and Compositions), Izd. Khimiya, Moscow, 1982, 232 pp
91. Yu S Lipatov *Fizicheskaya Khimiya Napolnennykh Polimerov* (Physical Chemistry of Filled Polymers), Izd. Khimiya, Moscow, 1977, 304 pp
92. Yu S Lipatov *Mezhfaznye Yavleniya v Polimerakh* (Interfacial Phenomena in Polymers), Izd. Naukova Dumka, Kiev, 1980, 259 pp
93. A F Burban, M T Bryk, S K Gordeev, et al. *Ukr. Khim. Zh.*, 1987, **53** 434
94. Yu S Lipatov, L V Karabanova, L M Sergeeva *Vysokomol. Soedin., Ser. A*, 1977, **19** 1073
95. E B Trostyanskaya, P G Babaevskii *Vysokomol. Soedin., Ser. A*, 1968, **10** 288

96. E B Trostyanskaya, P G Babaevskii *Usp. Khim.*, 1971, **40**(1) 117 [English translation in *Russ. Chem. Rev.*, 1971(1)]
97. V I Irzhak, B A Rozenberg, N S Enikolopyan *Setchatye Polimery: Sintez, Struktura, Svoistva* (Network Polymers: Synthesis, Structure, and Properties), Izd. Nauka, Moscow, 1979, 248 pp
98. O B Salamatina, E L Akopyan, S N Rudnev, et al. *Vysokomol. Soedin., Ser. A*, 1983, **25** 179
99. V V Korshak *Khimicheskoe Stroenie i Temperaturnye Kharakteristiki Polimerov* (The Chemical Structure and Temperature Characteristics of Polymers), Izd. Nauka, Moscow, 1970, 420 pp
100. V I Kortsovnik, B A Rozenberg *Vysokomol. Soedin., Ser. A*, 1979, **21** 2154
101. E M Filyanov, T V Krasnikova, N N Peschanskaya *Vysokomol. Soedin., Ser. A*, 1985, **27** 1487
102. N N Peschanskaya, V A Stepanov, E M Filyanov *Fiz. Tverd. Tela*, 1982, **24** 3262
103. V A Bershtein, N N Peschanskaya, V A Stepanov *Vysokomol. Soedin., Ser. A*, 1980, **22** 2246
104. A A Askadskii *Deformatsii Polimerov* (Deformation of Polymers), Izd. Khimiya, Moscow, 1973, 448 pp.
105. T E Lipatova, L S Sheinina *Kataliz i Mekhanizm Reaktsii Obrazovaniya Polimerov* (Catalysis and the Mechanisms of Polymer Formation Reactions), Izd. Naukova Dumka, Kiev, 1980, p. 128
106. I D Simonov-Emel'yanov, A M Chebotar' *Plast. Massy*, 1976(11) 41

Translated from *Uspekhi Khimii* 63 684–709 (1989) U.D.C. 541.183.1

Ion exchangers based on modified mineral carriers

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ABSTRACT. Methods for the synthesis of ion exchangers based on modified mineral carriers, such as chemical modification of the surface by organosilicon compounds, adsorption and chemical modification of the surface by low-molecular-weight and polymeric organic compounds, the polymerisation of monomers on the surface of mineral carriers, and the hydrolytic polycondensation of organosilicon compounds, have been examined. A list of the most widely encountered commercial sorbents has been given. The possibilities provided by the use of ion exchangers based on mineral carriers for the sorption and separation of inorganic ions, in the high-performance liquid chromatography of organic compounds and biopolymers, and also in catalysis, have been demonstrated.

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I. Introduction

Until recently, two main classes of ion exchanger were known: synthetic organic polymers containing ionogenic functional groups, and inorganic materials, primarily silica, aluminium oxide, and zeolites. The extensive practical application of organic polymeric ion exchangers is due to their universal action, the high concentration of ionogenic groups, the ease of regeneration, and the possibility of varing widely the nature and concentration of the functional groups and hence the sorptive and catalytic characteristics of these materials. The advantages of inorganic ion exchangers are their mechanical strength, their stability to heat and radiation, and the fact that they do not swell in solvents. In general, it can also be said that they have better mass-exchange characteristics, as is clearly seen by comparing the sorptive properties of meso-porous and large-pore mineral materials and organic sorbents with a gel structure. In addition, certain types of inorganic ion exchanger have unique catalytic properties.

At the same time, the development of chemistry and biochemisty has raised problems, for the solution of which both known classes of ion exchanger have proved unsuitable. For example, the use of organic ion exchangers in the intensively developing high-performance liquid chromatography is prevented by their poor average mass-exchange characteristics and the fact that the volume of the sorbent layer in the chromatographic column is not constant. Although mineral sorbents do not have these disadvantages, they can be used to solve only a restricted range of problems, because of the non-uniformity and narrow variability of the surface properties.

It has thus become necessary to create materials of a new type, combining the advantages of the previously known classes of ion exchanger. The mechanical and mass-exchange characteristics of these materials should be determined primarily by the rigid wide-pore mineral framework of the carrier, and their ion-exchange characteristics by the nature of the attached functional groups. The production of these materials has involved the modification of the surface of inorganic materials by organic compounds containing ion-exchanger functional groups.

The ion exchangers being considered form part of an extensive class of modified mineral carriers which find varied applications in sorption, chromatography, catalysis, and other branches of science and technology. The methods of preparation, properties, and applications of these materials have been described in a large number of publications (see for example the published monographs[1–11] and reviews[12–19]), but no general review of ion exchangers based on modified mineral carriers has been published. Such a review is appropriate, because of the specific characteristics of the synthesis of these materials and the fields of application in which only these materials are used, such as high-pressure ion chromatography, the ion-exchange chromatography of proteins and other natural compounds, and acid–base and phase transfer catalysis.

The present review describes methods for obtaining ion exchangers based on mineral carriers, some of their properties, and their applications in sorption, catalysis, and chromatography.

II. Methods for obtaining ion exchangers based on modified mineral carriers

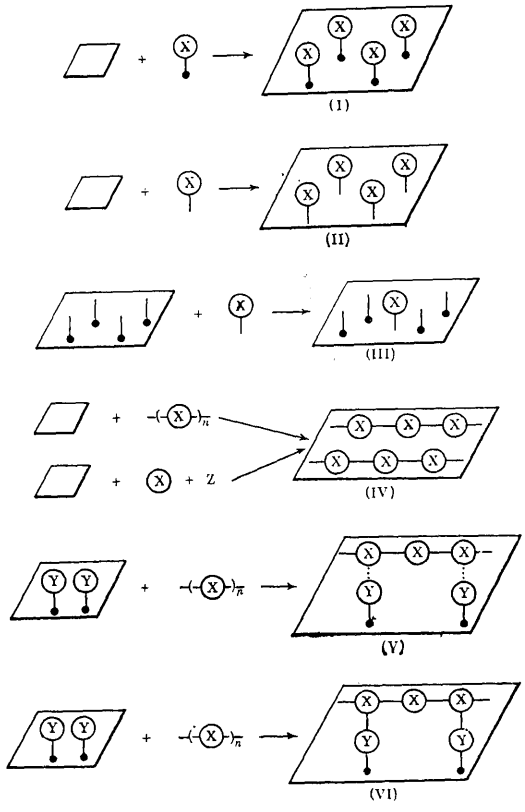
A large number of functional groups capable of taking part in ion exchange have been attached to the surface of mineral carriers. It was decided to restrict the present review to a narrow range of classical ion exchangers. Thus the cation exchangers examined include strongly, moderately, and weakly acidic materials containing sulphonic, phosphonic, and carboxylic acid groups, and the anion exchangers include strongly basic materials with quaternary ammonium and phosphonium groups and weakly basic materials with mono- and polyamine groups. The last sorbents, and also phosphonic and carboxylic acid cation exchangers, in a number of cases may show complex-forming power. The properties and applications of these sorbents associated with complex formation are not examined in the present review. Other materials excluded from the present review are modified mineral carriers with grafted tertiary phosphines or ionogenic molecules of aminoacids, dithiocarbamates, dithiocarboxylic acids, hydroxamic acids, and other compounds for which complex-forming properties or affinity are most characteristic.

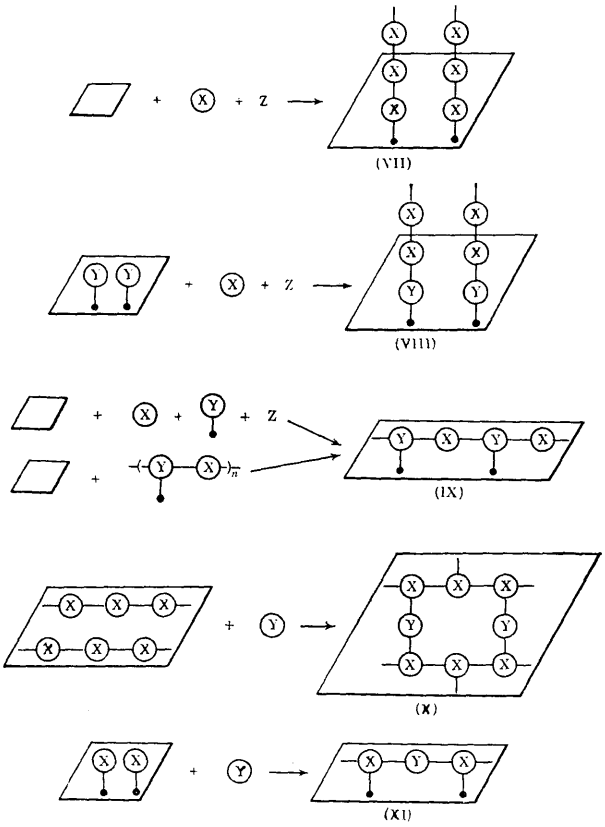
A wide range of mineral materials are used as carriers for the attachment of organic compounds, primarily silica, and also aluminium,[20–24] titanium,[22–26] zirconium,[22,27] tin(IV),[25,26,28] ruthenium(IV),[25,29] etc. oxides. The great majority of studies have been devoted to the attachment of organic compounds to silica, since this material has been extensively studied, is easily modified, and is readily available. Subsequently, except in certain special cases, the discussion will deal with the modification of the surface of silica. It should be noted that the approaches to the modification of the surface of different oxides are identical, and in most cases are based on the reaction with the hydroxyl groups of the surface. The regular features of the modification established for silica can in a first approximation be extended to other oxide carriers.

Ionogenic groups cannot be attached directly to the surface of mineral carriers, because of the instability (primarily to hydrolysis) of the bonds Si–O–C, Si–N, Si–S, Si–O–S, Si–P, Si–O–P, etc. This makes it necessary to introduce an organic "binder" joined to the carrier surface, and then to attach ion-exchanger groups to it by strong covalent bonds.

A large number of methods for modifying the surface of mineral carriers have now been developed, making it possible to vary the nature of the organic modifying layer (monomeric, polymeric) and the nature of the bond between the carrier and the organic modifier (covalent, ionic, hydrogen bonds, topological fixation). The variety of methods of preparation and structures formed on the surface is illustrated in Scheme 1. Additional possibilities for the synthesis of modified mineral carriers are provided by the conversion of attached functional groups X into other ion-exchanger groups.

Scheme 1





= the surface of the mineral carrier;

● = the anchoring group forming a covalent bond with the carrier;
– = a hydrocarbon chain;

Ⓧ = an ionogenic group or molecule containing an ionogenic group;

Ⓨ = a cross-linking molecule or group with no ion-exchange properties;

Z = initiation (in polymerisation).

The synthesis paths represented in the scheme are based on the use of prepared mineral carriers. An alternative method for obtaining modified silicas is by the hydrolytic polycondensation of organosilicon compounds.

Specific examples of the synthesis of ion exchangers based on modified mineral carriers can now be considered.

1. Covalent attachment of monomeric organic compounds (structure I)

Modification of the carrier surface by organosilicon compounds has been most widely used to synthesise ion exchangers based on silica:

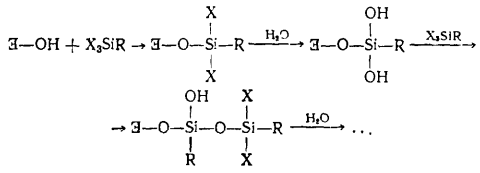
$$\exists\text{—OH} + XX^1X^2SiR \rightarrow \exists\text{—O—}\underset{|}{\overset{|}{Si}}\text{—R},$$

where ∃ represents the surface of the mineral carrier, X (and possibly X^1 and X^2) = Cl or OAlk, and R represents an organic group, which may include the required functional group.

The attachment of organosilicon compounds to the carrier surface may give two types of grafted-layer structure: "brush" and "polymeric". When the brush structure is formed, the molecules of the modifier are attached to the carrier surface as a result of their reaction

with the hydroxyl groups of the carrier, giving a uniform monomolecular layer. The surface concentration of grafted compounds is determined by the size of the XX^1X^2Si anchor group, and for ion exchangers with the brush structure it does not exceed 2–3 molecule nm^{-2}. For carriers with $S_{sp} = 100\ m^2\ g^{-1}$, this quantity is ~ 0.4 mmol g^{-1}, which is much lower than that for organic polymers.

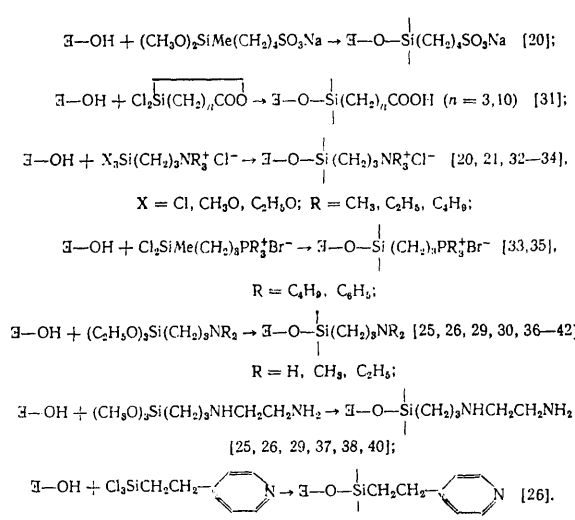
The surface concentration of grafted organic compounds can be increased by carrying out the modification in the presence of water. The following processes take place, giving the grafted layer a polymeric structure:



Sorbents with a polymeric structure have a higher surface concentration of grafted organic molecules, compared with sorbents with a brush structure, but when more than four molecules nm^{-2} are attached to the surface, a uniform covering cannot be expected.[30]

Not all hydroxyl groups of the carrier surface react with organosilicon compounds. Residual silanol groups, which show weakly acidic ion-exchange properties and are also capable of bringing about the specific adsorption of many organic molecules, in many cases have an unwanted influence on the properties of ion exchangers particularly when they are used in high-performance liquid chromatography (HPLC). The surface concentration of silanol groups can be decreased by using so-called monofunctional monomers $XSiMe_2R$ or by carrying out additional silanisation by small silanising agents, usually trimethylchlorosilane or hexamethyldisilazane.

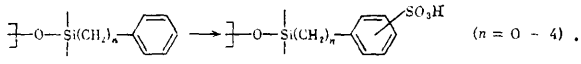
In principle, all the ion exchangers considered can be obtained by single-stage modification of the carrier surface:



Of the modifiers listed, however, only the organosilicon derivatives of amines, primarily γ-aminopropyltriethoxysilane (trade mark AGM-9), are readily available. Research workers therefore prefer first to attach a relatively simple and readily available organosilicon compound to the surface, and then to introduce into it the required ion-exchange group, using familiar reactions of organic synthesis.

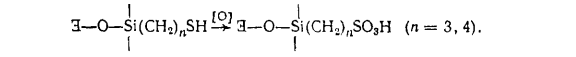
The yields of the reactions on the surface are usually not quantitative, and this leads to the presence of functional groups of different types. When selecting a method for synthesising an ion exchanger, it is preferable that the original functional groups to be subjected to subsequent transformations, and also the intermediate products of their transformation, should not have ion-exchange properties.

Strongly acidic cation exchangers are most frequently obtained by sulphonating aromatic compounds attached to the surface:[43–48]



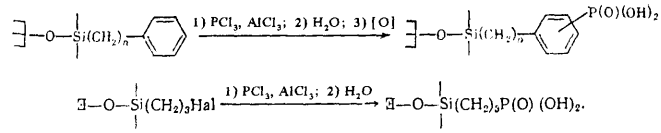
The advantages of this method are the availability of the original organosilicon modifiers and the high degree of sulphonation, which reaches 100% when chlorosulphonic acid is used as sulphonating agent.

The oxidation of grafted thiols is equally effective:[49,50]



Other methods of synthesis include radical chlorosulphonation of attached alkyl groups,[49] the reaction of grafted halogenoalkyl groups with sodium sulphite[51] or ammonia,[49] the reaction of a grafted glycidyl ester with sodium sulphite,[52] and the oxidation of a grafted isothiouronium salt.[20]

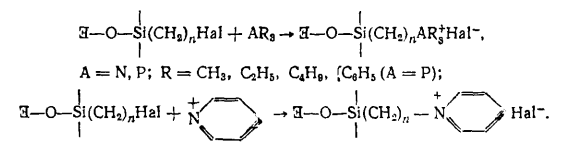
The following methods can be recommended for synthesising phosphonate cation exchangers:[53,54]



The attachment and hydrolysis of esters of alkyl or phenyl hydrogen phosphates[55,56] and the chlorides of alkyl hydrogen phosphates[57] have also been described.

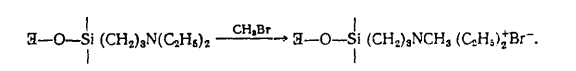
The best method for obtaining carboxylic acid cation exchangers is by the acid hydrolysis of attached esters[44,58,59] and nitriles,[46,58] where the yields are quantitative.

The most widely used method for synthesising strongly basic anion exchangers is by the reaction of attached halogenoalkyl groups with tertiary amines,[45,46,60,61] phosphines,[33,35,62] or pyridine:[61]



When an aromatic compound is grafted initially to the silica surface, it is first chloromethylated, for example with methyl chloromethyl ether in the presence of zinc chloride, and then aminated.[48,63] The advantage of the method is the high yield (>80%) at all stages of the transformation.

It is possible in principle to synthesise strongly basic anion exchangers by the exhaustive alkylation of attached amines, for example:[33]



However, since there is no guarantee that the reaction on the surface will be quantitative, the product may contain not only the required tetra-alkylammonium compounds but also alkylamines, which also have ion-exchange properties.

The method of synthesis on the surface in the production of weakly basic anion exchangers is usually employed to attach polyamine groups:[40,64]

$$\equiv Si{-}O{-}Si{\equiv}\,(CH_2)_3Hal + NH_2(CH_2CH_2NH)_nH \rightarrow \equiv Si{-}O{-}Si{\equiv}\,(CH_2)_3NH(CH_2CH_2NH)_nH.$$

Extensive synthetic possibilities are provided by the use of silica specimens modified by epoxy-groups.[52] The sorbents are obtained by treating silica with γ-glycidoxypropyltrialkoxysilanes followed by reaction with compounds capable of opening the epoxy-ring:

$$\equiv Si{-}OH + (RO)_3Si(CH_2)_3OCH_2CH{-}CH_2 \rightarrow$$

$$\rightarrow \equiv Si{-}O{-}Si{\equiv}\,(CH_2)_3OCH_2CH{-}CH_2 \xrightarrow{HX} \equiv Si{-}O{-}Si{\equiv}\,(CH_2)_3OCH_2CHOH{-}CH_2X,$$

$$X = N(C_2H_5)_2,\ OCH_2CH_2N(CH_3)_2,\ OCH_2CH_2N(C_2H_5)_2,$$
$$(NHCH_2CH_2)_nNH_2,\ OCH_2COOH,\ SO_3H.$$

When silica with grafted epoxy-groups is treated with water at pH 3, the product is a sorbent with grafted diol groups (X = OH). This sorbent and its derivatives are widely used in the chromatography of biopolymers, since there is no non-specific adsorption of proteins. It may also be noted that the oxidation of a grafted alcohol by a mixture of sodium metaperiodate and potassium permanganate in a weakly alkaline medium provides a convenient method for obtaining weakly acidic carboxylic acid cation exchangers.

The advantages of the method involving the covalent attachment of monomeric organosilicon compounds also include the possibility of obtaining polyfunctional sorbents (so-called multi-phases); chromatographic separation on these sorbents involves the coordinated combination of reactions of two or more types between the substances being analysed and the sorbent. The need for sorbents of this kind arises most frequently in the analysis of biopolymers, where the use of only one method of separation (for example reversed-phase or ion-exchange methods) does not give the required selectivity. To solve this problem, the carrier surface is modified using a mixture of organosilicon compounds, and the required functional groups are introduced to give sorbents of the following type:[65–68]

$$\equiv Si{-}O{-}Si(CH_3)_2(CH_2)_nCH_3$$
$$\equiv Si{-}O{-}Si(CH_3)_2(CH_2)_3R$$

$$R = C_6H_4SO_3H,\ N^+(CH_3)_2CH_2C_6H_5.$$

The best ratio of "hydrophobic" and ion-exchange interactions in the separation can be achieved by varying the quantities of the original organosilicon compounds. These results often cannot be achieved simply by mixing two different sorbents.

An alternative method of varying the contributions of the "hydrophobic" and ion-exchange interactions in retention is by changing the length of the hydrocarbon chain connecting the ionogenic group to the carrier surface.[69] This method gives sorbents with highly reproducible properties, but the need for the special synthesis of a set of organosilicon modifiers restricts its application.

A promising method for synthesising ion exchangers with variable ion-exchange capacity has been proposed;[70] the first stage involves the exhaustive modification of the silica surface by diol groups (using γ-glycidoxypropyltriethoxysilane), and in the second stage these groups are acylated using the cyclic anhydrides of dibasic acids. The concentration of carboxyl groups introduced can be varied to give the best ion-exchange retention of proteins; the complete shielding of the surface by the diol groups ensures that non-specific adsorption of proteins does not take place.

The covalent attachment of monomeric organosilicon compounds to the surface of mineral carriers ensures uniformity of the sorption centres and high reproducibility and predictability of the synthesis. In the case of sorbents with a brush structure, the modifier forms a lining in all the pores of the carrier consisting of a thin regular layer, allowing the diffusion of the substances from the solution into the interior of the particle and ensuring a high rate of mass exchange. This gives modified sorbents of this type a dominant position in HPLC. At the same time, these sorbents have a number of disadvantages.

Firstly, these sorbents have a low stability to hydrolysis. Modified silica specimens in which the grafted layer has a brush structure are not recommended for use at pH < 1 and pH > 9. The degradation of weakly basic anion exchangers is often observed on prolonged use even at pH > 7. The hydrolytic stability of sorbents in the alkaline range up to pH 10 can be increased by using other inorganc carriers, in particular aluminium oxide and aluminated or zirconated silica specimens.

Secondly, the exchange capacity of these sorbents is several times lower than that of ion exchangers based on organic polymers. This represents a significant obstacle to their use in technological sorption processes, and restricts their sphere of application to mainly analytical problems.

Thirdly, their synthesis is relatively complicated, and the use of organosilicon compounds which in many cases are expensive and difficult to obtain increases their cost considerably, compared with their organic-polymer analogues.

Thus the search for other methods for synthesising ion exchangers based on modified mineral carriers is continuing.

2. The attachment of monomeric organic compounds by adsorption (structures II and III)

The adsorption of organic ionogenic compounds on the surface of a mineral carrier is undoubtedly the simplest method for synthesising the sorbents being considered. The earliest studies in this field (see for example Ref.71), however, revealed its main disadvantage, namely the low stability, due to the continuous elution of the deposited substance into the solution. This stimulated the development of methods for the covalent attachment of organic compounds to the surface.

Nevertheless, recent experience has shown that adsorption systems can be used successfully even in HPLC. The surface modifier is a compound which is firmly adsorbed on silica, for example tetraethylenepentamine,[72] or a compound which has a low solubility in the eluant, for example cetyltrimethylammonium bromide or n-hexadecylpyridinium chloride when working with aqueous eluants.[73] Silica with adsorbed tetraethylenepentamine has been used to separate carbohydrates and polyalcohols at pH 8–9; even under these conditions, it was necessary to add the modifier to the eluant to keep the column characteristics constant. Silica with adsorbed long-chain ammonium salts shows practically no change in its characteristics when used to separate mixtures of inorganic anions.[73]

An increase in the stability of adsorption-bonded systems can be achieved by using reversed-phase sorbents as the original carrier, for example silica specimens modified by octyl- or octadecylsilanes. The thin hydrophobic layer grafted to the surface ensures the strong retention of ionogenic substances containing long-chain alkyl groups: $C_nH_{2n+1}SO_3Na$,[74] $C_nH_{2n+1}OSO_3Na$,[74,75] $(C_nH_{2n+1})_4N^+Cl^-$,[74,75] and

$C_{16}H_{33}N(CH_3)_3^+Cl^-$.[76,77] This method is essentially the limiting case of ion-pair chromatography. The modified columns are made from organic materials. Aqueous solutions are mainly used as eluants in the chromatographic analysis. Under these conditions, high stability of the column operation is achieved; according to Ref.77, the exchange capacity remains unchanged during continuous operation for at least 80 d in the separation of mixtures of inorganic anions.

This method for obtaining sorbents is attractive chiefly because of the ease of variation of the nature and sorption characteristics of the ion exchangers based on the most readily available reversed-phase columns.

3. The attachment of polymers

The greatest variety of possible sorbent structures among the ion exchangers being considered is provided by mineral carriers with organic polymers attached to their surface. Initially, the interest in these materials was due to the possibility of their application as polymer fillers.[8,15,16,24,78–99] In recent years, these materials have been used increasingly as sorbents and catalyst carriers.[22,28,100–121]

The interest of research workers in materials of this class is due to the following potential advantages over mineral carriers with covalently attached monomeric organic compounds: 1) higher stability of action, resulting from the multi-point attachment of the polymeric modifier to the surface or from the more effective shielding of the surface; 2) the greater sorptive capacity, resulting from the increase in the proportion of the organic component; and 3) the simpler (in some cases) synthesis, which makes it possible to avoid the use of organosilicon modifiers.

Two main approaches are used in the production of these materials: modification of the surface by prepared polymers[22,100,104,112–121] and polymerisation of monomers on the surface.[24,28,41,78–99,101–103,105–111,122]

Modification by prepared polymers (structures IV–VI, IX, X). The simplest version of the modification is the adsorption of organic polymers on the surface of a mineral carrier to give so-called film or pellicular sorbents.[123] The best results are obtained using heterochain nitrogen-containing oligomers based on polyethyleneimine (PEI),[112–116] which are firmly adsorbed on the surface of hydroxyl-containing carriers. By changing the molecular mass of the oligomer used, it is possible to vary the thickness of the grafted layer over a wide range, beginning from the values characteristic of brush structures. For example, the use of branched PEI oligomers with a molecular mass of 600 gives layers with a thickness of 3–4 nm;[115] the best selectivity in the separation of oligonucleotides is shown by silica specimens with pore dimensions of 70–100 nm, modified by PEI with a molecular mass of 35 000.[121]

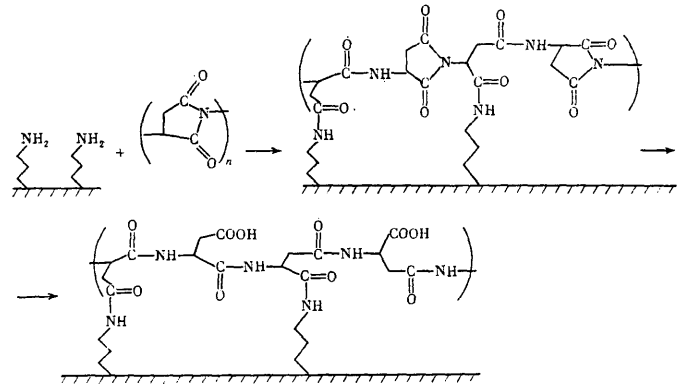
PEI attached by adsorption will obviously be transferred to the solution to some extent, particulary on treatment with acidic eluants. To increase the stability of action of these systems, Regnier and co-workers[112–115] proposed the cross-linking of the adsorbed oligomers using bifunctional and polyfunctional reagents: dibromoalkanes, epichlorohydrin, and cyanuryl chloride. The compounds most widely used for this purpose contain two or more epoxy-groups, which react with amines under mild conditions, and, when the epoxy-ring is opened, give additional alcohol groups which increase the hydrophilic nature of the sorbent. A similar approach was used in Ref.118, where adsorbed polyvinylpyrrolidone was cross-linked by the thermal decomposition of dicumyl peroxide or by using radiation.

When the adsorbed oligomers have been cross-linked, the particle of inorganic carrier is included in a "network" of organic polymer by so-called topological fixation; the components cannot be separated without complete breakdown of the sorbent. The sorbents with the greatest hydrolytic stability have been obtained by using titanium or aluminium oxides, or zirconated silica, as carrier: when these sorbents are kept at pH 14 for 24 h, only slight transfer of PEI to the solution is observed.[22]

Sorbents containing cross-linked PEI have the properties of weak anion exchangers, but they can easily be converted into strongly basic anion exchangers by quaternisation using methyl iodide[113] or into weakly acidic cation exchangers by reaction with halogenocarboxylic acids or with the anhydrides of dibasic carboxylic acids.[116,124]

To obtain film ion exchangers based on non-porous particles, the charged macro-particles are brought into contact with positively charged particles with colloidal dispersion. As a result of super-equivalent adsorption, the macro-particles acquire a charge opposite to the original charge. On these macro-particles it is possible in turn to deposit other micro-particles of opposite charge. Thus in Ref.104, particles of Amberlite XE-225 (a strongly basic polymeric anion exchanger) with dimensions of 100–500 nm were deposited from solution on glass particles with dimensions of 24–52 μm, followed by negatively charged particles of Ludox-AM with dimensions of 15 nm; these operations were repeated three times, to give an anion exchanger with a specific surface of 0.5 $m^2 g^{-1}$. Because of the low specific surface of these sorbents, their sorptive capacity is low and does not exceed $n \times 10$ μg-equiv g^{-1}, which is much lower than that of sorbents with a brush structure and, more particularly, the sorbents with adsorbed PEI described above.

To ensure stronger bonding of the oligomers to the carrier surface, in a number of cases the original carrier has been chemically modified using organosilicon compounds capable of forming covalent bonds with the functional groups of the oligomers.[116,119,120] Thus in Ref.116, PEI was attached using grafted carboxyl groups; in Ref.120, polyaspartic acid was attached to the surface of aminopropylsilica by the chemisorption and subsequent hydrolysis of polysuccinnimide.



Sorbents with an analogous structure are also obtained by modifying the carrier with polymers containing organosilicon anchor groups, for example polyethyleneimine containing $(CH_3O)_3Si(CH_2)_3$ groups[125] or a copolymer of 4-chloromethylstyrene and vinylmethyldichlorosilane.[117] The presence of active chlorobenzyl groups in the copolymer provides a method for synthesising a wide range of cation and anion exchangers. An advantage of this method of grafting is that the characteristics of the original polymer are usually well known.

Polymerisation on the surface (structures IV, VII–IX, XI). The polymerisation of monomers on the surface of mineral materials is one of the most general methods of synthesising modified mineral carriers.[8,15,16] The simplest method involves polymerisation on the surface of non-modified carriers. Weakly acidic cation exchangers are

synthesised by polymerising acrylic acid[24,28,79,103,122] (in the polymerisation of methyl methacrylate[24,84,86,93] or acrylonitrile,[24] subsequent hydrolysis is necessary). Extensive synthetic possibilities are provided by the polymerisation of styrene;[100–103,122] sulphonation of the polymer layer on the surface gives sulphonic acid cation exchangers,[100–103, 122] and chloromethylation followed by amination gives strongly basic anion exchangers.[100,122] A promising monomer is chloromethylstyrene.[126–128] In some cases,[100–103,126–128] these vinyl monomers are copolymerised with divinylbenzene.

Various methods are used to initiate polymerisation: mechanochemical treatment,[80,81] ultraviolet irradiation,[90,129] and electrical discharge.[82] In most studies, polymerisation has been carried out using special initiators and using radiation. In the first case, the adsorption of the monomer on the carrier surface is accompanied by the adsorption of benzoyl peroxide,[24,100] t-butyl peroxide,[101] azobisisobutyronitrile,[28,127,128] or ammonium persulphate.[24] In the second case,[84–88,93] two methods are used: irradiation of the carrier with an adsorbed layer of monomer, or post-radiation grafting, where the carrier is subjected to the action of radiation and then treated with the monomer. The lifetime of the reaction centres on the surface may reach 20 d.[130]

All these cases give the homopolymer and a so-called non-extractable polymer, the proportion of which may reach 90–100%. For polymerisation under the influence of radical initiators or an electrical discharge, covalent bonds are not formed between the polymer and the carrier, and the modifying layer is held on the surface by adsorption forces or geometric factors. On mechanochemical treatment or the action of radiation or ultraviolet light on systems with adsorbed quinone,[90] radicals such as $\equiv Si-O^{\cdot}$,[15,16,80,90,93] which initiate polymerisation, may be formed on the carrier surface. In this case the polymer is joined to the surface by an $Si-O-C$ bond, which is not stable to hydrolysis and which is decomposed by the action of small quantities of moisture, so that it cannot be said that covalent bonds are formed between the polymer and the carrier surface.

An effective procedure which makes it possible to use milder polymerisation conditions in the surface layer and at the same time guarantees the formation of a strong carrier–polymer covalent bond involves the preliminary modification of the carrier by organosilicon compounds. The most widely used methods are those involving the attachment of vinyltrichlorosilane[91,93,105–109] and other vinyl derivatives[94,96] to the carrier surface. Treatment with γ-rays or radical initiators is then used to bring about the polymerisation of acrylic acid,[106,108,109] methyl methacrylate,[93,94] styrene,[94,96,105,107–109] or vinylpyridines[91] on the surface of the modified carrier. In a number of cases, cross-linking of the grafted polymer chains is brought about by carrying out the polymerisation in the presence of divinylbenzene.[105]

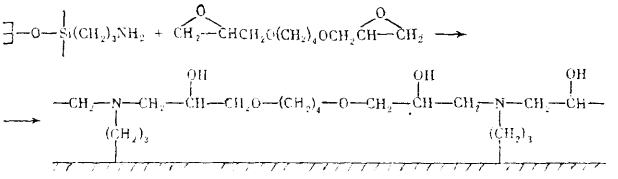
It is possible to attach to the surface not only vinyltrichlorosilane but also other organosilicon compounds capable of initiating radical polymerisation, in particular peroxides[23,92,97,131] and ozonides.[98] A method has also been described for attaching to the carrier surface compounds with the general formula $Cl_2(CH_3)Si(CH_2)_3X$, where $X = N(CH_3)_2$, $N(C_2H_5)_2$, and $OCOCCl_3$, with subsequent graft polymerisation of methyl methacrylate or styrene under the influence of visible light (λ = 400–500 nm) in the presence of manganese carbonyl,[95] fluorenone, or related organic compounds.[37]

A fundamental and as yet not fully resolved problem concerns the structure of the grafted layer in these materials. Analysis of data obtained by different authors indicates that only a small proportion of the silanol groups of the surface or grafted organosilicon compounds initiate the growth of a polymer chain. This leads to "islet" modification of the surface, and complete covering of the surface by the organic polymer requires a large quantity of the monomer, up to 3–6 effective monolayers (see for example Ref.84). In the initial stage of the polymerisation (at concentrations up to one third of an effective monolayer), linear macromolecules with a narrow molecular-mass distribution are formed; with increase in the degree of conversion there is an increase in the contribution of processes of chain transfer to the polymer, leading to branching of the macromolecules and marked broadening of the molecular-mass distribution.[85] This may lead to additional non-uniformity of the characteristics of the grafted layer.

The conformation of the grafted chains is determined by their chemical character, in particular their affinity for the surface hydroxyl groups of the carrier. Infrared spectroscopy has established that a large number of hydrogen bonds are formed between polymethyl methacrylate and an aerosil surface.[78,86] With a small quantity of deposited polymer, its molecules have a branched conformation, whereas at high concentrations they form a non-planar coil. Similar effects are observed in the polymerisation of vinylpyridines on an aerosil surface or of acrylic acid on an aminopropylaerosil.[79,88] The formation of hydrogen bonds between the functional groups of the polymer and the carrier leads to uniform covering of the surface and increases the strength of attachment of the polymer and the degree of shielding of the surface. It should be noted, however, that in systems with a strong adsorption interaction there is a sharp decrease in the rate of polymerisation.[79,88]

An increase in the strength of the bonding of the polymers to the carrier surface is achieved by copolymerising vinyl monomers with unsaturated organosilicon compounds containing reactive chorosilyl or ethoxysilyl groups, for example $(C_2H_5O)_3SiCH=CH_2$[99,105] and $(C_2H_5O)_2Si(CH_3)CH_2OCOC(CH_3)=CH_2$.[94] In Ref.99 it is stated that the grafted polymer obtained in this way cannot be separated from the carrier even by treating with HF; this is attributed to the many-point grafting of the polymer and the marked shielding of the carrier surface.

The last method of synthesis gives sorbents whose structures are identical to those of the specimens obtained by modifying the carrier surface with prepared polymers containing active organosilicon groups[117,125] (see above). A third method of obtaining sorbents of this kind involves the two-dimensional cross-linking of grafted monomeric organosilicon compounds. An example is provided by the cross-linking of grafted primary amines with diepoxides:[110]



After treatment in this way, the time of stable operation of the sorbent increases from several days to several months.

The data in the present section show that, on the average, mineral carriers modified by polymers have a higher stability to hydrolysis than sorbents with a brush structure. In a number of cases they can be synthesised without using organosilicon compounds. They are characterised by an increase in the exchange capacity to 2.5 mg-equiv g^{-1}. The capacity of ion exchangers based on organic polymers is generally much higher, but this difference is counterbalanced slightly by the large bulk density of the sorbents based on mineral carriers. Thus the exchange capacity of a sulphonic acid cation exchanger based on silica is 2.2 mg-equiv g^{-1}, which corresponds to 1 mg-equiv cm^{-3}; for Dowex 508 the corresponding quantities are 5 mg-equiv g^{-1} and 1.7 mg-equiv cm^{-3}.[108,109]

The disadvantages of the methods described, particularly those involving polymerisation on the surface, include the difficulty of controlling the course of the reaction and the unpredictable change in the structural characteristics of the sorbents; in many cases the specific surface decreases by a factor of 2.5–10, with almost the same decrease in the specific pore volume.[108,109] The mass-exchange characteristics of sorbents with thick polymeric modifier layers are close to those of organic ion exchangers, and are much inferior to those of sorbents with a brush structure; in the general case, this lowers the efficiency of chromatographic columns (see for example Ref.132). Nevertheless, the use of these sorbents is often justified even in HPLC, when the efficiency of separation is limited by another parameter of the process, for example the diffusion of the compounds being analysed in the chromatography of proteins.

4. Hydrolytic polycondensation of organosilcon compounds

The essential feature of the method being considered is the hydrolysis of trichloro- or trialkoxysilanes X_3SiR to give polysiloxanes. Since this gives a three-dimensional structure of $-Si-O-Si-O-$ bonds, these materials, despite the fact that they do not contain silicon dioxide, are in many respects analogous to modified silica specimens. If the hydrocarbon group R does not contain ionogenic functional groups, these are introduced into the prepared polysiloxane.

Ion exchangers are formed directly by the hydrolytic polycondensation of $Cl_3SiCH_2C_6H_4SO_3H$,[133] $Cl_3SiC_6H_4C_6H_4PCl_2$ (after oxidising the phosphonite group to phosphonate),[134], $Cl_3SiC_6H_4POCl_2$,[135] 1,1-dichloro-1-silalactones,[31,136] $Cl_3Si(CH_2)_nCOCl$ (n = 3,10),[31] $(C_2H_5O)_3Si(CH_2)_3NHCH_2CH_2NH_2$,[137] $[(C_2H_5O)_3Si(CH_2)_3]_2NCH_3$,[138] and $[(CH_3O)_3Si(CH_2)_3]_4N^+Cl^-$.[138] The exchange capacities of these sorbents are 2–6 mg-equiv g^{-1}. Convenient intermediate materials for synthesising ion exchangers are provided by the hydrolysis products of $X_3Si(CH_2)_nC_6H_5$ (X = Cl, C_2H_5O; n = 0–2),[139–142] Cl_3SiCH_2Cl,[143] $(C_2H_5O)_3SiCH_2SH$,[144] and $(CH_3O)_3Si(CH_2)_3SH$.[142]

Of all modified mineral carriers, ion exchangers based on polysiloxanes have the highest exchange capacity, only slightly lower than that of organic ion exchangers. This advantage, however, does not compensate the disadvantages associated with the fact that they do not contain a rigid silicon dioxide matrix. Polysiloxanes are less stable, and, like organic ion exchangers, undergo considerable swelling in various solvents, so that they are unsuitable for use in HPLC. The ionogenic groups of these ion exchangers differ considerably in their accessibility; the inner groups are inaccessible to large organic molecules, and this restricts the possibilities for the application of ion-exchange polysiloxanes in sorption and catalysis. Moreover, considerable difficulties are encountered in the preparation of polysiloxanes with required values of the specific surface, specific volume, and pore dimensions, whereas in other known methods of synthesis these parameters are easily varied by selecting an appropriate carrier.

The mechanical and mass-exchange characteristics of polysiloxanes can be improved by carrying out the simultaneous polycondensation of functional organosilicon compounds with tetraethoxysilane or polyethoxysiloxanes,[141,142,145,146] but the exchange capacity is lowered, and the synthesis is more complicated.

Hydrolytic polycondensation may provide a useful method for the synthesis of film ion exchangers.

III. Industrial ion exchangers based on modified mineral carriers

A number of firms in other countries now produce ion exchangers based on silica, chiefly for use in chromatography. The principal sorbents and the firms producing them are listed below (in most cases, in the sorbent names, the numbers denoting the particle size of the sorbent or the average pore diameter are omitted).

Sorbents for the HPLC of organic compounds

Weakly basic ion exchangers: Nucleosil NH_2, Nucleosil $N(CH_3)_2$, Polygosil NH_2, Polygosil $N(CH_3)_2$ (Macherey-Nagel, FRG–Switzerland); Zorbax NH_2 (Du Pont, USA); Bondapak NH_2 (Waters, USA); Aminopropyl-Daltosil 100, DEAE-Daltosil 100 (Serva, USA); DEAE 2SW Spherogel TSK-IEX (Beckman, USA); Lichrosphere 100 NH_2 (Merck, FRG); Vydac 601 SC (Separations Group, USA); Silasorb DEA (Lachema, Czechoslovakia).

Strongly basic anion exchangers. Nucleosil SB (Macherey-Nagel, FRG–Switzerland); Partisil 10 SAX (Whatman, UK); SAX Ultrasil (Beckman, USA); TEAB-Daltosil 100, TEAP-Si 100 (Serva, USA); Zorbax SAX, Zipax SAX (Du Pont, USA); Supelcosil LC-SAX (Supelco SA, Switzerland); Vydac 301 SC, Vydac 301 TPB (Separations Group, USA); Silasorb S (Lachema, Czechoslovakia).

Weakly acidic cation exchangers. Carboxymethyl-Daltosil 100, Carboxymethyl-Si60 (Serva, USA); CM 2SW Spherogel TSK-IEX (Beckman, USA).

Strongly acidic cation exchangers. Partisil SCX (Whatman, UK); Zorbax SCX, Zipax SCX (Du Pont, USA); Nucleosil SA (Macherey-Nagel, FRG–Switzerland); SCX Ultrasil (Beckman, USA); Vydac 401 SC, Vydac 401 TPB (Separations Group, USA); Supelcosil LC-SCX (Supelco SA, Switzerland); Sulfopropyl-Daltosil 100, Sulfopropyl-Si100 (Serva, USA).

Sorbents for the chromatography of biopolymers

Weakly basic anion exchangers: Ultropac TSK 545 DEAE (LKB, Sweden); SynChropak AX, SynChropak CATSEC, SynChroprep AX, SynChropak ASC (SynChrom, USA); Zetaprep DEAE (Molecular Separations Division, USA); Aminopropyl-Si100, DEAE-Si100 (Serva, USA); Nucleogen-DEAE (Macherey-Nagel, FRG–Switzerland); Spherogel TSK IEX 530 DEAE (Beckman, USA); TSK Gel IEX-545 DEAE SIL (Toyo Soda, Japan); Zorbax Bio-Series WAX-300 (Du Pont, USA); Shimadzu Shim-pack WAX1(2) (Shimadzu, Japan).

Strongly basic anion exchangers. SynChropak Q, SynChroprep Q, SynChropak QSC (SynChrom, USA); Zetaprep QAE (Molecular Separations Division, USA); Sep-Pak Accell QMA (Waters, USA); Zorbax Bio-Series SAX-300 (Du Pont, USA).

Weakly acidic cation exchangers. Ultropak TSK 535 CM (LKB, Sweden); SynChropak CM, SynChroprep CM, SynChropak CSC (SynChrom, USA); Zetaprep CM (Molecular Separations Division, USA); Carboxymethyl-Si300, Carboxypentyl-Si500 (Serva, USA); Sep-Pak Accell CM (Waters, USA); Spherogel TSK IEX 540 CM (Beckman, USA); Zorbax Bio-Series WCX-300 (Du Pont, USA); Shimadzu Shim-pack WCX-1 (Shimadzu, Japan).

Strongly acidic cation exchangers: Nucleosil SA Catecholamine (Macherey-Nagel, FRG–Switzerland); Zorbax Bio-Series SCX-300 (Du Pont, USA).

Sorbents for ion chromatography

Strongly basic anion exchangers: Partisil SAX (Whatman, UK); Vydac 302 SC (Separations Group, USA); Wescan Anion (Wescan Instruments, USA); Zipax SAX (Du Pont, USA); Supelcosil LC-IC (Supelco SA, Switzerland); Nucleosil Anion (Macherey-Nagel, FRG–Switzerland); R Sil An (Alltex Association, USA); TSK Gel IC-Anion SW (Toyo Soda, Japan).

Strongly acidic cation exchangers: Partisil SCX (Whatman, UK); Vydac CX (Separations Group, USA); Zipax SCX (Du Pont, USA).

Unfortunately, detailed information on the structures of most of these sorbents is not available either in the firms' literature or in the original papers; the methods of synthesis are not known, and in some cases it is not possible to say anything about the composition of the functional groups on the surface. It may be noted that the carrier most frequently employed is porous silica with an average pore diameter of 6–30 nm; sorbents for separating biopolymers have a large pore diameter, reaching 100 nm. In a number of cases (the sorbents Zipax, Vydac SC, Corasil, SynChropak ASC), the carriers are particles with a non-porous glass core and a porous external layer of silica with a thickness of about 1 μm.

Most of these sorbents consist of silica with chemically grafted monomeric organosilicon compounds. The weakly basic anion exchangers contain the groups $-NH_2$, $-N(CH_3)_2$, $-N(C_2H_5)_2$ (DEAE sorbents). The strongly basic anion exchangers contain different grafted tetra-alkylammonium salts. The weakly acid cation exchangers contain $-CH_2COOH$ groups (sorbents of the Carboxymethyl, CM series). In strongly acidic cation exchangers, attached aryl and alkyl sulphonic acids are used to equal extents. The synthesis of sorbents for the chromatography of biopolymers (in particular the sorbents of the DEAE and CM series) is often carried out with preliminary modification of the surface by a γ-glycidoxypropyltrialkoxysilane followed by the introduction of the required functional group.

Sorbents with polymers attached to the surface have appeared in recent years. Thus sorbents of the SynChropak series are obtained by modifying the surface with polyethyleneimine; the cation exchanger Zipax SCX contains a sulphonated layer of a fluorocarbon polymer on its surface.

The range of mineral carriers used is being extended. In particular, sorbents of the Zorbax Bio-Series are based on zirconated silica gel.

In the near future there should be an increase in the proportion of sorbents with deposited polymers and also sorbents based on mineral carriers with an increased stability to hydrolysis in alkaline media.

IV. Applications of ion exchangers based on modified mineral carriers

1. The concentration and separation of inorganic anions

One of the principal fields of application of ion exchangers based on organic polymers is the extraction from solution and separation of inorganic ions (see for example Ref.147). In recent years, however, the sorption of transition metal ions has been carried out increasingly using complexing sorbents,[148] which ensure high stability and selectivity of the binding of the metal ions. On this basis, research workers studying the synthesis of sorbents for metal ions immediately began to graft complex-forming groups on to the surface of silica, so that the number of publications on the applications of ion exchangers based on silica on this field is comparatively small (p.321 of Ref.9, and Refs.53–56, 64, and 149–165).

The most interesting results have been obtained on the sorption of noble metal ions. In strongly acidic media (2–4 M HCl), the quantitative sorption of rhodium(III) and iridium(IV) by aminosilica is observed,[157,162] and this makes it possible to separate these elements from other noble metals and a 10^4-fold excess of non-ferrous metals and iron(III). Anion exchangers based on silica can be used to separate gold from a large excess of non-ferrous metals[64,159] and silver from platinum and palladium.[153] Palladium(II), platinum(IV), osmium(VI, VIII), and ruthenium(IV) are sorbed by anion exchangers based on silica in the weakly acidic range;[157,160–162,164,165] the mechanism of sorption has not yet been established.

Sulphonic acid[151,154,155] and phosphonic acid[53–56] cation exchangers based on silica show an increased affinity for multiply-charged metal ions, in particular aluminium(III), scandium(III), zirconium(IV), and thorium(IV), so that these metals can be separated selectively from materials with complex compositions, for example alloy steels.

Silica with grafted ethylenediamine has proved effective for the anion-exchange binding of $Cr_2O_7^{2-}$, MnO_4^-, WO_4^{2-}, MoO_4^{2-}, AsO_4^{3-}, SeO_4^{2-}, and uranium(VI) as carbonate complexes (p.321 of Ref.9, and Refs.149, 150, and 152), so that it can be used to extract these anions from sea water.

In all the works cited it is pointed out that the main advantage of silica sorbents is the high rate of attainment of sorption equilibrium which makes it possible to work at high rates of flow of the solution being analysed through the column containing the sorbent (up to 100 ml min^{-1} cm^{-2}); this is particularly important in the extraction of ions from large volumes of dilute solutions. In most cases, quantitative desorption of the ions from the surface is achieved using small volumes of eluant, so that the concentration coefficient in a single "sorption–desorption" cycle is 10^2–10^3, which is appreciably greater than that for the organic-polymer analogues. The higher selectivity of sorbents based on silica is also noteworthy. The advantages of modified silicas include the possibility of determining sorbed ions on the surface by a wide range of physical methods: X-ray fluorescence,[9,37,38,149,150–152,156,157,162] luminescence,[151,158] and spectral methods.[151,166] This makes it possible to lower the detection limits of elements and to reduce the time taken for analysis.

2. High-pressure in chromatography

For a long time, high-performance liquid chromatogray did not find application in inorganic analysis, and the few published papers dealt chiefly with the separation of complexes of metals with organic ligands using reversed-phase methods (see the published reviews[167,168]). A powerful stimulus to work in this field was provided by the classical study of Small, Stevens, and Bauman,[169] who proposed the use of ion-exchange stationary phases combined with a conductometric detector. Subsequent studies (see the published monographs[170,171] and review[172]) fundamentaly altered existing views on many traditionaly difficult problems in inorganic analysis. Thus when ion chromatography is used, the time taken to analyse mixtures of the anions Cl^-, Br^-, I^-, NO_2^-, NO_3^-, and SO_4^{2-} and mixtures of the cations Li^+, Na^+, K^+, Rb^+, and Cs^+ or all the lanthanide elements at concentrations of 0.1–1 μg ml^{-1} is 5–20 min.

The most popular materials used in ion chromatogray are strongly basic anion exchangers (for the separation of anions) and sulphonic acid cation exchangers (for separating cations); the structure and

characteristics of the sorbents are varied over a wide range, depending on the eluant and the detection system.

When a conductometric detector is used, the eluant should have a low conductivity; the low concentration of the eluant makes it necessary to use specially synthesised sorbents with a low capacity (0.01–0.1 mmol g^{-1}), in which the ion exchange groups are concentrated chiefly on the outer surface of the granule.[170] In the analysis of anions by the so-called two-column version of ion chromatography with conductometric detection, weakly alkaline carbonate–bicarbonate solutions are used as eluants; under these conditions, silica sorbents are unstable, and it is necessary to use ion exchangers based on zirconated silica specimens or organic polymers.

When other methods of detection are used, for example spectrophotometric,[73–75,77,173–177] refractometric,[178–180] potentiometric (at a copper electrode),[181] emission (using an inductively bound plasma),[182] and atomic absorption[183] methods, the stability and capacity requirements to be satisfied by the sorbents are not so severe, so that it is possible to use the same ion exchangers as in the HPLC of organic compounds. In the ion chromatography of ions, extensive use is made of dynamically modified sorbents obtained by the adsorption of long-chain quaternary ammonium salts on silica[73] or reversed-phase sorbents.[74,75,77,173,174,184,185] An attractive feature is the possibility of easily varying the sorptive capacity of the ion exchangers, and the use of aqueous eluants ensures the high stability of these phases modified by adsorption.

The problems of the ion-chromatographic analysis of mixtures of alkali metal cations and various mixtures of the anions of inorganic acids have now been fully solved. Specific examples of the use of ion exchangers based on silica for these purposes can be found in the literature of the firms producing these materials, and in published monographs[170,171] and original papers.[73–75,77,132,173–180,184]

The efforts of research workers are now concentrated on the problems of analysing the alkaline earth and transition metals.[181,183,186–196] A number of complexing sorbents have been proposed for this purpose, in particular silica specimens with grafted 8-quinolinol,[195,196] crown ethers,[193] and related compounds,[194] but data in other papers indicate that the use of traditional cation exchangers makes it possible to achieve equal selectivity and efficiency of separation. The selectivity and retention are controlled by adding to the eluant complexing reagents such as hydroxyisobutyric,[190,191] citric,[181,189] and tartaric acids,[181,187,188] and ethylenediamine.[181] The ions are detected spectrophotometrically; for this purpose they are converted at the outlet from the analytical column into complexes with highly sensitive reagents such as PAR[183,187,188,191] or Arzenazo I.[190] It is possible in principle to use eluants to which the photometric reagent, for example Arsenazo III,[186] has been added beforehand; in this case the ion-exchange separation of the complexes of the metal ions with this reagent takes place. An interesting example is the use of EDTA solution as eluant; the metal ions being determined are converted into negatively charged complexes with EDTA, which are separated on a strongly basic anion exchanger followed by conductometric or spectrophotometric detection; an important feature is that the accompanying anions can be determined simultaneously.[192]

3. The chromatography of organic compounds

In the high-performance liquid chromatography of organic compounds, sorbents based on silica with grafted monomeric organosilicon compounds are mainly used. The most widely used substrates are organc acids, amines, and aminoacids. The dependence of the retention of the compounds being separated on the nature of the grafted ion-exchange group, the structure of the compounds being separated, and the composition of the eluant has been studied in detail. Thus the order of the elution of carboxylic acids coincides with the order of increase in their acidic dissociation constants.[108,197,198] The dependence of the retention of organic acids by a weakly basic anion exchanger on the acidity of the eluant is given by a curve with a maximum;[197] the retention on the ion exchangers is inversely proportional to the ionic strength of the eluant.[46,199]

The most extensive use of the HPLC of ionogenic organic compounds is in medicine and for the control of environmental pollution. A large number of studies[46,200–204] have been devoted to the determination of catecholamines—dopamine, noradrenalin, adrenalin, and dihydroxyphenylalanine—using a strongly acidic cation exchanger. Considerable attention is being paid to the determination, in blood and other biological materials, of various medicines and drugs—caffeine, aspirin,[45] morphine, cocaine, quinine,[199] codeine, heroin,[205] nicotine,[46] and penicillamine.[206] Data have been published on the use of ion exchangers based on silica to separate aminoacids,[204,207] carboxylic acids,[45,108,197,198,202,208–211] alkyl sulphonates,[212] aliphatic and aromatic amines,[202,213] pyridinium aldoximes,[214] and other pyridine derivatives.[46] In recent years, organic acids and other compounds have often been determined by ion chromatography with conductometric detection.[208,209,211,212]

An interesting feature is the use of strongly basic and weakly basic anion exchangers based on silica in the exclusion chromatography of cationic polymers, for example polyethyleneimines and polyvinylpyridines.[110,215,216] The use of fixed groups with the same charge on the carrier surface completely suppresses the desorption of the polymers.

4. The chromatography of biopolymers

Judging from the number of publications, the main field of application of ion exchangers based on mineral carriers is the chromatography of biopolymers. This is not surprising, since the role of biotechnology is steadily increasing, and the only acceptable method for analysing, separating, and purifying the complex mixtures in these processes is liquid chromatography, in particular ion-exchange chromatography, which is the most universal method for compounds of this class. Previously, the analysis and separation of biopolymers was carried out almost exclusively using sorbents based on polymers and soft gels, which show appreciable non-specific sorption. The high degree of swelling and low mechanical strength of wide-pore sorbents based on organic matrices, however, made them unsuitable for HPLC, so that attention was transferred to mineral sorbents. An advantage of these sorbents is that they are unaffected by biological action and withstand various forms of sterilisation.

Various aspects of the application of ion exchangers based on silica in the chromatography of biopolymers have been described in detail in various monographs[6,7,11] and reviews.[12,217–220] In the present review, therefore, only some of the most important features will be examined, and references will be given to various specific applications.

One of the basic requirements to be satisfied by sorbents for the chromatography of biopolymers is that the pore size of the sorbent should correspond to the dimensions of the molecules of the compounds being separated. Here it is necessary to take account of the fact that increase in the pore diameter of the sorbent leads to a decrease in its surface area and hence in the sorptive capacity and efficiency of the sorbent. A large number of studies have therefore been devoted to the optimisation of the porous structure of the sorbent to solve various specific problems (see for example Refs.52, 115, 121, 221, and 222).

A characteristic feature of proteins is their strong non-specific interaction with the surface of silica, which leads to their irreversible sorption and often to the loss of the biological activity of the compounds being separated.[223] It is therefore necessary to effectively shield the silica surface from reaction with proteins; this is achieved by modifying the surface beforehand by dipolar groups[27,52,70,224] or polyethyleneimine.[112–116,121,225] Moreover, protein molecules are capable of many-point ion-exchange bonding to the sorbent, so that to decrease the retention, sorbents with a low surface concentration of ion-exchange groups are used.[34,65–68,70,112]

The ion-exchange separation of biopolymers is most frequently carried out in a weakly alkaline medium, that is in the range of hydrolytic instability of silica sorbents. The chromatography of biopolymers is therefore often carried out using sorbents with adsorbed or grafted polymers[12,112–116,119–121,124,225–229] or sorbents based on zirconated silica specimens.[22,27,230]

The ion-exchange retention of proteins, viruses, and other biological adsorbates depends on many parameters, in particular the composition, acidity, and ionic strength of the eluant. Detailed experimental studies of these topics have been described.[226,227,230–233] The selection of the best conditions is assisted by data on the adsorption isotherms for proteins on ion exchangers[234] and the results of theoretical studies.[235,236] Thus a correlation has been established[235] between the retention of a protein and the number of charges involved in the adsorption–desorption process.

Ion exchangers based on silica are used in the chromatographic analysis of mixtures of basic proteins, α-chymotrypsin, cytochrome C, and lysozyme,[27,70,116,124,229,231,237] nucleosides,[45] nucleoside phosphates,[34,238] nucleic bases,[239] oligonucleotides,[66,67,69,113,221, 224,225,240–243] ribonucleic acid,[113,221,244] and DNA restriction fragments,[67,68,221,245–247] and to separate growth factors.[233,248,249]

Ion exchangers based on minerals are being more widely used for the preparative separation of biological compounds,[219,220,250,251] in particular interferon,[252] and also for their purification by chromatofocussing.[228,253]

5. Catalysis

Ion exchangers based on organic polymers, primarily sulphonic acid cation exchangers, are widely used in catalysis[147,254] in hydrolysis, hydration, esterification, alkylation, condensation, etc. The range of reactions catalysed is determined in practice only by the chemical nature of the ionogenic group, so that the replacement of an organic polymer by an inorganic matrix should not influence the catalytic properties. At the same time, it should be expected that ion exchangers based on mineral carriers will make it possible to carry out processes requiring a higher temperature or accompanied by strong exothermic effects leading to local superheating with consequent degradation of the catalyst.

The mesoporous structure of the carrier ensures that all the reaction centres are accessible, so that the specific activity (calculated for one centre) of ion exchangers based on mineral carriers should be much greater than that of organic polymer resins. In spite of the greater exchange capacity of organic ion exchangers, their activity calculated for unit mass or unit volume may be lower. This effect should be greatest for reactions involving large organic molecules.

The limit of the thermal stability of sulphonic acid cation exchangers based on silica and obtained by polycondensation is more than 100 K higher than that of the organic-polymer analogue Amberlite 15.[142] In the hydrothermal treatment of sulphonic acid cation exchangers, the greatest stability is shown by catalysts in which the silicon atom is joined to an aliphatic carbon atom.

Sulphonic acid cation exchangers based on silica have been used to catalyse the alkylation of alcohols by isobutylene to obtain alkyl t-butyl ethers (in particular methyl t-butyl ether)[255,256] and of phenol by dec-1-ene,[257] the dehydration of alcohols,[142] esterification,[142] and the gas-phase nitration of benzene by nitrogen dioxide.[142] Comparison of the activity of sulphonic acid cation exchangers based on silica with that of analogous cation exchangers based on organic polymers (KU-2, Amberlite 15, Lewatit SPC 108/H) showed that the former in many cases have a higher specific activity, calculated both for one centre and for unit mass or volume, in spite of the lower concentration of sulphonic acid groups.

Strongly basic silica anion exchangers with grafted optically active aminoalcohols and alkaloids are used to catalyse Michael asymmetric addition.[258,259] It was unexpectedly found that by varying the length of the chain joining the active centre to the carrier, and the accessibility of the silanol groups of the surface, it is possible to reverse the enantio-selectivity of the addition. This indicates that the carrier plays an active part in the formation of the intermediate substrate–catalyst complex.

A second method of using ion exchangers based on silica in catalysis is by the attachment of transition metal complexes. The heterogeneous metal-complex catalysts obtained in this way combine the high activity and selectivity of homogeneous metal-complex catalysts with the technology of traditional heterogeneous catalysts.[4,5] The metal complexes are usually attached by the coordination of ligands grafted to the carrier, but in a number of cases ion-exchange attachment is preferred. Examples include the attachment of chloro-complexes of platinum(II) and platinum(IV) to anion exchangers with grafted quaternary ammonium and phosphonium groups to obtain catalysts for the industrially important reaction of hydrosilylation of unsaturated compounds.[33,62] The ion-exchange attachment of platinum gives more stable catalysts than attachment by coordination (bonding through the phosphine group), and the catalyst can be used repeatedly without loss of activity. The selectivity of the formation of the β-isomer in the hydrosilylation reaches 100%. Unlike catalysts with a polymeric matrix, the silica carrier ensures the activity of all the platinum atoms.

Modified silica specimens can also be used to catalyse inter-phase transfer, as shown for the alkylation of phenol,[35] the synthesis of esters,[260] and halide exchange.[61,261] The catalytic properties of strongly basic phosphonium ion exchangers based on silica differ considerably from those of their polymer-based analogues and hexadecyltributylphosphonium bromide.[35,261]

References

1. G V Lisichkin, G V Kudryavtsev, A A Serdan, et al *Modifitsirovannye Kremnezemy v Sorbtsii Katalize i Khromatografii* (Modified Silicas in Sorption, Catalysis, and Chromatography), Izd. Khimiya, Moscow, 1986, 248 pp
2. I E Neimark *Sinteticheskie Mineral'nye Adsorbenty i Nositeli Katalizatorov* (Synthetic Mineral Adsorbents and Catalyst Carriers), Izd. Naukova Dumka, Kiev, 1982, 216 pp
3. V B Aleskovskii (Editor) *Napravlennyi Sintez Tverdykh Veshchestv* (The Directed Synthesis of Solid Substances), No.1, Izd. Leningrad. Gos. Univ., Leningrad, 1983, 196 pp
4. Yu I Ermakov, V A Zakharov, B N Kuznetsov *Zakreplennye Kompleksy na Okisnykh Nositelyakh v Katalize* (Complexes Attached to Oxide Carriers in Catalysis), Izd. Nauka, Novosibirsk, 1980, 190 pp

5. G V Lisichkin, A Ya Ioffa *Geterogennye Metallokompleksnye Katalizatory* (Heterogeneous Metal-Complex Catalysts), Izd. Khimiya, Moscow, 1981, 160 pp
6. L A Osterman, *Khromatografiya Belkov i Nukleinovykh Kislot* (The Chromatography of Proteins and Nucleic Acids), Izd. Nauka, Moscow, 1985, 536 pp
7. V M Kolikov, B V Mchedlishvili *Khromatografiya Biopolimerov na Makroporistykh Kremnezemakh* (The Chromatography of Biopolymers on Macro-porous Silicas), Izd. Nauka, Leningrad, 1986, 190 pp
8. M T Bryk *Polimerizatsiya na Tverdoi Poverkhnosti Neorganicheskikh Veshchestv* (Polymerisation on the Surface of Inorganic Solids), Izd. Naukova Dumka, Kiev, 1981, 288 pp
9. *Silylated Surfaces* (Edited by D E Leyden, W T Collins), Gordon and Breach, New York, 1980, 379 pp
10. K K Unger *Porous silica, its properties and use as support in column liquid chromatography* Elsevier, Amsterdam, 1979, **16** 336 pp (J. Chromatogr. Library)
11. H Parvez, Y Kato, S Parves (Editors) *Progress in HPLC, V.1: Gel permeation and ion-exchange chromatography of proteins and peptides* VNU Science Press, Utrecht, 1985, 223 pp
12. F E Regnier *Methods Enzymol.*, 1984, **104** 170
13. H H Weetall, A M Filbert *Methods Enzymol.*, 1974, **32** 59
14. G V Lisichkin, S M Staroverov *Zhur. Vses. Khim. Obshch. im. D. I. Mendeleeva*, 1983, **28** 47
15. S S Ivanchev, A V Dmitrenko, *Usp. Khim.*, 1982, **51** 1178 [English translation in *Russ. Chem. Revs.*, 1982(7)]
16. M A Bruk *Usp. Khim.*, 1987, **56** 148 [English translation in *Russ. Chem. Revs.*, 1987(1)]
17. G V Lisichkin, G V Kudryavtsev, P N Nesterenko *Zh. Anal. Khim.*, 1983, **38** 1684
18. V M Ivanov, G V Kudryavtsev, G V Lisichkin, P N Nesterenko *Opredelenie Malykh Kontsentratsii Elementov* (The Determination of Low Concentrations of Elements), (Edited by Yu A Zolotov) Izd. Nauka, Moscow, 1986, p.107
19. R W Murray *Electroanal. Chem.*, 1984, **13** 191
20. BRD P. 2426306; *Chem. Abstr.*, 1976, **84** 80210
21. Japan. P. 105757; *Chem. Abstr.*, 1982, **96** 87834
22. R M Chicz, Z Shi, F E Regnier *J. Chromatogr.*, 1986, **359** 121
23. N V Yablokova, Yu A Aleksandrov, O M Titova *Vysokomol. Soedin.*, 1986, **28A** 1908
24. V N Petrik, L L Kuznetsova, R M Livshits *Vysokomol. Soedin.*, 1974, **16B** 110
25. P R Moses, L M Wier, J C Lennox, et al. *Anal. Chem.*, 1978, **50** 576
26. P R Moses, R W Murray *J. Am. Chem. Soc.*, 1976, **98** 7435
27. R W Stout, S I Sivakoff, R D Ricker, et al. *J. Chromatogr.*, 1986, **352** 381
28. B.P. 1456974; *Chem. Abstr.*, 1977, **86** 172662
29. P R Moses, R W Murray *J. Electroanal. Chem.*, 1977, **77** 393
30. G V Kudryavtsev, S V Markin, G V Lisichkin *Vestn. Mosk. Gos. Univ., Ser. 2: Khim.*, 1983, **24** 509
31. M V Sobolevskii, K P Grinevich, A I Demchenko, et al. *Plast. Massy*, 1977, 68
32. USSR P. 727653; *Byull. Izobret.*, 1980, (15)
33. V S Brovko, N K Skvortsov, A Yu Ivanov, V O Reikhsfel'd, *Zh. Obshch. Khim.*, 1983, **53** 1831
34. H Engelhardt, E Schweinheim *Chromatographia.*, 1986, **2** 425
35. P Tundo, P Venturello *J. Am. Chem. Soc.*, 1979, **101** 6606
36. J H Knox, G Vasvari *J. Chromatogr. Sci.*, 1974, **12** 449
37. D E Leyden, G H Luttrell *Anal. Chem.*, 1975, **47** 1612
38. D E Leyden, G H Luttrell, A E Sloan, et al. *Anal. Chim. Acta*, 1976, **84** 97
39. O I Voroshilova, A V Kiselev, Yu S Nikitin *Kolloidn. Zh.*, 1980, **42** 223
40. G V Lisichkin, G V Kudryavtsev *Dokl. Akad. Nauk SSSR*, 1979, **247** 117
41. A K Andrianov, A V Olenin, V P Zubov, et al. *Vysokomol. Soedin.*, 1983, **25A** 1987
42. A A Chuiko, V A Tertykh, G E Plavnik, I E Neimark *Kolloidn. Zh.*, 1965, **27** 903
43. I E Neimark, V M Chertov *Dokl. Akad. Nauk SSSR*, 1961, **138** 877
44. S Z Bernadyuk, G V Kudryavtsev, S V Markin, G V Lisichkin, *Zhur. Vses. Khim. Obshch. im. D. I. Mendeleeva*, 1982, **27** 586
45. G B Cox, C R Loscombe, M J Slucutt, et al. *J. Chromatogr.*, 1976, **117** 269
46. P A Asmus, C Low, M Novotny *J. Chromatogr.*, 1976, **123** 109
47. K Unger, K Berg, D Nyamah, T Lothe *Colloid. Polym. Sci.*, 1974, **252** 317
48. BRD P. 2225904; *Chem. Abstr.*, 1974, **80** 113118
49. N Weigand, I Sebestian, I Halasz *J. Chromatogr.*, 1974, **102** 325
50. B B Wheals *J. Chromatogr.*, 1979, **177** 263
51. Europ. P. 8902; *Chem. Abstr.*, 1980, **93** 150369
52. Shung Ho Chang, K M Gooding, F E Regnier *J. Chromatogr.*, 1976, **120** 321
53. T E Vertinskaya, V I Fadeeva, D V Mil'chenko, et al. *Zh. Anal. Khim.*, 1986, **41** 1067
54. G V Kudryavtsev, D V Mil'chenko, S Z Bernadyuk, et al. *Teor. Eksper. Khim.*, 1987, **23** 711
55. E I Sinyavskaya, L V Tsymbal, V M Bogatyrev, et al. *Adsorbtsiya i Adsorbenty*, 1984(12), 51
56. USSR P. 887462; *Byull. Izobret.*, 1981(45)
57. E I Sinyavskaya, K B Yatsimirskii, V M Bogatyrev, et al. *Katalizatory, Soderzhashchie Nanesennye Kompleksy* (Catalysts Containing Deposited Complexes), (Edited by Yu I Ermakov) Izd. IK Sibir. Otd. Akad. Nauk SSSR, Novosibirsk, 1980, Part 1, p. 93
58. G V Kudryavtsev, G V Lisichkin *Adsorbtsiya i Adsorbenty*, 1984(12), 33
59. S M Staroverov, P N Nesterenko, G V Lisichkin *Vestn. Mosk. Gos. Univ., Ser. 2: Khim.*, 1980, **21** 370
60. USSR P. 743717; *Byull. Izobr.*, 1980(25)
61. P Tundo, P Venturello, E Angeletti *J. Amer. Chem. Soc.*, 1982, **104** 6547
62. V S Brovko, N K Skvortsov, V O Reikhsfel'd *Zh. Obshch. Khim.*, 1981, **51** 487
63. D C Locke, J T Schmermund, B Banner *Anal. Chem.*, 1972, **44** 90
64. I P Alimarin, P N Nesterenko, V M Ivanov *Dokl. Akad. Nauk SSSR*, 1983, **271** 627
65. J B Crowther, R A Hartwick *Chromatographia*, 1982, **16** 349
66. J B Crowther, S D Fazio, R A Hartwick *J. Chromatogr.*, 1983, **282** 619
67. T R Floyd, S E Cicero, S D Fazio, et al. *Anal. Biochem.*, 1986, **154** 570
68. T R Floyd, L W Yu, R A Hartwick *Chromatrographia.*, 1986, **21** 402
69. S M Staroverov, A A Serdan, G V Lisichkin *J. Chromatogr.*, 1986, **364** 377
70. M E Landgrebe, D Wu, R R Walters *Anal. Chem.*, 1986, **58** 1607

71. A A Morozov *Khromatografiya v Neorganicheskom Analize* (Chromatography in Inorganic Analysis), Izd. Vys. Shkoly, Moscow, 1972, 217 pp
72. D L Hendrix, R E Lee, J G Baust, H James *J. Chromatogr.*, 1982, **210** 45
73. T Takeuchi, E S Yeung *J. Chromatogr.*, 1986, **370** 83
74. R M Cassidy, S Elchuk *Anal. Chem.*, 1982, **54** 1558
75. I Molnar, H Knauer, D Wilk *J. Chromatogr.*, 1980, **201** 225
76. J H Knox, G R Laird *J. Chromatogr.*, 1976, **122** 17
77. R M Cassidy, S Elchuk *J. Chromatogr. Sci.*, 1983, **21** 454
78. L V Pavlova, S A Pavlov, M A Bruk *Vysokomol. Soedin.*, 1987, **29A** 1518
79. S A Pavlov, M A Bruk *Vysokomol. Soedin.*, 1987, **29A** 118
80. V A Kargin, N A Plate *Vysokomol. Soedin.*, 1959, **1** 330
81. L P Yanova, G S Blyskosh, A M Chigishove, et al. *Kolloidn. Zh.*, 1971, **33** 171
82. D Berg, H G Tiller, I Kopka, B Langguth *Z. Chem.*, 1978, **18** 219
83. L A Negievich *Ukr. Khim. Zh.*, 1975, **41** 101
84. Yu L Morozov, L I Plotnikova, S R Rafikov, B L Tsetlin *Vysokomol. Soedin.*, 1967, **9A** 1627
85. M A Bruk, E Ya Yunitskaya, A L Izyumnikov, T T Velichko *Vysokomol. Soedin.*, 1980, **22B** 138
86. S L Mund, M A Bruk, A D Abkin *Vysokomol. Soedin.*, 1976, **18A** 2631
87. G S Blyskosh, L P Yanova, A B Taubman, G G Ryabchikova *Vysokomol. Soedin.*, 1969, **11A** 900
88. S A Pavlov, M A Bruk, A D Abkin *Adsorbtsiya i Adsorbenty*, 1982(9), 61
89. L A Negievich *Ukr. Khim. Zhur.*, 1977, **43** 176
90. N I Litsov, A A Kachan *Vysokomol. Soedin.*, 1976, **18B** 182
91. V V Korshak, L B Zubakova, N V Kachurina, O B Balashova *Vysokomol. Soedin.*, 1979, **21A** 1132
92. S S Ivanchev, N S Enikolopyan, B V Polozov *Vysokomol. Soedin.*, 1981, **23A** 2064
93. A V Olenin, A L Khristyuk, V B Golubev, et al. *Vysokomol. Soedin.*, 1983, **25A** 423
94. S S Ivanchev, A V Dmitrenko, V A Demidova, A K Dabagova *Vysokomol. Soedin.*, 1985, **27A** 1086
95. A K Andrianov, A V Olenin, O N Saprygin, et al. *Vysokomol. Soedin.*, 1984, **26A** 2599
96. S S Ivanchev, A V Dmitrenko, V A Demidova, N E Shadrina *Vysokomol. Soedin.*, 1986, **28A** 2095
97. USSR P. 787411; *Byull. Izobret.*, 1980(46)
98. USSR P. 765271; *Byull. Izobret.*, 1980(35)
99. K Hayakawa, K Kawase, H Yamakita *J. Appl. Polym. Sci.*, 1977, **21** 2921
100. C G Horvath, B A Preiss, S R Lipsky *Anal. Chem.*, 1967, **39** 1422
101. US P. 4140653; *Chem. Abstr.*, 1979, **90** 170825
102. R E Bareiss, U Buechel, H G Elias *Angew. Makromol. Chem.*, 1976, **55** 129
103. N K Boardman *J. Chromatogr.*, 1959, **2** 388
104. US P. 3488922; *Chem. Abstr.*, 1970, **72** 70984
105. B.P. 1456865; *Chem. Abstr.*, 1977, **86** 190835
106. B B Wheals *J. Chromatogr.*, 1975, **107** 402
107. P Gareil, A Heritier, M Caude, R Rosset *Analusis.*, 1976, **4** 71
108. M Caude, R Rosset *J. Chromatogr. Sci.*, 1977, **15** 405
109. J P Lefevre, A Divry, M Claude, R Rosset *Analusis.*, 1975, **3** 533
110. D M Wonnacott, E V Patton *J. Chromatogr.*, 1987, **389** 103
111. G Schomburg, J Köhler, H Figge, et al. *Chromatographia.*, 1984, **18** 265
112. W Kopaciewicz, M A Rounds, F E Regnier *J. Chromatogr.*, 1985, **318**, 157
113. R R Drager, F E Regnier *Anal. Biochem.*, 1985, **145** 47
114. A J Alpert, F E Regnier *J. Chromatogr.*, 1979, **185** 375
115. G Vanecek, F E Regnier *Anal. Biochem.*, 1982, **121** 156
116. S P Gupta, E A Pfannkoch, F E Regnier *Anal. Biochem.*, 1983, **128** 196
117. V A Davankov, A A Kurganov, A B Tevlin *J. Chromatogr.*, 1983, **261** 223
118. J Köhler *Chromatographia.*, 1986, **21** 573
119. A J Alpert *J. Chromatogr.*, 1986, **359** 85
120. A J Alpert *J. Chromatogr.*, 1983, **266** 23
121. V I Ofitserov, V F Yamshchikov *Bioorg. Khim.*, 1983, **9** 1248
122. E V Egorov *Summary of Candidate's Thesis, Institute of Chemical Physics, Academy of Sciences of the USSR–All Union Scientific Research Institute for Chemical Reagents and Highly Pure Chemical Substances, Moscow*, 1967, 24 pp
123. G Horvath, *Bonded stationary phases in chromatography* (Edited by E Grushka, H D Durst, E J Kikta) Ann Arbor: Ann Arbor Science, 1974, 237 pp
124. W Kopaciewicz, F E Regnier *J. Chromatogr.*, 1986, **358** 107
125. US P. 4551245; *Chem. Abstr.*, 1986, **104** 90080
126. O Itabashi, T Goto, H Moriya *Nippon Kagaku Kaishi*, 1987, 1600; 1987, **107** 155295
127. T M Suzuki, O Itabashi, T Goto, et al. *Anal. Sci.*, 1986, **2** 391
128. O Itabashi, T Goto *Chem. Ind. (London)*, 1986, 287
129. A A Kachan, V A Shrubovich *Fotokhimicheskoe Modifitsirovanie Sinteticheskikh Polimerov* (The Photochemical Modification of Synthetic Polymers), Izd. Naukova Dumka, Kiev, 1973, 159 pp
130. Binh Dinh Ngoc, J G Rabe, W Schnabel *Angew. Macromol. Chem.*, 1975, **46** 23
131. B.P. 1456865; *Ref. Zh. Khim.*, 1977, 15S216P
132. P R Haddad, P E Jackson, A L Heckenberg *J. Chromatogr.*, 1985, **346** 139
133. F Runge, W Zimmermann *Prakt. Chem.*, 1955, **4** 283
134. USSR P. 429074; *Byull. Izobret.*, 1974(39)
135. USSR P. 523911; *Byull. Izobret.*, 1977(3)
136. USSR P. 429073; *Byull. Izobret.*, 1974(39)
137. USSR P. 475378; *Byull. Izobret.*, 1975(35)
138. BRD P. 3120195; *Chem. Abstr.*, 1982, **97** 128601
139. USSR P. 418497; *Byull. Izobret.*, 1974(30)
140. BRD P. 2357184; *Chem. Abstr.*, 1975, **83** 137376
141. S Suzuki, K Tohmori, Y Ono, *Chem. Lett.*, 1986, 747
142. S Suzuki, Y Ono *The 8th Japan USSR Catalysis Seminar. Catalysis by new materials*, 29–30 Oct. 1986, Tokyo, Japan. p. 211
143. I B Slinyakova, M G Voronkov, I E Krot *Kolloidn. Zh.*, 1973, **35** 480
144. USSR P. 585187; *Byull. Izobret.*, 1977(7)
145. K K Unger, N P Becker, P Roumeliotis *J. Chromatogr.*, 1976, **125** 115
146. I B Slinyakova, L I Kurennaya *Adsorbtsiya i Adsorbenty*, 1972(1), 83
147. B P Nikol'skii, P G Romankov *Ionity v Khimicheskoi Tekhnoloii* (Ion Exchangers in Chemical Technology), Izd. Khimiya, Leningrad, 1982, 416 pp

148. K M Saldadze, V D Kopylova-Valova *Kompleksoobrazuyushchie Ionity (Kompleksity)* (Complex-Forming Ion Exchangers), Izd. Khimiya, Leningrad, 1980, 336 pp
149. D E Leyden, G H Luttrell, W K Nonidez, D B Werho *Anal. Chem.*, 1976, **48** 67
150. D E Lyeden, M L Steele, B B Jablonski, R B Somoano *Anal. Chim. Acta.*, 1978, **100** 545
151. I P Alimarin, V I Fadeeva, G V Kudryavtsev, et al *Talanta.*, 1987, **34** 103
152. S E Northcott, D E Leyden *Anal. Chim. Acta.*, 1981, **126** 117
153. M Grote, A Schwalk, A A Kettrup *Fr. Z. Anal. Chem.*, 1982, **313** 297
154. I M Loskutova, V I Fadeeva, T I Tikhomirova, G V Kudryavtsev *Zh. Anal. Khim.*, 1984, **39** 471
155. T I Tikhomirova, I M Loskutova, V I Fadeeva, et al. *Zh. Anal. Khim.*, 1984, **39** 1630
156. V I Fadeeva, I M Loskutova, T I Tikhomirova, et al. *Vestn. Mosk. Gos. Univ., Ser 2: Khim.*, 1985, **26** 194
157. I R Zmievskaya, A T Savichev, V I Fadeeva, et al. *Zh. Anal. Khim.*, 1987, **42** 1467
158. USSR P. 1 122 613; *Byull. Izobret.*, 1984(41)
159. USSR P. 1 057 060; *Byull. Izobret.*, 1983(44)
160. V M Ivanov, G N Gorbunova, G V Kudryavtsev, et al. *Zh. Anal. Khim.*, 1984, **39** 504
161. I R Zmievskaya, G V Kudryavtsev, T I Tikhomirova, V I Fadeeva *Zh. Vses. Khim. Ova. im. D.I.Mendeleeva*, 1985, **30** 354
162. I R Zmievskaya, A T Savichev, V I Fadeeva, et al. *XIII Vsesoyuznoe Chernyaevskoe Soveshchanie po Khimii, Analizu i Tekhnologii Platinovykh Metallov. Tezisy Dokladov* (Summaries of Papers Presented at the Thireteenth All Union Chernyaev Conference on the Chemistry, Analysis, and Technology of the Platinum Metals), 1986, **2** 153
163. V I Fadeeva, T I Tikhomirova, N S Smirnova, I M Loskutova *Zh. Anal. Khim.*, 1987, **42** 1436
164. V P Goncharik, L P Tikhonova, L I Kozhara *Zh. Anal. Khim.*, 1984, **39** 1853
165. V M Ivanov, N Y Yatsmiriskaya, A I Shchadrina *Zh. Anal. Khim.*, 1985, **40** 2226
166. P N Nesterenko, G V Kozyreva, V M Ivanov, et al. *I Vsesoyuznoe Soveshchanie po Khimii, Tekhnologii i Analizu Zolota i Serebra. Tezisy Dokladov* (Summaries of Papers Presented at the First All Union Conference on the Chemistry, Technology, and Analysis of Gold and Silver), Novosibirsk, 1983, p. 107
167. A R Timerbaev, O M Petrukhin, Yu A Zolotov *Zh. Anal. Khim.*, 1981, **36** 1160
168. B Steinbrech *J. Liquid Chromatogr.*, 1987, **10** 1
169. H Small, T S Stevens, W C Bauman *Anal. Chem.*, 1975, **47** 1801
170. F C Smith, R C Chang *The practice of ion chromatography* (John Wiley: New York), 1983, 218 pp
171. J S Fritz, D T Gjerde, C Pohlandt *Ion Chromatography* (Translated into Russian), Izd. Mir, Moscow, 1984, 221 pp
172. O A Shpigun, Yu A Zolotov *Zavod. Lab.*, 1982, **48** 4
173. F G P Mullins *Analyst (London)*, 1987, **112** 665
174. R N Reeve *J. Chromatogr.*, 1979, **177** 393
175. P J Naish *Analyst (London).*, 1984, **109** 809
176. R A Cochrane, D E Hillman *J. Chromatogr.*, 1982, **241** 392
177. H J Cortes *J. Chromatogr.*, 1982, **234** 517
178. F A Buytenhuys *J. Chromatogr.*, 1981, **218** 57
179. B Luckas *Fr. Z. Anal. Chem.*, 1985, **320** 519
180. B Rössner, G Schwedt *Fr. Z. Anal. Chem.*, 1985, **320** 566
181. P R Haddad, P W Alexander *J. Chromatogr.*, 1985, **324** 319
182. J P McCarthy, J A Caruso *J. Chromatogr. Sci.*, 1983, **21** 389
183. D Yan, E Stumpp, G Schwedt *Fr. Z. Anal. Chem.*, 1985, **322** 474
184. C M Riley, L A Sternson, A J Repta *J. Chromatogr.*, 1981, **217** 405
185. D J Barkley, T E Dahms, K N Villeneuve *J. Chromatogr.*, 1987, **395** 631
186. J Toei *J. High Resol. Chromatogr., Chromatogr. Commun.*, 1987, **10** 111
187. D Yan, G Schwedt *Fr. Z. Anal. Chem.*, 1987, **327** 503
188. D Yan, G Schwedt *Fr. Z. Anal. Chem.*, 1985, **320** 325
189. R M Cassidy, S Elchuk *J. Chromatogr. Sci.*, 1980, **18** 217
190. S Elchuk, R M Cassidy *Anal. Chem.*, 1979, **51** 1434
191. A Mazzucotelli, A Dadone, R Frache, F Baffi *J. Chromatogr.*, 1985, **349** 137
192. S Matsushita *J. Chromatogr.*, 1984, **312** 327
193. M Lauth, P Gramain *J. Chromatogr.*, 1987, **395** 153
194. J Chmielowiec, W Simon *Chromatographia.*, 1978, **11** 99
195. K H Faltynski, J R Jezorek *Chromatographia.*, 1986, **22** 5
196. C H Risner, J R Jezorek *Anal. Chim. Acta.*, 1986, **186** 233
197. J H Knox, A Pryde *J. Chromatogr.*, 1975, **112** 171
198. J H Knox, G Vasvari *J. Chromatogr. Sci.*, 1974, **17** 449
199. P J Twitchett, A E P Gorvin, A C Moffat *J. Chromatogr. Sci.*, 1976, **120** 360
200. B M Eriksson, B A Persson *J. Chromatogr.*, 1982, **228** 143
201. B M Eriksson, S Gustafsson, B A Persson *J. Chromatogr.*, 1983, **278** 255
202. H Thomas, W Stammel, A Brossi *J. Chromatogr. Sci.*, 1983, **21** 481
203. K Kemper, E Hagemeier, K S Boos, et al. *Chromatographia.*, 1984, **19** 288
204. A Himuro, H Nakamura, Z Tamura *J. Chromatogr.*, 1983, **264** 423
205. J H Knox, J Jurand *J. Chromatogr.*, 1973, **82** 398
206. F Kreuzig, J Frank *J. Chromatogr.*, 1981, **218** 615
207. A P Williams *J. Chromatogr.*, 1986, **373** 175
208. R S Bowman *J. Chromatogr.*, 1984, **285** 467
209. K Harrison, W C Beckham, T Yates, C D Carr *Int. Lab.*, 1986, 90
210. G J Peters, E J Laurensse, A Leyva, H M Pinedo *Anal. Biochem.*, 1987, **161** 32
211. S P Bag *Talanta.*, 1985, **32** 779
212. J R Larson *J. Chromatogr.*, 1986, **356** 379
213. J C Liao, C R H Vogt *J. Chromatogr. Sci.*, 1979, **17** 237
214. C E Kientz, A Verweij, H L Boter *J. Chromatogr.*, 1983, **282** 643
215. E V Patton, D M Wonnacott *J. Chromatogr.*, 1987, **389** 115
216. G B Guise, G C Smith *J. Chromatogr.*, 1982, **235** 365
217. K M Gooding *Biochromatography.*, 1986, **1** 34
218. G K C Low *High Perform. Liq. Chromatogr.*, **1** 34
219. R D Johnson *Dev. Ind. Microbiol.*, 1987, **27** 77
220. I Marsaroff, F E Regnier *J. Liq. Chromatogr.*, 1986, **9** 2563
221. M Colpan, D Riesner *J. Chromatogr.*, 1984, **296** 339
222. G Vanecek, F E Regnier *Anal. Biochem.*, 1980, **109** 345
223. V N Borisova, B V Mchedlishvili, L A Nakhapetyan *Sinteticheskie Makroporistye Kremnezemnye Sorbenty v Khromatografii Biopolimerov* (Synthetic Macroporous Silica Sorbents in the Chromatography of Biopolymers), Izd. ONTITEI, Mikrobioprom, Moscow, 1979, 58 pp

224. T Ueda, Y Ishida *J. Chromatogr.*, 1987, **386** 273
225. S I Yastrebov, S G Popov *Bioorg. Khim.*, 1986, **12** 661
226. W Kopaciewicz, F E Regnier *Anal. Biochem.*, 1983, **133** 251
227. W Kopaciewicz, F E Regnier *Anal. Biochem.*, 1982, **126** 8
228. G W Wagner, F E Regnier *Anal. Biochem.*, 1982, **126** 37
229. K M Gooding, M N Schmuck *J. Chromatogr.*, 1984, **296** 321
230. R W Stout, S I Sivakoff, R D Ricker, L R Snyder *J. Chromatogr.*, 1986, **353** 439
231. Yu A El'tekhov, A V Kiselev, T D Khokhlova, Yu S Nikitin *Chromatographia.*, 1973, **6** 187
232. H Engelhardt, D Mathes *Chromatographia.*, 1981, **14** 325
233. C A Frolik, L L Dart, M B Sporn *Anal. Biochem.*, 1982, **125** 209
234. J.-X Huang, C Horvath *J. Chromatogr.*, 1987, **406** 285
235. W Kopaciewicz, M A Rounds, J L Fausnaugh, F E Regnier *J. Chromatogr.*, 1983, **266** 3
236. E S Parente, D B Wetlaufer *J. Chromatogr.*, 1986, **355** 29
237. K M Gooding, M N Schmuck *J. Chromatogr.*, 1983, **266** 633
238. B Burnette, C R McFarland, P Batra *J. Chromatogr.*, 1983, **277** 137
239. H Yuki, T Yajima, H Kawasaki, A Yamaji *Anal. Biochem.*, 1979, **97** 203
240. T G Lawson, F E Regnier, H L Weith *Anal. Biochem.*, 1983, **133** 85
241. C R Newton, A R Greene, G R Heathcliffe, et al. *Anal. Biochem.*, 1983, **129** 22
242. E Hagemeier, S Bornemann, et al. *J. Chromatogr.*, 1982, **237** 174
243. T Kremmer, M Boldizsar, L Holczinger *J. Chromatogr.*, 1987, **415** 53
244. J Alonso, M V Nogues, et al. *J. Liquid Chromatogr.*, 1985, **8** 299
245. Y Kato, K Komiya, T Hashimoto *J. Chromatogr.*, 1982, **246** 13
246. R Hecker, M Colpan, D Riesner *J. Chromatogr.*, 1985, **326** 251
247. T A Ratko, J M Pezzuto *J. Chromatogr.*, 1985, **324** 484
248. R C Sullivan Y N Shing, P A D'Amore, M Klagsbrun *J. Chromatogr.*, 1983, **266** 301
249. A J M Van Den Eijnden-Van Raaij, I Koornneef, T M J Van Oostwaard, et al. *Anal. Biochem.*,1987, **163** 263
250. D Josic, W Hofmann, W Reutter *J. Chromatogr.*, 1986, **371** 43
251. M N Schmuck, D L Gooding, K M Gooding *J. Chromatogr.*, 1986, **359** 323
252. R A Wolfe, J Casey, P C Familletti, S Stein *J. Chromatogr.*, 1984, **296** 277
253. L A A Sluyterman, O Elgersma *J. Chromatogr.*, 1978, **150** 17
254. L G Polyanskii *Kataliz Ionitami* (Catalysis by Ion Exchangers), Izd. Khimiya, Moscow, 1973, 214 pp
255. USSR P. 1 142 465; *Byull. Izobret.*, 1985(8)
256. G V Lisichkin, G V Kudryavtsev, S Z Bernadyuk *Zh. Vses. Khim. Obshch. im. D.I. Mendeleeva*, 1983, **28** 712
257. S Z Bernadyuk, N A Gasheeva, G V Lisichkin, et al. *Vestn. Moskov. Gos. Univ., Ser. 2: Khim.*, 1986, **27** 407
258. V V Krotov, S M Staroverov, P N Nesterenko, G V Lisichkin *Zh. Obshch. Khim.*, 1986, **56** 2460
259. V V Krotov, S M Staroverov, P N Nesterenko, G V Lisichkin *Zh. Obshch. Khim.*, 1987, **57** 1187
260. G Bram, G Decodts *Tetrahedron Lett.*, 1980, **21** 5011
261. P Tundo, P Venturello *J. Am. Chem. Soc.*, 1981, **103** 856

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Van der Waals radii and their application in chemistry

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ABSTRACT. Published systems of van der Waals radii (VR) have been examined and compared. The many ways of using VR in various branches of chemistry, in particular in crystal chemistry, stereochemistry, and X-ray diffraction (primarily to describe and interpret molecular conformations and crystal structures and to determine new structures) have been analysed. Particular attention has been paid to the detection of specific non-valence interactions (both inter- and intramolecular). Various structural-biological problems, in particular the production of 'incorrect' pairs of bases in DNA and the use of VR to explain the physicochemical properties of substances, have been examined. The properties of crystals determined by the effective volume, dimensions, and shape of the molecules, and the characteristic features of the structures of inclusion compounds, clathrates, and organic conductors, have been discussed. The use of VR to investigate the mechanism and predict the possibility of various chemical reactions has been described. The bibliography contains 173 references.

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I. Introduction

Quantum-mechanical ideas play an exceptionally important role in present-day chemistry, yet the classical theory of the structure of molecules and classical stereochemistry, whose foundations were laid by Butlerov, Kekulé, Van't Hoff, Le Bel, and Werner, today still remain the basis of organic and coordination chemistry. In recent years they have been supplemented significantly by the quantitative geometric characteristics of molecular systems, based mainly on empirical generalisations of the results of studies by X-ray diffraction and other physical methods.

One such generalisation is the system of covalent radii, which makes it possible to estimate the lengths of valence bonds. However, as a consequence of the variety of valence states and the significant deviations from additivity, the use of covalent radii has been extremely limited. For practical purposes, tables of 'standard' bond lengths,[1] which together with 'standard' values of the valence angles make it possible to construct in a first approximation a rod-and-sphere model of a molecule, are more useful. Even these concepts are inadequate, however, since they do not make it possible to take account of non-valence intramolecular interactions and cannot be used to analyse the packing of molecules.

The need for a comprehensive discussion of the geometry of molecules and their packing made it necessary to develop the concept of van der Waals radii (VR), which is now widely used in various branches of chemistry. It might seem that with the present availability of such effective means of taking account of non-valence interactions as atom–atom potentials,[2,3] it would be possible to carry out a more rigorous and accurate quantitative analysis of the geometry of molecular systems. The universal nature, simplicity, and clarity of the VR concept, however, make it appropriate for use in preliminary qualitative estimates, and often for the final solution of many problems of practical importance.

II. Systems of van der Waals radii and the dispersion of intermolecular contacts

The first attempts to relate the distances between the atoms of neighbouring molecules in crystals to the corresponding radii of the atoms (or atomic groups)[4–6] included the first representations of large molecules as overlapping van der Waals spheres and of crystal structures as close-packed molecules in contact. Pauling[7] gave the first table of VR, consisting of the rounded values of the ionic radii. It was Kitaigorodskii,[8] however, who fully recognised the value of this approach for chemistry and molecular physics and who laid the foundations of the theory of the close-packing of molecules.

Table 1. Van der Waals atomic radii (Å) of the elements of organic compounds.

Element	Pauling, 1939 (Ref.7)	Kitaigorodskii, 1955 (Ref.8)	Kitaigorodskii, 1971 (Ref.9)	Bondi, 1964 (Ref.16)***	Zefirov and Zorkii, 1974 (Ref.11)
C	1.85*	1.72**	1.80	1.70	1.71
H	1.2	1.17	1.17	1.20	1.16
O	1.40	1.36	1.52	1.52	1.29
N	1.5	1.57	1.58	1.55	1.50
Cl	1.80	1.78	—	1.75	1.90
S	1.85	2.02	—	1.80	1.84 [15]

* Half the thickness of an aromatic molecule (in the third edition of his book,[7] Pauling changed this quantity to 1.70 Å, leaving the other quantities unchanged).

** The radius of the carbon atom in aromatic molecules; the radius of aliphatic carbon is given as 1.80 Å (in his next publication,[9] Kitaigorodskii adopted the universal value 1.80 Å).

*** Radii for atoms forming only single bonds (for aliphatic compounds in the case of hydrogen).

The VR values proposed by Kitaigorodskii[8] were extremely close to those of Pauling[7] (Table 1). Later Kitaigorodskii[9] modified his table slightly (in the present authors' opinion making it less satisfactory). A common disadvantage of these VR systems was that they were constructed from extremely limited structural data (sometimes the value of a VR was established from only one structure). Although the proposed VR values in many cases were close to the best values, the VR are in principle essentially statistical quantities, and should be determined by averaging over a large number of structures.

The starting point for the construction of a system of VR is essentially the basic postulate of the theory of the close-packing of molecules, according to which the molecules, bounded by the outer surface of intersecting van der Waals atomic spheres, touch one another in the crystal, that is they do not penetrate one another and are not suspended in a cavity. The problem is to select suitable VR values. Kitaigorodskii[8] showed that a satisfactory solution to this problem exists.

The quantities $\Delta r_{ij} = r_{ij} - (R_i + R_j)$, where R_i and R_j are the van der Waals radii, and i and j are the indices of atoms belonging to neighbouring molecules, will be used. If the VR are known, it is possible, for each pair of molecules, to find the smallest value of Δr_{ij}, that is $(\Delta r_{ij})_{\min}$. This postulate implies that the quantity $(\Delta r_{ij})_{\min}$ is never negative and is equal to zero for a certain number of molecule–molecule contacts, whose existence is sufficient to ensure a three-dimensional system of contacts (significant contacts) in the crystal.

In fact, the accuracy of this postulate is extremely low (the deviations exceed the uncertainty of the X-ray diffraction data by factors of 10–100). To make it more realistic, it is better to take for the significant contacts not the equality $\Delta r_{\min} = 0$ but the inequality $|\Delta r_{\min}| < \delta$, assuming that $\Delta r_{\min}$ may also be negative (that is that overlap of the van der Waals spheres is possible), but that the quantity δ is fairly small. Kitaigorodskii[8] assumed that the postulate applies if it is assumed that $\delta = 0.05 r_{ij}$. However, firstly some deviations are still observed even in this case, and, secondly, the objectively justified selection of a specific value of δ guaranteeing a correct description of a wide range of molecular packing is apparently in general impossible. A more fundamental analysis makes it necessary to adopt a statistical approach to VR with allowance for the dispersion of intermolecular contacts.

The dependence of the energy of interaction φ of two free atoms A and B on the distance r between them is given by a potential curve (Fig. 1*a*) with a minimum at the equilibrium distance r_0. If however the atoms A and B are in molecules, the 'contact' distance r_{AB} between them is less than r_0. This can be demonstrated by the hypothetical example shown in Fig. 1*b*. For simplicity, it is assumed that the atoms in the triatomic molecules being considered are identical; it will be assumed that the molecules can approach one another only by translation along a certain axis. If the energy of interaction of the molecules is regarded as the sum of the atom–atom potentials $\sum_{ij}\varphi_{ij}$, it follows that in the equilibrium position of the molecules, $r_{AB} < r_0$, since in the interaction of atoms which are not in direct contact, attraction predominates over repulsion, and with increase in the size of the molecules (Fig. 1*c*), the difference $r_0 - r_{AB}$ should increase. This difference naturally also depends on the orientation of the molecules.

Thus strictly speaking, the VR of an atom is in general not a physical constant. As a result of the rapid increase in the energy φ with decrease in r_{AB}, however, this distance rapidly reaches a quasi-limiting value. This in fact justifies the existence of tabulated values of R. It may be assumed, however, that shorter intermolecular contacts should be observed for large molecules.

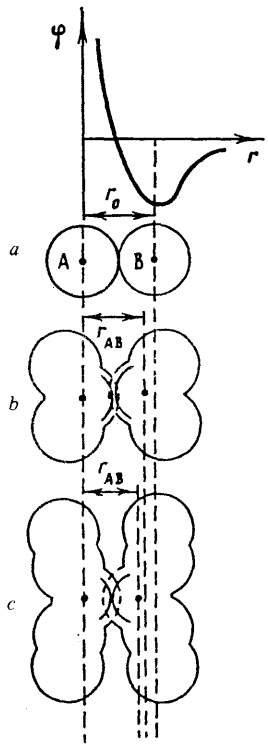


Figure 1. Dependence of the length of an atom–atom van der Waals contact on the composition and geometry of the molecule: *a*, interaction of free atoms A and B; *b*, interaction of atoms A and B in triatomic molecules; *c*, the same for penta-atomic molecules.

In fact, this tendency is masked by the individual characteristic features of the composition, shape, and packing of the molecules. The picture is much more complicated when the arrangement of not two but several molecules is considered. The tendency to adopt a packing ensuring the lowest energy of the crystal structure as a whole may lead to the appearance of local more closely packed and less closely packed regions, whose arrangement in space is specific for each specific crystal. The interatomic distances corresponding to the significant contacts of a given type A...B may differ considerably in different molecular crystals, but should be distributed within a certain range. For a specific structure, the VR give only the most probable (*a priori*) values of the intermolecular contacts.

Another important feature complicating the analysis of intermolecular contacts using VR is that the postulate formulated above assumes that the VR are additive, that is it is based on a combination rule according to which $\bar{r}_{AB} = (\bar{r}_{AB} + \bar{r}_{BB})/2 = R_A + R_B$, where $\bar{r}$ is the average length of the significant contact. Although at first sight this rule appears obvious, in fact it does not follow from any more general considerations. Moreover, the presence of effective charges on the atoms indicates that there will be deviations from additivity.

Good and Hope[10] examined possible combination rules for equilibrium distances, and gave preference to the equation $r_0(AB) = \sqrt{r_0(AA) \cdot r_0(BB)}$. When applied to intermolecular contacts, this corresponds to the expression $\bar{r}_{AB} = 2\sqrt{R_A R_B}$, which shows better agreement with experiment than the additivity usually assumed, but this is revealed only by a statistical analysis.[11]

Mean-statistical values of the VR of the elements of organic compounds were found[11] by treatment of X-ray diffraction data for 75 organic crystal structures without intermolecular hydrogen bonds. For each of these structures, significant contacts ensuring the existence of a three-dimensional framework of contacts were selected. The minimum number of such contacts is 4 when the molecules are in general positions, and 6 when they are at a centre of inversion. Even in the selection of the significant contacts it is necessary to specify some VR system. In a first approximation, the radii of Kitaigorodskii[8] were taken (except for the Cl atom, for which the value 1.86 Å [12] was used). Since the final (refined) VR values given in Table 1 were found to be fairly close to the original values, the significant contacts on the whole were apparently selected correctly.

Table 2, taken from the paper by Zefirov and Zorkii,[11] gives the values of $\bar{r}_{ij}$ for significant contacts of different types. The mean-statistical VR were selected to give best agreement between $\bar{r}_{ij}$ and $2\sqrt{R_i R_j}$; as already noted and as can be seen from Table 2, this is more effective than using the $R_i + R_j$ values. This last feature can apparently be interpreted as follows. If the atoms i and j are atoms of the same kind, then $R_i = R_j$ and $R_i + R_j = 2\sqrt{R_i R_j}$; if however they are atoms of different kinds, then $R_i + R_j > 2\sqrt{R_i R_j}$, that is according to statistical data when these atoms are in contact there is a tendency for the van der Waals spheres to overlap slightly. Since atoms of different kinds often have effective charges of opposite sign, their approach may be due to electrostatic attraction.

Table 2. Interatomic distances in the 'significant' intermolecular contacts, and comparison with the van der Waals radii.

Contact	$R_i + R_j$			$2\sqrt{R_i R_j}$	$\bar{r}_{ij}$	r_{ij} (min)	r_{ij} (max)	n *
	(Ref.8)	(Ref.9)	(Ref.11)	(Ref.11)				
C...C	3.44	3.60	3.42	3.42	3.41	3.32	3.53	31
H...H	2.34	2.34	2.31	2.31	2.31	2.04	2.58	58
C...H	2.89	2.97	2.87	2.81	2.81	2.57	3.12	160
O...C	3.08	3.32	3.00	2.97	2.97	2.85	3.11	12
O...H	2.53	2.61	2.45	2.44	2.44	2.25	2.59	44
N...C	3.29	3.38	3.21	3.20	3.17	3.03	3.27	24
N...H	2.74	2.75	2.66	2.63	2.64	2.53	2.84	51
Cl...H	2.95	—	3.06	2.96	2.96	2.88	3.03	26

* n is the number of contacts over which the averaging was carried out.

The similarity in the values of $\bar{r}_{ij}$ and $2\sqrt{R_i R_j}$ makes it possible to base the determination and application of VR on the condition $|(r_{ij} - 2\sqrt{R_i R_j})_{min}| \leqslant \delta$, where δ is sufficiently small. Bound by tradition, however, research workers more frequently use the classical and more obvious relationship $|r_{ij} - (R_i + R_j)| \leqslant \delta$, even when the radii proposed by Zefirov and Zorkii[11] are used. Strictly speaking, this is incorrect, but since the difference between $2\sqrt{R_i R_j}$ and $R_i + R_j$ is usually small, its does not lead to significant errors, and in the present review, in some cases, the authors of the works cited will be followed, and the intermolecular (or non-valence intramolecular) contacts will be compared with the sum of the VR, without this being specially pointed out.

For a correct understanding of the physical significance of the comparison of r_{ij} with $2\sqrt{R_i R_j}$ or with $R_i + R_j$, it is important to characterise the distribution of the values of r_{ij} corresponding to significant contacts of a definite type (that is to contacts between atoms of a definite type). For this purpose it is convenient to use the observed limiting values of r_{ij}(min) and r_{ij}(max), given in Table 2, and also the values of $\Delta_1 = \bar{r}_{ij} - r_{ij}$(min) and $\Delta_2 = r_{ij}$(max) $- \bar{r}_{ij}$. The values of Δ usually do not exceed 0.3 Å, or 0.15 Å for contacts not including H atoms. The values of $2\sqrt{R_i R_j}$ 'centre' fairly satisfactorily the range between r_{ij}(min) and r_{ij}(max), that is the distribution is close to normal. The values of $R_i + R_j$ for atoms of different kinds, however, are usually displaced considerably towards the upper limit.

The most familiar and most frequently used systems of VR are compared in Table 1.† As noted above, the most important VR obtained by Zefirov and Zorkii[11] are extremely close to those given by Kitaigorodskii,[8] except for the VR of the S and Cl atoms (in the last case the discrepancy is due to the fact that Kitaigorodskii[8] did not take account of the specific nature of the Cl...Cl contacts; see section III below). Subsequently, however, a much larger value was adopted[9] for the O atom, coinciding with that recommended by Bondi.[16] Bondi[16] used a statistical approach, but with extremely few data, and the final results were distorted by a number of significant errors.

Thus according to the original postulate of the theory of close-packing, significant contacts should be used to determine VR. This obvious feature was overlooked by Kitaigorodskii[9] and Bondi,[16] so that the VR of the O atom was too high. Thus when using Bolton's data[17] to examine the shortest interatomic distances between two neighbouring molecules of chloranil $C_6O_2Cl_4$, Bondi[16] used the 'contacts' O...O 3.26 Å and O...C 3.06 Å, without noticing that there is also an O...C distance of 2.85 Å (corresponding to a significant contact), which cannot be reconciled with the adopted value $R_0 = 1.52$ Å. A similar error was made by Kitaigorodskii[9] in the examination of the structure of alloxan $C_6H_2O_4$: he took as 'contacts' the O...O distances 2.94, 3.05, and 3.07 Å, which gave the average value $R_0 = 1.51$ Å, but the diagram given shows that this structure contains the significant contacts O...C 2.79 Å and O...H 2.38 Å and 2.47 Å, indicating that this VR value leads to unacceptable overlap of the van der Waals spheres.

A completely unreasonable statistical procedure, called 'revision of van der Waals atomic radii', was recently used by Nyburg and Faerman,[18] who determined VR using the Cambridge Structural Data Bank and determined all the shortest distances between atoms of the same kind in neighbouring molecules. The fact that many of them did not correspond to atom 'contacts' was completely ignored. A rational approach to the problem being discussed requires a correct analysis of the packing of the molecules in each of the structures being considered.

It is also important to emphasise the following significant feature. Contacts between atoms of the same kind are most convenient for determining VR. It is these contacts, however, which often show specific properties, making it impossible to obtain at this level a system of universal VR showing additivity (or satisfying the rule

† The mean-statistical VR of the F, Br, and I atoms[13,14] can be added to the data in Table 1.

$\bar{r}_{ij}$ (significant) $\simeq 2\sqrt{R_iR_j}$). Thus oxygen atoms, which (together with fluorine) have the highest electronegativity, usually carry an appreciable effective negative charge. It is for this reason, and also because of their relatively small size, that O atoms rarely form significant contacts with one another. An exception is provided by compounds rich in oxygen (for example containing a large number of nitro-groups). Even if a significant contact O...O is formed, however, it will generally be longer than twice the universal VR, because of the strong electrostatic repulsion. Special account can and must be taken of features of this kind (in particular, a special oxygen VR can be introduced just for O...O contacts), but the tabulated value of R_0, suitable for analysing ordinary contacts such as O...C, O...N, etc., obviously should not be derived from O...O distances.

For F...F contacts, in certain cases, another situation arises. Zefirov and Porai-Koshits[13] obtained the VR of fluorine by examining the significant contacts F...F in the crystals of compounds with the general formulae $(MF_5)_4$ and EF_6. This was possible, because in the molecules of these compounds the high negative charge on the F atoms is compensated by the 5 or 6 times larger positive charge on the M or E atoms, but in organofluorine compounds, the average F...F distances should be longer (greater than $2R_F$).

The contacts between other halogen atoms of the same kind (Γ...Γ) show another characteristic feature: here, a stronger exchange interaction is often superimposed on the purely van der Waals interaction. Contacts involving these interactions, described as specific interactions (see section III), are naturally unsuitable for determining VR. If this feature is not taken into account the VR obtained for the halogens are too low (as for example in data given by Kiraigorodskii[8] and Bondi[16]). Γ...Γ contacts can still be used to find the VR of halogens, however, if contacts with specific interactions are excluded. Zefirov and Porai-Koshits[14] determined the angular geometric characteristics corresponding to these contacts. This made it possible to exclude them from the set of distances examined and to obtain for the VR of the Cl, Br, and I atoms the values 1.90, 1.97, and 2.14 Å respectively. The value of R_{Cl} obtained by Zefirov and Porai-Koshits[14] coincided with that previously obtained by Zefirov and Zorkii[11] from an examination of the significant contacts between chlorine and other atoms.

III. The application of van der Waals radii in crystal chemistry, stereochemistry, and X-ray diffraction

Since they are based on X-ray diffraction data on the structure of crystals, VR are naturally used primarily to describe and interpret crystal structures, and also to determine new structures. When intermolecular interactions are considered, contacts of two types are examined: normal contacts corresponding to ordinary van der Waals interactions, and shortened contacts, where specific intermolecular interactions are revealed. A remarkable feature is that although they represent a geometric approach to the structure of a substance, VR can also be used to examine its energy, since they are used to obtain atom–atom potential functions, which now represent the most universal and effective means of calculating the energy of interaction of comparatively complex molecules. Although intermolecular contacts represent the source of data for compiling tables of van der Waals radii, one of their most important uses is in the analysis of the non-valence interactions within molecules and in the related discussion and prediction of molecular conformations.

1. Normal intermolecular contacts

Since a system of VR together with data on the dispersion of the lengths of the significant contacts reflects the usual picture of the packing of molecules in crystals, in the study of each new substance a comparison of the shortest intermolecular (atom–atom) distances with the sums of the VR or the quantities $2\sqrt{R_iR_j}$ usually makes it possible to establish the 'normal' character of the intermolecular interactions and confirms that the crystal does in fact consist of discrete molecules. Data on the shortest intermolecular distances (selected using VR) are often given as standard tables (see for example Ryabova and co-workers[19] and Romanenko and co-workers[20]).‡

For coordination compounds, the determination of the molecular character of a crystalline substance is often difficult, and the result is difficult to predict. An example is provided by the study[21] of a structure which was found to contain dimeric anions $[Cu_2(OCH_3)_2.\{2,6\text{-}(NO_2)_2C_6H_3O\}_4]^{2-}$, each joined by hydrogen bonds to two piperidinium cations $C_5H_{12}N^+$ forming the second coordination sphere of the complex. There are no contracted intermolecular contacts between these associates, so that the structure could be described as molecular.

The use of VR makes it possible to introduce the concept of molecular coordination number (MCN), which provides an extremely useful means of describing the structure of molecular crystals.[8,22] The distribution of the values of Δr_{min} (see section II) on a numerical axis usually appears approximately as shown in Fig. 2*a*, which gives the distribution of the Δr_{min} values for 3,3,'-bithienyl. Figures indicating the multiplicity of the given molecule–molecule contact are given above the vertical lines corresponding to the Δr_{min} values. A characteristic feature is the gap between the two values of Δr_{min} denoted μ and ν, where μ corresponds to the molecule with the largest Δr_{min} still in the coordination sphere, and ν corresponds to the molecule with the smallest Δr_{min} not included in the coordination sphere. The larger the gap between μ and ν, the more clearly defined the coordination sphere.§ Later,[23] this qualitative approach to the determination of the MCN was supplemented by the quantitative conditions: 1) $\nu - \mu \geqslant 0.6$ Å, and 2) -0.3 Å (or -0.15 Å) $\leqslant \mu \leqslant 1.0$ Å; this value in brackets corresponds to contacts not involving hydrogen atoms. In all 155 examples of the coordination environment of molecules examined,[23] it was possible, in the distribution of the Δr_{min} values, to select values of μ and ν satisfying the above conditions. At the same time, in 25% of cases, a picture similar to that shown in Fig. 2*b* was observed. Here, two appreciable gaps are observed in the sequence of Δr_{min} values, making it possible to distinguish a coordination sphere between the first and second spheres (a 'sesqui-sphere'). The MCN in these cases is written as a sum (for example 12 + 2). The quantitative criteria for the coordination 'sesqui-sphere' are: 1) $\nu_1 - \mu_1 \geqslant 0.3$ Å; 2) $\nu_2 - \mu_2 \geqslant 0.6$ Å; 3) $\mu_1 \geqslant -0.3$ (-0.15) Å; and 4) $\mu_2 \leqslant 1.0$ Å. Here it is assumed that $\nu_2 > \mu_2 \geqslant \nu_1 > \mu_1$.

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‡ The advantages of a table of this kind over a table of distances shorter than some single value for contacts of all types are obvious; intermolecular distances selected without comparison with VR usually by themselves do not carry any valuable information.

§ The definition of MCN, previously introduced by Kitaigorodskii,[8] as the number of molecules having at least one contact with the molecule being considered does not make it possible to determine this quantity objectively.[22]

In homomolecular crystals, a continuous series of MCN from 9 to 18 has been observed. The most common values are 14 (about half of the structures) and 12 (about one third of the structures). An expanded form of notation for the MCN (in layers and in chains) has been proposed and analysed[24,25] for a more detailed characterisation of the coordination environment of molecules.

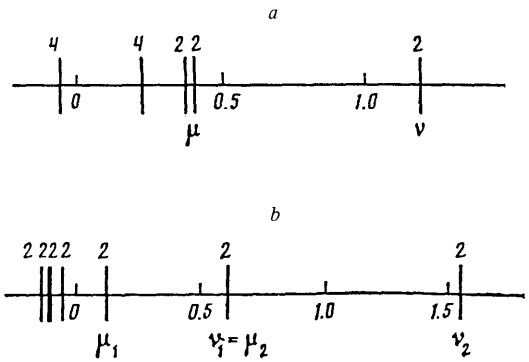


Figure 2. Diagrams illustrating the determination of the molecular coordination number (the values of Δr_{min} are shown on the numerical axis): *a*, structure of 3,3′-bithienyl; *b*, hypothetical structure with a coordination 'sesqui-sphere'.

In X-ray diffraction studies it is often pointed out that the intermolecular distances are greater than the ordinary values, and that this might indicate loosening of the packing. These conclusions are not sufficiently reliable, however, and are usually reached without taking account of the natural dispersion of the significant contacts.¶

On the other hand, the existence of anomalously short contacts indicates either that the X-ray diffraction data are unreliable or (when there is crystal-chemical justification) the existence of specific intermolecular interactions (see next section).

In some X-ray diffraction studies, VR are used to identify atoms. For example, in the determination of the structure of methylammonium hexachloroferrate(II) hydrate,[26] difficulties were encountered in identifying the nitrogen and carbon atoms, which give electron density maxima of similar height. The formation of a short intermolecular contact (2.76 Å) between an oxygen atom and one of the atoms difficult to identify indicated that this was a nitrogen atom, since this distance for the nitrogen and oxygen atoms, with allowance for their van der Waals radii, is normal, whereas it is too short for carbon and oxygen atoms.

The detection of unrealistic intermolecular contacts using VR plays an important part in the analysis of crystal structures with incomplete ordering. These structures are often described as a statistical sequence of molecules in which one of a number of possible positions of some atomic group is realised. For example, in an X-ray diffraction study[27] of the selenium derivative of biepoxycyclopentyl $C_{16}H_{16}O_4Se$ it was suggested that randomly distributed molecules with different angles of rotation of the phenyl groups coexist in the structure (the angle between two positions of the ring is close to 90°). It was shown,[28] however, that this model unavoidably leads to extremely short intermolecular contacts. A detailed analysis made it possible to construct a model of the structure consisting of enantiomorphic domains in which the molecules are packed in accordance with the usual VR values (the ways in which these domains are connected were also studied).

A domain structure was also proposed[29] for the crystals of 3-bromobicyclo[3.3.1]non-2-en-4-one, where random arrangement of the oxygen atoms leads to shortened O...O contacts with a length of 2.31 Å. Unrealistically short intermolecular Cl...Cl contacts (2.33 Å) were also noted[30] in the random structure of $Ni(p\text{-}H_2NC_6H_4OCH_3)_4(Cl_3CCOO)_2$. In the last two studies, however, the problem was not fully analysed, and a model which does not contradict the observed diffraction pattern and at the same time is consistent with crystal-chemical considerations has not yet been constructed.

The modelling of non-valence interactions by means of VR was an essential part of such outstanding and familiar studies as the determination of the structure of the α-helix of polypeptides[31] and the double helix of DNA.[32] At the present time also, the initial models of proteins and other biological materials are constructed using VR (these models are subsequently verified and refined by X-ray diffraction and NMR spectroscopy).

VR have recently been used[33] to solve structural-biological problems associated with the formation of 'incorrect' pairs of bases in DNA. In the transfer of inherited information, an exceptionally important role is played by the so-called 'Watson–Crick pairs' adenine–thymine (uracil) or guanine–cytosine. The use of mean-statistical VR values and allowance for the dispersion of van der Waals contacts showed that the nucleic acids of the incorrect pairs of bases in the usual tautomeric forms can be arranged in a double helix without producing shortened interatomic contacts or significant distortion of the sugar–phosphate core. It was found that the sugar–phosphate core is sufficiently flexible to allow the arrangement in a double helix of nucleotide pairs having dimensions approximately 2 Å larger (the inosine–adenine pair) and 2 Å smaller (the uracil–cytosine pair) than the canonical Watson–Crick pairs, and also pairs in which one base is displaced relative to the other by ~2 Å along a two-fold axis (the guanine–uracil pair).

The systems examined above contain only normal intermolecular contacts. This last feature is an experimental fact or is postulated on the basis of empirical generalisations, so that the requirement that the contacts be normal can be used to construct or correct structural models. At the same time, as already noted, shortened intermolecular contacts also arise regularly in certain systems; these systems are examined in the next section.

2. Shortened intermolecular contacts (SInterC)

The detection of anomalously short (shortened) contacts in crystal structures is of particular importance, since these contacts usually indicate the existence of specific intermolecular interactions which are appreciably stronger than ordinary van der Waals interactions and which have a significant influence on the structure and properties of molecular crystals. The most common example of specific interactions (SI) is the hydrogen bond. Metal–metal, halogen–halogen, sulphur–sulphur, and various other intermolecular SI are less well known. The detailed study of SInterC will undoubtedly lead to the detection of new types of SI which have not yet been studied.

¶ An exception is provided by crystals made up of very small molecules (containing a small number of atoms), studied at relatively high temperatures.

The term shortened intermolecular contacts is used to describe the distances r_{ij} between the atoms of different molecules if $r_{ij} < R_i + R_j - \delta$ or $r_{ij} < 2\sqrt{R_iR_j} - \delta$,[34] where δ is the overlap of the van der Waals spheres acceptable for a normal contact. Many workers discussing SInterC assume that $\delta \simeq 0$, which has no physical significance. As noted above, statistical analysis shows that it is appropriate to take $\delta = 0.15$ Å for contacts not involving hydrogen atoms, and $\delta = 0.30$ Å for contacts involving hydrogen atoms.

Contacts for which $2\sqrt{R_iR_j} - \delta < r_{ij} < 2\sqrt{R_iR_j}$ can be described as contacted. More or less contracted contacts are sometimes regarded as indicating van der Waals interactions of increased strength.[35] It should be borne in mind, however, that there is no direct relationship between the length of the shortest intermolecular contact in van der Waals interaction and the energy of interaction of the corresponding molecules. Thus contracted contacts cannot be regarded as a sign of specific intermolecular interactions.

The study of hydrogen bonds occupies a unique place in the investigation of SInterC. As data on hydrogen bonds have accumulated and become more detailed, a number of geometric criteria for the existence of an H-bond have been proposed.[36–39] All these criteria are based on an examination of the distances $r(X \ldots Y)$ or $d(H \ldots Y)$ in a system XH ... Y, although in fact the strength of a bond is also determined to a large extent by its linearity, that is by the angle X–H–Y.† The general idea is that the length of the contact between atoms involved in an H-bond is shorter than the distance between the same atoms joined by only van der Waals interaction. These criteria differ, however, in the use of different VR systems and different values of δ. The general trend has been that the criteria have been made more rigid as it has been found that in some cases they 'do not work'.

The criterion of Pimentel and McClellan,[36] the first to be proposed, is based on a comparison of the length of the contact X...Y with sum of the van der Waals radii of X and Y; δ is taken as zero. When it became possible to locate H atoms in X-ray diffraction studies, criteria based on the comparison of the lengths of the contacts H...Y with the sum of the VR of the H and Y atoms began to be used. These are the criteria of Hamilton and Ibers[37] ($d < R_H + R_Y$ or $d < R_H + R_Y - 0.2$ Å), Zefirov[38] ($d < 2\sqrt{R_HR_Y} - 0.35$ Å), and Rahim and Barman[39] ($d < r_{XH} + R_H + R_Y$).

The use of various criteria of this kind without introducing additional information, however, may lead to erroneous conclusions, particularly when the hydrogen atoms have not been located. It has been shown[40] by infrared spectroscopy that OH...O contacts are not H-bonds in the following crystals: citric acid[41] (O...O 2.84 Å), methyl-α-*D*-glucopyranose[42] (O...O 2.93 Å and H...O 2.19 Å), *L*-ascorbic acid[43] (O...O 2.93 Å and H...O 2.23 Å), and tartronic acid[44] (O...O 3.02 Å and H...O 2.23 Å). In all these cases, the use of the criteria of Pimentel and McClellan with the VR of Bondi,[16] $d(O \ldots O) < 3.04$ Å, Rahim and Barman, $d(O \ldots O) < 3.68$ Å, Hamilton and Ibers, $d(O \ldots H) < 2.6$ Å, and a modification of the latter, $d(O \ldots H) < 2.4$ Å would have led to errors, since according to these criteria, all the above contacts should correspond to an H-bond.

† For very large deviations from linearity, for example if $\angle XHY \leqslant 90°$, the concept of H-bond apparently loses significance.

Strictly speaking, the existence and strength of an H-bond should be judged by energy calculations, for example by Poltev's method,[45,46] where account is taken of the angular dependence of the energy of the H-bond. The energy of approach (particularly when the value of the angle XHY is taken into account) unavoidably leads to the conclusion that there is no rigid boundary between the 'bond' and 'no bond' situations. This makes it obvious that any geometric criteria are arbitrary, although they may be useful for practical purposes. Moreover, the correct use of geometric parameters combined with VR is a most important (if not the principal) source of information on H-bonds. An important auxiliary role may be played by crystal-chemical (crystal-structural) considerations: the assumption that an H-bond is formed is often essential to establish the factors leading to a given mode of packing of the molecules.

The magnitude of the decrease in the length of a contact compared with the normal value, defined as $2\sqrt{R_iR_j}$ (or $R_i + R_j$) often makes it possible not only to detect an H-bond but also to deduce its strength. Thus a comparison of H-bonds of different types (NH...Cl and OH...O) from the differences $\Delta r_{HY} = r_{HY} - 2\sqrt{R_HR_Y}$, where the VR were taken from Zefirov and Zorkii,[11] showed that the structure of *trans*-chloro(*L*-prolinato-N,O)[(+)-α-methylbenzylamine-N]platinum(II) [47] contains pseudo-dimers of complexes formed by the stronger H-bonds NH...Cl; the pseudo-dimers are connected in layers by the weaker bonds OH...H.

Among the large number of H-bonds detected using VR, various types of bond which have been little studied are of particular interest. Thus an X-ray diffraction study[48] with location of the H atom has proved objectively that the crystal of (benzoylmethyl)-triphenylphosphonium bromide ($PhCOCH_2P^+Ph_3)Br^-$ contains H-bonds of the type CH...Br^-. The geometric parameters of this bond are: C...Br^- 3.457 Å, H...Br^- 2.26 Å, C–H 1.20 Å, angle $CHBr^-$ 172°. The distance H...Br is 0.41 Å shorter than the value of $2\sqrt{R_HR_{Br}} - 0.35$ Å, equal to 2.67 Å. In the crystal of (p-$CH_3OC_6H_4)_2Te(NSO_2C_6H_4CH_3$-$p$), one of the aromatic rings at the Te atom forms a short contact with the N atom (C_{16}...N 2.96 Å, H_{16}...N 2.25 Å, CHN 124°).[49] This contact is very short, so that it was assumed that the crystal contains a CH...N H-bond, analogous to the familiar CH... O bonds.

SInterC of the type Γ...Γ, where Γ = Cl, Br, I, are fairly frequently observed in crystal structures (fluorine does not form shortened contacts[13]). The greatest of the shortened contacts increases from chlorine to iodine. The significant contacts I...I show a practically continuous series of distances from twice the van der Waals radius to twice the covalent radius of iodine.[50] The production of Γ...Γ SInterC is attributed to the specific interactions between the halogen atoms, that is to the greater or lesser contribution of exchange forces.

The lower limits of the distances for the contacts C–Γ...Γ–C have been determined;[51] they are given effectively by the equation $r_{ij} = d - 0.15$ Å, where d is the length of the shortest contact in the structure of the corresponding halogen ($d = 3.28$ Å for Cl_2,[52] 3.32 Å for Br_2,[53] and 3.50 Å for I_2 [54]). Later, the 'upper limits' (r_{max}) of the distances r_{ij} for the specific interactions Γ...Γ in organic crystals were established.[14] The angular characteristic φ—the greater of the two angles C–Γ...Γ for each contact—was used. The data for 123 structures established that for $r_{ij} < r_{max}$, the angle $\varphi \geqslant 130°$, and that for $r_{ij} > r_{max}$, much smaller values of φ are also observed. On this basis, the value of r_{max} (3.65 Å for Cl, 3.79 Å for Br, and 4.14 Å for I) was taken as the 'upper limit' of the SI. A remarkable feature is that the relationship $r_{max} + 0.15$ Å $\simeq 2R_Γ$ is satisfied with a fairly high accuracy.

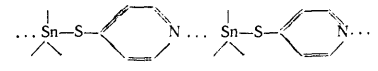
It is important to emphasise, however, that the concept of the 'upper limit' of specific interactions Γ...Γ is conditional. If $r_{ij} < r_{max}$, the interaction can be regarded as specific; if however $r_{ij} > r_{max}$, additional information is required to determine the nature of the interaction. The Γ...Γ atom–atom potentials taking account of the possible production of SI are unknown, but it is clear that with increase in the distance, the modulus of the energy of this bond decreases more smoothly than that of the covalent bond. In various crystals of organic halogen derivatives, the packing of the molecules is clearly determined by the tendency towards maximum approach of the Γ atoms. Thus the specific character of an interaction may be indicated (but not necessarily) by the characteristics of the arrangement of the molecules in the crystalline substance.

The use of VR combined with an energy calculation has shown how the successive introduction of F, Cl, Br, or I atoms into the molecule influences the packing of the molecules in the crystals of 1,5-dihalogenoanthraquinones $C_{14}H_6O_2\Gamma_2$.[55] All these crystals contain clearly defined molecular chains with similar structures. These chains resemble one another particularly closely in $C_{14}H_6O_2F_2$, $C_{14}H_6O_2Cl_2$, and $C_{14}H_6O_2Br_2$, but the ways in which they are superimposed in these structures differ considerably. When the structure is modified by the successive replacement of the H atoms in positions 1 and 5 of anthraquinone by halogen atoms, three factors are important: 1) the increase in the size of the atoms (the increase in their covalent and van der Waals radii), 2) the appearance (beginning at Cl) of SI, which to some extent may compensate the increase in the size of the atoms, and 3) the magnitude of the gap (or overlap) between the van der Waals spheres of the atoms belonging to neighbouring molecules. In particular, in anthraquinone the H atoms in positions 1 and 5 (or 4 and 8) in the chain do not give contacts close to the sum of the VR,‡ but the hydrogen atoms of neighbouring chains are in direct contact with them. The difference in the VR (ΔVR) of the F and H atoms is 0.24 Å; the difference in their covalent radii is ΔCR = 0.34 Å. Since SI are not characteristic of F atoms, their introduction into the anthraquinone molecule produces little change in the structure of the chains, but alters the way in which they are packed. The structure of $C_{14}H_6O_2F_2$ contains short contacts involving F atoms ($\Delta r_{ij} = r_{ij} - \Sigma VR = -0.12$ Å for F...H and 0.00 for F...C). Since ΔVR(Cl and F) = 0.50 Å and ΔCR(Cl and F) = 0.35 Å, the replacement of F atoms by Cl leads to a change in the packing.

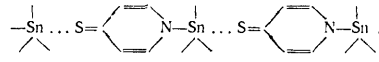
In addition to Γ...Γ SInterC, S...S InterC are fairly frequently encountered in organic crystals. Thus Zefirov and Zorkii,[34] using published data,[56] reported 14 short S...S distances, seven of which were much shorter than twice the VR of the S atom, and apparently appeared as a result of SI between the sulphur atoms.

In crystals formed by molecules or ions containing metal atoms, SI and hence SInterC involving these atoms may be produced (for example metal...metal, metal...oxygen, etc. SI). Thus the packing of the molecules in the crystals indicates the existence of the specific interactions Cu...O in copper salicylideneiminate, and Cu...Cu in copper salicylidenemethyliminate.[57] It is difficult to discuss this question, however, since there are no reliable VR values for metal atoms. For example, the published VR of the mercury atom vary from 1.5 Å [8,58] to 1.9 Å or more,[59,60] although the VR of this atom have apparently been more extensively discussed than those of any other metal.

The question of the production of SI in a structure is sometimes important for establishing the formula of a substance. For example, the use of VR detected an Sn...N specific interaction in the structure of the triphenyltin derivative of 4-thiopyridine,[61] and from this it was concluded that in the crystal the compound is an organotin derivative of pyridinethiol, and not thiopyridine, and that its structure is described by the formula



and not



If only normal intermolecular contacts are observed in a molecular crystal, the recognition of molecular agglomerates (dimers, chains, layers) of physical significance using only VR usually cannot be carried out completely correctly; in this case an energy calculation is required.[62] When SI with energies much greater than the energy of ordinary van der Waals atom–atom interactions are present, however, the agglomerates are usually distinguished quite clearly, giving a physically justified description of the structure. Thus the structure of triphenylmethyl bromide[63] consists of dimers formed by Br...Br specific interactions; the crystals contain two types of dimer, with Br...Br distances of 3.181 Å§ ($\Delta r = -0.76$ Å) and 3.466 Å ($\Delta r = -0.47$ Å). The structure of zinc 7-methylthio-8-mercaptoquinolinate[64] contains a short contact S...S 3.29 Å ($\Delta r = -0.39$ Å); these contacts join the molecules in centrosymmetric dimers.

Infinite chains −O...Sn−N−C−O...Sn−N−C−O... parallel to the long axis of the acicular crystal were detected in the structure of triphenyltin isocyanate;[65] here, the Sn...O distance is 2.81 Å ($\Delta r \lesssim -0.5$ Å). The chains can be distinguished even more clearly in the above-mentioned structure of the triphenyltin derivative of 4-thiopyridine with Sn...N 2.62 Å [61] ($\Delta r \lesssim 0.9$ Å).

The packing of the BF_3 molecules in the crystal structure of boron trifluoride at −145 °C is extremely interesting.[66] As a result of the coordinative unsaturation of the boron atom, the planar-trigonal coordination is brought up to trigonal bipyramidal by the fluorine atoms of neighbouring molecules. The BF_5 trigonal bipyramids share vertices to form infinite layers in the crystal. The intermolecular B...F distances are 2.663–2.704 Å, which is appreciably smaller than the sum of the VR of the atoms F (1.40 Å)[13] and B (2.13 Å).[16]

3. *A priori* calculation of close packing

The determination of an optimum structure by theoretical calculation generally involves the search for arrangements of the molecules with minimum energy. In the absence of specific interactions, the tendency towards close packing models with a certain accuracy the tendency towards an energy minimum, so that the minimisation of the energy can be replaced by the search for close-packed arrangements.

‡ In the work cited,[55] the numerical data were replaced by analogous quantities calculated from refined[11,13,14] VR values.

§ This SInterC is the shortest known C−Br...Br−C contact, and almost reaches the lower limit of 3.17 Å found by Zefirov.[51]

Using VR, molecules can be represented as three-dimensional bodies, and crystal structures as the packing of these bodies. As noted above, representations of this kind first appeared in works by Sidgwick,[5] Albrecht and Corey,[6] and Pauling;[7] for Kitaigorodskii[8] they provided the starting point for the development of the theory of the close packing of molecules in crystals. This theory established not only the existence of a three-dimensional system of molecules 'in contact' but also the production of intermolecular contacts according to the 'projection into cavity' principle. Zorkii,[67] who refined the formulation of the basic postulates of the theory of the close packing of molecules, pointed out that not all molecule–molecule contacts are made according to this principle, but that each structure necessarily contains 'projection into cavity' combinations which act as 'catches' fixing the structure. The existence of 'projection into cavity' contacts by itself, however, does not ensure a high packing density.

When molecules are represented as three-dimensional bodies, the question of the possibility of predicting crystal structures as close-packed arrangements of these bodies arises. In general, for three-dimensional packing, this problem is extremely complex. For the two-dimensional packing of planar molecules, it has been solved by the method of flow trajectories,[62,68,69] which makes it possible to find graphically the close-packed arrangement of figures whose outer contour is formed by intersecting circles.

Specific calculations have been carried out[62] for Ni dimethylglyoximate (Ni-DMG) and Cu salicylidenemethyliminate (Cu-SMI), in whose crystals a unique situation is produced: the planes of the molecules coincide exactly with the planes of the 'layers',¶ so that even a two-dimensional analysis can be used to discuss the possibility of an *a priori* prediction of the structure.

For both substances, a series of minima was obtained on the curves giving the dependence of the quantity $1/k$, where k is the packing density coefficient, on the parameters of the structure. In both cases the actual packing of the molecules was found to be very close to 'incompressible', that is it corresponds approximately to certain minima on the $1/k$ curves, and the packing density coefficient cannot be increased by small translations and rotations. At the same time, these structures were not the most compact; they did not correspond to the deepest minima on the $1/k$ curves. This result can be seen particularly clearly for Cu-SMI, for which it was possible to construct a packing with $k = 0.91$, which is appreciably more compact than the packing with $k = 0.87$, close to the actual packing. Thus when discussing compact molecular packing, it is necessary to be careful when using terms such as 'close-packed' and 'closest-packed'.[8,9]

If the packing of molecules in the crystals were not only incompressible but also close-packed, this would mean that the values of $1/k$ and the energy of the structure not only changed in the same sense but also were proportional to one another. Such complete mutual correspondence between a formal geometric characteristic and a thermodynamic function can hardly be expected. The arrangement of molecules in a crystal is certainly determined not only by the compactness of the packing but also by the relative orientation of the multiple moments.

At the same time, calculations have shown that there are not many examples (15–20) of closest packing corresponding to structures close to the real structures of Ni-DMG and Cu-SMI. This means that it is possible to construct a comparatively small number of hypothetical structures and to select from them the most probable structure by making use of additional methods, for example by examining the optimum arrangement of the multipoles or by using experimental data on the lattice parameters.† For structures in which the analysis of the packing cannot be reduced to a two-dimensional calculation, however, this method is naturally unrealistic.

Considerable progess in the *a priori* prediction of molecular (mainly organic) crystal structures has been achieved by using atom–atom potential functions (AAPF).[2,3,71] A remarkable feature is that VR have also played an important role in the development of organic crystal chemistry (after the theory of close packing). The VR are used to specify the equilibrium distances r_0, which appear in the parameters of the AAPF (see Fig. 1). Here, a common error is made: the sum of the VR found from the crystal structures is taken as the equilibrium distance, without taking account of the 'compression' of the molecules in the crystal. An empirical relationship between these quantities, $r_0/\Sigma VR \simeq 1.16$, has been pointed out.[72]

4. The conformations of molecules

In the mechanical model of a molecule, its conformation is regarded as resulting from the valence and non-valence interactions of the atoms.[73] The lengths of the covalent bonds, fixed in a fairly narrow range, and their directed character are the universal stereochemical factors which practically always are of decisive importance. The part played by non-valence interactions is particularly clearly revealed in three cases: 1) for non-rigid molecules, for example molecules in which rotation about single bonds is possible; 2) when there is steric hindrance; and 3) when there are intramolecular SI (they are often called attractive interactions, in contrast to steric hindrance, where forces of repulsion are most important).

In the last two cases, shortened intramolecular contacts (SIntraC) arise, and although the nature of the shortening is completely different in this case, its geometric consequences are analogous, and are revealed in the deviation of the bond lengths and more particularly the valence angles from the ideal values (the deformation of valence angles involves a much smaller expenditure of energy than the compression or elongation of covalent bonds). The use of VR makes it possible to detect SIntraC, and to follow their influence on the conformation of molecules or to conclude that effects of this kind are not observed.

¶ The characteristic features of the crystal structures of Ni-DMG and CU-SMI are due to the specific intermolecular metal–metal bonds perpendicular to the 'layer'. The word 'layer' is here put in inverted commas, since in contrast to the usual practice the word is used in the purely geometric sense. The strongest intermolecular interactions in these crystals lead to the formation of chains (perpendicular to the 'layers'), but it is in the 'layers' being considered that the tendency towards close packing should be detected.

† The two-dimensional approach (the method of flow trajectories) has also proved extremely effective for the *a priori* prediction of the packing of the chains of $PdCl_2$ and $BeCl_2$ [12,70] (in the crystal, these chains are joined to one another only by van der Waals interaction). The high symmetry and the relatively simple form of the chains obtained by modelling using VR made it possible to calculate successfully the most compact incompressible packing; the actual structure of $PdCl_2$ was found to be the third most compact, and the actual structure of $BeCl_2$ to be the most compact.

If relatively mobile fragments of a molecule are not joined by SI and there is no steric hindrance between them, free internal rotation often arises.[74] This has a significant influence on the physicochemical properties of substances, as discussed below (see section IV).

A number of examples of the distortion of valence angles as a result of the overlap of the van der Waals spheres of valence-non-bonded atoms can be considered. In the radical-ion salt $[C_{14}H_8S_4]^+ \cdot [PtBr_5S(CH_3)_2]^-$,[75] the octahedral configuration of the Pt atom is distorted by the mutual repulsion of the atoms of the methyl groups and Br. In the cobalt complex of Vitamin PP, that is nicotinamide (NA), with the composition $[Co(NA)_2(H_2O)_4](CH_3COO)_2.2H_2O$,[76] the inequality of the exocyclic angles at the C atom of the heterocyclic ring joined to the C atom of the amide group (119.5° and 122.0°) is due to the difference in the VR of the N and O atoms of the amide group, and also to the repulsion between an H atom of the heterocyclic ring on the one hand and an H atom of the amide group on the other ($\Delta r = -0.36$ Å).

The VR values have a characteristic influence on the conformations of polyethylene and substituted polyethylene polymers. The van der Waals diameter of the H atom is 2.31 Å, and the identity period along a completely *trans*-carbon chain is 2.54 Å, so that the polyethylene molecules can (and do) have a planar zigzag conformation. This period of the *trans*-carbon chain, however, does not ensure sufficient space for other atoms replacing H atoms, and more particularly for groups of atoms. For example, the van der Waals diameter of the F atom is 0.26 Å larger than the identity period, so that in polytetrafluoroethylene, a planar zigzag conformation cannot be produced. In this case the crowding is reduced by slight bending of the chain to give a slightly twisted spiral.[77] Isotactic stereoregular hydrocarbon polymers with the general formula $-(CH_2-CHR)_n-$ have similar spiral conformations,[78] since even for R = CH_3 (VR $\simeq$ 2.0 Å), crowding of the chain does not allow the production of a planar conformation.

In a number of cases, VR can be used to explain the difference in the values of the dihedral angles in related compounds. Thus the decrease by 21.4° in the dihedral angle between the planes of the benzene rings of the phenothiazine unit in the molecule of 1,3-dinitro-10-phenylphenothiazine[79] compared with the corresponding angle in non-substituted phenothiazine, equal to 153.3°, makes it possible to avoid steric hindrance in the molecule of the derivative, since the hydrogen atoms of the N-phenyl substitute 'touch' the atoms of the lateral rings of the phenothiazine unit in the *peri*-positions. The distances are H...H 2.33 Å and H...N 2.61 Å, which are very close to the values $2R_H$ = 2.31 Å and $2\sqrt{R_H R_N}$ = 2.64 Å.[11] With increase in the dihedral angle, these contacts would be shortened. The presence of a shortened N...O contact (2.719 Å) explains the folded conformation of the arabinofuranose molecule.[80]

The use of VR makes it possible not only to explain various details of the conformations of molecules but also in many cases to reach other conclusions about their structure, primarily the possibility or impossibility of conjugation, the reasons for breakdown of planarity, etc. Measurements of the dipole moments and the molecular Kerr constants have been used to study the conformation of a number of triarylphosphine oxides $(XC_6H_4)_3PO$ and the dependence of the orientation of the aryl rings relative to the phosphoryl group on the nature of the substituents.[81] From the spatial arrangement of the *d* orbitals of phosphorus, it might have been assumed that the most favourable conditions for the conjugation of these orbitals with the aryl rings are created when the angle φ is equal to zero or 90°; here, φ is the angle of rotation of the aryl rings about the P–C bonds, and the zero value corresponds to the position of the rings in which their planes pass through the C_3 symmetry axis. A graphical analysis of three-dimensional models using the VR given by Zefirov and Zorkii[11] showed, however, that the conformations with an angle of φ equal to zero or 90° are impossible, because of the overlap of the van der Waals spheres of the *ortho*-hydrogen atoms of the aryl rings. Steric hindrance is absent only for values of φ in the range 30–60°. The values of φ calculated from the anisotropy of the polarisability were as follows:

X	H	*p*-Cl	*p*-CH_3	*m*-Cl	*m*-CH_3
φ, °	55	65	60	49	52.

Assuming that the range of angles φ > 45° is more favourable than the range φ < 45°, the authors cited attributed the increase in φ when substituents are introduced into the *para*-position to the increase in the conjugation of the phosphoryl group with the aryl rings (for the *p*-chloro-derivative, slight steric hindrance predominates). In the opinion of the authors cited, the corresponding substituents in the *meta*-position lower the electrostatic repulsion, leading to a decrease in the angle φ.

A study[82] of the structure of dichlorobis(vinylbenzotriazole)-cobalt(II) showed that steric hindrance interferes with the π-conjugation of the vinyl groups with the benzotriazole rings: the terminal C atoms of the vinyl groups form extensively shortened (by 0.32 Å and 0.35 Å) contacts with the N atoms. Rotation of the free ends of the vinyl groups not towards the N atoms but in the opposite direction, however, would have led to even greater steric hindrance.

The rotation of the phenyl rings in the molecule of tricarbonyl-(1,4-diphenylbutadiene)iron $C_4H_4Ph_2Fe(CO)_3$ [83] is due to steric strain in the ligand (similar to that observed in biphenyl), as indicated by the shortening of the intramolecular non-valence distances C...C and C...H between the atoms of the phenyl rings and the butadiene system. In spite of the rotation of the phenyl groups relative to the plane of the butadiene system, however, these contractions remain fairly large: C...C 2.83–2.89 Å and C...H 2.55–2.65 Å. This strain in the ligand indicates[83] its tendency towards coplanarity and hence the presence of conjugation, which is apparently preserved despite the rotations indicated. The preservation of the planarity of a system in spite of a considerable number of contracted intramolecular contacts (compared with the sum of the VR), as for example in the cation of the salt $C_{18}H_{17}O_2^+ClO_4^-$,[84] ‡ indicates extensive delocalisation of the π-electrons.

Steric strains are sometimes reduced by their distribution among several neighbouring sites in a molecule. Thus the presence in the structure of di-(2,8-diphenylindolizin-3-yl)disulphide[85] of short intramolecular contacts S...C 3.330 Å and 3.342 Å (the sum of the VR of the S and C atoms is 3.55 Å) with the phenyl groups in positions 2 and 2′ leads to an increase in two triads of valence angles (on two triads of neighbouring carbon atoms) by 4–19° compared with the other exocyclic angles at these atoms.

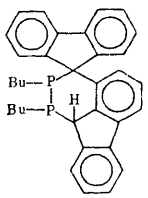
In some cases, VR have made it possible to detect an increase in the length of valence bonds as a result of steric hindrance. This effect is particularly important, since it is most directly related to the stability of chemical compounds.

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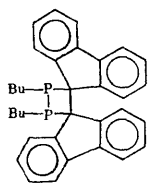
‡ In this structure the planarity of the system is preserved, despite a whole series of not only contracted but also shortened contacts, for example C...O 2.73 Å and 2.79 Å (Δr = –0.24 Å and –0.18 Å) and C...C 3.01 Å and 320 Å (Δr = –0.41 Å and –0.22 Å).

The presence of bulky substituents in the *ortho*-positions of a benzene ring influences the lengths of the bonds in the ring. Thus the presence of neighbouring phenyl and C_2F_5 groups in the molecule of 'fluoroterphenyl'[86] (shortest non-valence distances F...C 2.236 Å and 2.940 Å; length of the 'normal' van der Waals contact F...C 2.236 Å and 2.940 Å; length of the 'normal' van der Waals contact F...C 3.09 Å [13]) leads to an increase in the length of the corresponding C–C bond in the ring of 1.415 Å. Steric crowding is also responsible for the increase in the length of the C–C bond to 1.563 Å compared with 1.488–1.511 Å for the other three bonds of the type $C_{sp^2}-C_{sp^3}$ in the molecular of 2-*p*-anisidino-2,5-bis(trifluoromethyl)-3-perfluoroisobutenyl-5-monohydroperfluorohex-3-ene.[87] An even greater increase in the lengths of the bonds compared with the standard values is sometimes observed.

In the molecule of 1,2-di-t-butyl-1,2-diphosphorinane-(6,5,4-*l*,*m*)-fluorene-3-spiro-9′-fluorene[88]



extensively shortened intramolecular contacts are observed between the t-butyl groups and the phenyl rings of the fluorene fragments (C...C 3.286 Å, C...H 2.52 Å), and between the benzene rings of neighbouring fluorene fragments (C...C 3.298 Å), together with short P...C contacts (3.215 Å; sum of the VR of the P and C atoms 3.62 Å).[89] For this reason, all the P–C distances in the molecule are longer than the usual length of a single P–C(sp^3) bond, 1.85 Å;[89] here, the P–C bond length of 1.951 Å is one of the longest observed in structural studies of derivatives of three-coordinate phosphorus. Charnega and co-workers[88] also studied the molecule of fluorene-9-spiro-1-(3,4-di-t-butyl)-3,4-diphosphetane-2-spiro-9′-fluorene



which in addition to the contracted non-valence contact P...C of length 3.404 Å also contains contracts shorter than those in the previous case, C...C 3.297, 3.178, and 3.170 Å, and C...H 2.41 Å. In this molecule, the lengths of the P–C bonds in the ring are 1.904 Å and 1.911 Å, that is they are not elongated as extensively as in the previous molecule, but on the other hand, as a result of the repulsion of the fluorene groups, the bond between the spiro-carbon atoms is elongated considerably (to 1.626 Å). The central C–C bond in the molecule of 2,3-bis(trifluoromethyl)-2,3-bis(*p*-fluorophenyl)hexafluorobutane is elongated to an even greater extent (to 1.671 Å); in this case, in addition to the central bond, all the C–CF_3 bonds are also elongated (1.559–1.582 Å). In the opinion of the authors who studied this structure,[90] this increase in the length of the bonds in the 'central' unit of the molecule cannot be attributed entirely to steric hindrance.

Bonds of other types, for example P–S, may also be elongated by steric hindrance. In the molecule of 1,5-di(*p*-tolyl)-3,7-diphenyl-3,7-dithio-1,5-diaza-3,7-diphosphacyclo-octane,[91] the central fragment is the eight-membered $P_2N_2C_4$ ring. Both P atoms in the ring have the tetrahedral bond configuration characteristic of a four-coordinated phosphorus atom. The P–S bond lengths, 1.936 Å and 1.948 Å, are slightly longer than the standard value of 1.91 Å, due to the appreciable steric hindrance between the S atoms and the phenyl rings (the S...C distances are 3.11 Å, and the sum of the VR 3.55 Å).

In polynuclear coordination compounds, steric hindrance leads to an increase in the length of metal–metal bonds. Thus in the molecule of rhodium thioacetate $[Rh_2(CH_3COS)_4(CH_3CSOH)_2]$,[92] the Rh–Rh distance (2.55 Å) is much greater than the length of the Rh–Rh bond (2.3855 Å) in the analogous rhodium(II) acetate.[93] The VR of the sulphur atom (1.84 Å) is much larger than that of the oxygen atom (1.29 Å). As a result, the S...O distance in the thioacetate groups is 0.37 Å greater than the O...O distance in the acetate groups of the comparable complexes, and this, together with the electronic factor, leads to the difference in the Rh–Rh bond lengths indicated above.

Another example of the use of VR to analyse steric hindrance in molecules is given by Sadykov.[94] Here, an examination of shortened intramolecular non-valence contacts and increased valence angles gave the order of conformational strain in the molecules of matrine and its derivatives: allomatrine < sophoridine < matrine ≃ isosophoridine ≃ tetrahydroneosophoramine < *cis*-matrine.

A paper by Pasynskii and co-workers[95] gives an example of the use of VR to explain various characteristics of the conformations of molecules resulting from an attractive interaction. The use of VR in a study of the structure of $Cp_2Nb(CO)(\mu\text{-}CO)Mn(CO)_4$ detected an additional interaction between the clino-sandwich dicyclopentadienyl fragment and the pentacarbonylmanganese group. The bond between these structural fragments involves chiefly a direct Nb–Mn interaction; there is also an additional bond formed by a carbonyl group (μ-CO) acting as a bridge, and the corresponding distance Nb...C is 2.781 Å. This last value is much greater than the length of the Nb–C bond with the terminal CO group (2.06 Å), but is much shorter than the length of the van der Waals contact.

In conclusion it is useful to note that VR are very often used to reach important (and non-trivial) conclusions about the absence of any significant strain in a molecule being considered.

IV. The physicochemical properties of substances

1. The packing density coefficient. Properties determined by the effective volume, dimensions, and shape of molecules

In the absence of specific intermolecular interactions, the macroproperties of condensed phases are determined not by individual atom–atom contacts but by the integral characteristics of the molecular packing. One such characteristic, in particular, is the packing density coefficient (k). The values of k for the great majority of organic crystals lie in the range 0.65–0.77, and for substances with $k < 0.6$, a change to the vitreous state with decrease in temperature[9] or poor quality of the single crystals[96] are observed. Morphotropic jumps in homologous series are accompanied by an increase in the packing density. Substances with high packing density coefficients usually have high values of the density, viscosity, surface tension, heat of volatilisation, and melting point. An inverse dependence on k is shown by the compressibility of crystals with similar structure. Experiment has shown[9,97] that for benzene,

naphthalene, and anthracene, on going from the solid to the liquid phase, k decreases from values greater than 0.68 to 0.58, and the value in the gas does not exceed 0.5.§

Particularly compact arrangements result if the projections of a molecule fit closely into the cavities of neighbouring molecules. On the other hand, molecules with projections and cavities which do not correspond to one another are not suitable for the production of a compact arrangement. Loose molecular packing may also be due to other factors. For example, in substances containing a large number of fluorine atoms, on which appreciable negative charges are usually localised, a large number of intermolecular contacts F...F are unavoidably produced. In this case their length corresponds to the right-hand edge of the distribution curve (see section II). Thus in the crystals of perfluoro-3,3,6,6,4′,4′,4″,4″-octamethyl-1,2:4,5-dicyclobutenocyclohexa-1,4-diene ($C_{18}F_{28}$), the shortest F...F distances are 2.9–3.0 Å (VR of fluorine 1.40 Å [13]), and this explains[98] the unusually high volatility of this compound.

The analysis of intermolecular contacts is also used to interpret such properties as solubility. The low solubility of many molecular crystals is often attributed either to a high packing density or to the existence of SI. The existence of both is established using VR. Thus in the crystals of 3-carboxymethylthio-1,5-diphenylformazan,[99] the molecules are joined by H-bonds O–H...O of length 2.67 Å to form centrosymmetric dimers; between the planes of the dimers there are shortened contacts, apparently corresponding to stronger interactions, and this explains the low solubility. Similarly, the decrease in the solubility and the increase in the stability of the crystal structure of $Hg[C_9H_5(SCH_3)NS]_2$ and the isostructural zinc 7-methylthio-8-mercaptoquinolinate are attributed[59] to the existence of additional intermolecular interactions in their crystals. In fact, in this structure the molecules are connected to form dimers by a specific interaction S...S 3.35 Å (twice the VR of sulphur is 3.68 Å [15]).

A different situation is observed in the crystals of tetrakis(chloromethyl)adamantane.[100] Comparison of the intermolecular contacts with the corresponding sums of the VR showed that in this case the molecular packing is determined only by purely van der Waals forces, but at the same time it is highly compact, since the side groups occupy the spaces between the adamantane rings and ensure strong adhesion of the molecules. This adhesion, despite the absence of SI, explains the very low solubility and high melting point of the substance.

The shape of molecules, established using VR, is revealed particularly clearly in their ability to form solid solutions. Similarity in the shape and size of the replacing molecules and the molecules being replaced is a necessary and sufficient condition for the formation of substitutional solid solutions of organic compounds. Kitaigorodskii[101] proposed that the extent of this similarity be estimated using the geometric similarity coefficient ε, calculated as follows. The molecules, modelled using VR, must be superimposed to give the smallest extent of non-overlapping parts. If the overlap volume is v, and the volume of non-overlapping parts V, then $\varepsilon = 1 - V/v$. The molecules of A are soluble in a crystal of B if $\varepsilon > 0.8$ and there is no significant breakdown of the packing if a molecule of B is replaced in imagination by a molecule of A. An example is provided by the biphenyl–bipyridyl system. The molecules of these substances have very similar shapes, so that A dissolves in B, and B dissolves in A (a continuous series of solid solutions is not formed, however; the reason for this has been discussed [101]).

In addition to substitutional solid solutions, inter-block solid solutions also exist, where the dissolved molecules are localised on the surfaces of single-crystal blocks (in a mosaic crystal). Partial geometric correspondence between the molecules of the matrix and the impurity is sufficient for the formation of these solutions. Inter-block solid solutions have been used successfully[102] to produce new luminescent crystals. The matrices were naphthalene crystals, and the activating additives were anthranilic acid, methyl anthranilate, 1,4-diphenylbuta-1,3-diene, and 1,6-diphenylhexa-1,3,5-triene. Comparison of the projections of models of the additive molecules, constructed using VR, with the projection of a model of naphthalene showed that with decrease in the geometric similarity, the influence of the additives on the optical properties of napthalene decreases. Partial geometric correspondence is also a necessary condition for selecting a matrix for obtaining quasi-linear impurity spectra.[103]

To facilitate the calculation of the volume of molecules, Kitaigorodskii[8] proposed the use of the volume increments of the atoms (ΔV_i) and atomic groups. The value of ΔV_i for the atom being considered is calculated as the difference between the volume of the van der Waals sphere of this atom and the volumes of the spherical segments cut off on the given sphere by neighbouring valence-bonded atoms. The increments calculated in this way have been widely used[104–106] to calculate a whole series of important physical characteristics of polymers: density, volume expansion coefficient, vitrification temperature, temperature of the start of intensive thermal degradation, melting point, refractive index, coefficient of optical sensitivity to strain, bulk modulus of elasticity, etc. An important feature is that all these characteristics can be calculated even before synthesising the polymers, using only the chemical structure of the repeat unit. All the equations used in the calculations contain the volumes of the repeat units of the polymer $\sum_i \Delta V_i$. In particular, the density of an amorphous polymer is given approximately by the equation $d = km/\Sigma\Delta V_i$, where $k = 0.681$ (the average value of the packing density coefficient characteristic of polymers), and M the mass of the repeat unit. This calculation generally gives an accuracy of 0.001 g cm^{-3}. Similar calculations have been carried out by van Krevelen.[107]

This equation for the density shows that the value of d depends chiefly on the ratio of the volumes and mass of the atoms in the macromolecule. A unique element in this respect is fluorine, which has a small volume and a comparatively large atomic weight. Their ratio is much greater for fluorine than for any other monovalent substituent, and when fluorine is introduced into macromolecules it leads to a sharp increase in the density. A characteristic example is provided by Teflon (polytetrafluoroethylene).[108]

If the experimental value of the density is known, the packing density coefficient of the polymer can be calculated. This calculation made it possible to explain[109] the decrease in the softening temperature of copolymers of α,ω-dimethylacryloyloctaphenyltetrasilane with methyl methacrylate (MMA) with increase in the concentration of the former in the copolymers. At the same time the value of k decreases slightly, that is slight loosening of the molecular packing of the chains is observed, leading to a decrease in the softening temperature. Comparison of the calculated and experimental

§ Since there is no periodic structure in the liquid and the gas, the quantity being considered is the ratio of the total volume of the molecules modelled using VR to the total volume occupied by the given phase.

vitrification temperatures of network copolymers can sometimes be used to establish their structure. The structures of network copolymers based on MMA and diallyl *m*-carboranedicarboxylate were determined in this way.[110]

Another example of the successful use of VR to analyse the structure of condensed phases can be found in a paper by Abramzon and Goloudina,[111] who studied monolayers of surface-active substances at a liquid–gas interface. The authors cited tried to show that under certain conditions these layers have a crystalline structure. The property of the monolayer studied was the packing density, or more accurately the free volume corresponding to one molecule or hydrocarbon chain: $V_{free}^{m(c)} = V^{m(c)} - V_0^{m(c)}$, where $V^{m(c)}$ is the experimentally determined volume occupied by the molecule (or chain), and $V_0^{m(c)}$ the characteristic volume of the molecule (or chain), calculated using the VR of the H and C atoms and the methyl group given by Kitaigorodskii.[8] The authors cited analysed the contraction isotherms for condensed monolayers of aliphatic acids and higher alcohols by comparing the values of V_{free} for the packing of the hydrocarbon chains in the monolayer and the molecules of n-alkanes. The range of existence of solid layers was then determined, and it was shown that the phase transformations in the condensed layers of the substances examined are due to changes in the packing density of the hydrocarbon chains and are similar to the phase transformations in n-alkanes. This last feature provides evidence that the condensed monolayer has a crystal structure. A similar conclusion was reached in an electron diffraction study[112,113] of films of surface-active substances. Van der Waals radii have also been used to study the structure of aqueous solutions of a number of metal thiocyanates.[114]

Particle size plays an important role in transfer phenomena, and if the particles are polyatomic ions or molecules, VR can be used to study these phenomena. An example can be found in a paper by Lesnichaya,[115] where in a study of the electrical conductivity of molten guanidinium chloride $C(NH_2)_3Cl$, a comparison of the dimensions of the guanidinium ions obtained using VR with the dimensions of the chloride ion indicated that in this case an important part in ion transfer is played by mobile protons.

The use of VR (together with other parameters of the molecules) also makes it possible to explain and to estimate quantitatively the changes in the lattice parameters on intercalation, that is when molecules or ions are introduced into the spaces between the layer in layer single crystals. Thus on the intercalation of dichlorobenzene molecules into single crystals of $(C_{10}H_{21}NH_3)_2CdCl_4$, the distance between neighbouring layers increases by 3.65 Å, and for the intercalation of chloronaphthalene molecules the corresponding increase is 3.75 Å (the unit cell parameter *c* of the single crystal increases by 7.3 Å and 7.5 Å respectively).[116] These distances correlate well with the diameter of the chlorine atom (3.80 Å), particularly if account is taken of the possibility that chlorine atoms are situated in the cavities in the layers of the single crystal.¶ A similar change is observed in the parameter *c* of a single crystal of $(C_9H_{19}NH_3)_2PbI_4$ when hexane molecules are introduced (the distance between the layers increases by the thickness of the hexane molecule).[116] In insertion compounds of graphite with the composition $C_{24}K(C_6H_6)_x$, the benzene molecules are arranged at right angles to the graphite layers;[117] in this case, however, two limiting orientations are possible: one of the C–C bonds of the benzene ring may be arranged at right angles to or parallel to the layer. Comparison of the experimentally determined distance between the graphite layers and the dimensions of the benzene molecule, a model of which was constructed using VR, made it possible to give preference to the first version.

The system of VR makes it possible to describe clearly and fairly accurately the dimensions and shapes of the cavities and channels in various crystal structures, and also the dimensions and shapes of the molecules capable of entering these cavities and channels. This is related to questions of the permeability of molecular sieves and membranes, which are of primary importance for the understanding, prediction, and practical realisation of many chemical and biological processes (in particular, transport reactions).

Zeolite crystals contain more or less extensive cavities with windows formed by the connection of *n* silicon–oxygen tetrahedra. Taking the VR of oxygen as 1.4 Å, it is possible to calculate the dependence of the diameter of the window on *n*:[118]

n	4	5	6	8	10	12
D, Å	1.2	2.0	2.8	4.5	6.3	8.0.

The value of *D* determines the size of the atoms (ions) and molecules capable of entering the zeolite cavities.

A particularly fine geometric analysis is required in the study of inclusion compounds (clathrates). Thus the formation of these compounds is prevented not only when the dimensions of the species to be introduced are too large, but also when they are too small, since mobility of the particles in the cavities is energetically unfavourable. For example, α-dextrin (cyclohexaglucan), which contains channels with a diameter of ~6 Å, can accommodate molecules of benzene derivatives containing a smaller number of substituents which are not too large; β-dextrin (cyclopentaglucan), which contains channels with a diameter of 7.5 Å, forms inclusion compounds with naphthalene derivatives, but in γ-dextrin (cyclo-octaglucan), the cavities with diameter of 9–10 Å are too large for most ordinary organic substances, and they show little tendency to form inclusion compounds.[119] Similarly, the molecules of normal alkanes can be accommodated in the channels of urea, but cannot be held in the channels of thiourea, which have a larger cross-section and cannot be filled sufficiently fully by the thin chains of normal alkanes.[119]†

The use of VR is also extremely important in the study of the cavities in globular protein molecules. To study the mechanism of the penetration of the substrate to the active centres (haemo-groups) of the enzyme catalase, an attempt was made to find intramolecular cavities and channels in the enzyme.[121] The coordinates of the atoms were used to calculate the filling function of the space within the molecule. This function takes a constant value within a sphere of radius *R* round any of the atoms, and the value zero at other points (*R* is the sum of VR of the given atom and a water molecule). The van der Waals radii were assumed to have the following values: Cα 1.95, O 1.50, N 1.55, C 1.7, S 1.8, Fe 1.35, H_2O 1.4 Å. Several fairly large cavities were found; one of them consists of a bent channel which becomes broader when it meets the surface of the molecule, where its diameter reaches 8 Å; the other end of the channel extends towards the haeme group, and ends at a distance of 7 Å from it. This cavity apparently allows the substrate molecules to penetrate to the active centres of the enzyme.

¶ Dolzhenko and co-workers[116] considered only the thickness of the aromatic ring (3.42 Å), whereas the chlorine atoms obviously play a more important role.

† Later more detailed studies of the stability of compounds of urea with n-alkanes using VR have been published.[120]

Van der Waals radii are also used in the study of adsorption phenomena. Thus in a study of the mechanism of flotation using xanthates, the dimensions of the pentyl xanthate anion and the area (28 Å^2) occupied by this anion (arranged at right angles to the surface of the mineral particle) were found. These data established that at the initial concentrations of xanthate in the pulp usually employed in flotation, the quantity of sorbent attached to the surface of the mineral particles undergoing flotation in a number of cases is sufficient for the formation of 4–5 continuous monomolecular layers with close packing of the sorbent molecules.[122]

2. The rotation of atomic groups and molecules in crystals

The physicochemical properties of substances depend on the dynamics of the molecule, in particular on the rotation of individual groups or entire molecules. Crystals in which rotation of the molecules takes place differ considerably from ordinary crystals in a number of properties, primarily their plasticity.

The possibility that molecules rotate in a crystal can be estimated using VR. A classical example (one of the first) is provided by methane. Its crystals have a cubic face-centred cell with an edge of 6.35 Å. The shortest distance between the centres of the molecules is 4.49 Å, which is exactly equal to twice the quantity $r_{C-H} + R_H$ and indicates free rotation (without free rotation, the shortest distance between the centres of the molecules would be smaller, since according to the principle of close packing the van der Waals spheres of the H atoms should enter the cavities of neighbouring molecules). A similar calculation using VR was carried out[8] to prove the possibility of coordinated rotation of the molecules of methyl-, ethyl-, and propylmercury chlorides round one of the axes in the crystals. A particular case of the rotational-crystalline state is provided by the H-phase of n-alkanes, in which the molecules rotating about their long axis form a hexagonal arrangement corresponding to the close packing of cylinders.

Not only whole molecules, but also individual groups, may rotate in a crystal. Using the mean-statistical VR values of the atoms of fluorine and chlorine, Antipin and co-workers[123] found that in the structure of 2-trichlorophosphazo-2-trifluoromethylperfluoropropane $Cl_3P=N-C(CF_3)_3$ the trifluoromethyl groups mesh with one another like gears. This should restrict their movement mainly to twisting vibrations about the C–C bonds. An analysis of the non-valence contacts using VR made it possible to estimate the relative contributions of intramolecular and intermolecular forces to the barrier to the reorientation of these groups. The possibility of the rotation of other groups in molecules in crystals has been discussed, for example, in papers by Bokii and co-workers[124] and Gachegov and Soifer.[125]

In some systems, free rotation about a σ-bond is restricted by the approach of non-bonded substituents which would be impossible according to the corresponding VR values. In these cases the conformers are in fact isomers, and can be separated. Sometimes, steric hindrance to free rotation leads to the appearance of optical isomerism, and it becomes possible to separate the optical antipodes.

3. Organic conductors

In the case of isotropic metallic and ionic conductors, the conductivity is characterised by a fairly well studied three-dimensional band structure. Organic substances (charge-transfer complexes, radical-ion salts) usually show one-dimensional, or less frequently two-dimensional, conductivity, the interpretation of which requires an analysis of the molecular packing using VR. Various regular features of this conductivity, usually related to the stacked packing and the magnitude of the interplanar distance (the distance between the parallel planes of the molecules in contact), have been established.[126–128]

The one-dimensional character of the properties of most organic conductors is due to the characteristic features of their structures: the large planar molecules are arranged in stacks in such a way that the overlap of the electronic wavefunctions along the stacks is smaller by several powers of ten:[127] the conductivity electrons (π-electrons) move more readily along the stacks than between them.

The most familiar one-dimensional organic conductors are 7,7,8,8-tetracyanoquinodimethane (TCNQ) and its radical-ion salts, whose conductivity at room temperature reaches $10-10^2\ \Omega^{-1}\ cm^{-1}$. A characteristic feature of the crystal structures of these salts is the existence of a conducting system consisting of infinite stacks of TCNQ molecules, and the interplanar distance between the stacks is practically the same throughout the stack (3.22–3.26 Å) [126] and shorter than twice the VR of the carbon atom (3.42 Å). The increase in the interplanar distance TCNQ...TCNQ to 3.43 Å in the salt Pb^+TCNQ^- leads to a decrease in the conductivity to $10^{-2}\ \Omega^{-1}\ cm^{-1}$ (the other characteristics of the conducting quasi-one-dimensional structures are preserved).[129]

For other compounds with a quasi-one-dimensional electronic system, such as the radical-cation salts of tetrathiotetracene (TTT), tetraselenotetracene (TSeT), and tetrathiofulvalene (TTF), the condition for the production of high metallic conductivity is again the presence of conducting chains, that is regular radical-cation or radical-anion stacks with an interplanar distance which is the same throughout the stack and which is shorter than the ordinary van der Waals distance, and with neighbouring radicals superimposed in identical fashion. Important features for the stabilisation of the metallic state apparently include not only strong interactions within the conducting chain but also an additional strong interaction between the chains, as indicated by the contracted (compared with the sum of the corresponding VR) intermolecular contacts.[126]

Among the radical-cation salts of TTT and TSeT with a high conductivity ($10^3\ \Omega^{-1}\ cm^{-1}$ at room temperature), three complexes can be distinguished: $(TTT)_2I_3$, $(TSeT)_2Cl$, and $(TSeT)_2I$. In their crystal structures,[126] the shortest interplanar distances in the conducting stacks are 3.32, 3.37, and 3.40 Å respectively, whereas in the complexes of TTT these distances lie in the range 3.32–3.63 Å (twice the VR of sulphur is 3.68 Å), and in the TSeT complexes they lie in the range 3.37–3.53 Å (twice the VR of selenium is 4.00 Å [7]). Moreover, the structures of these three compounds contain extensively shortened intermolecular contacts: Se...Se 3.47 Å and 3.45 Å [in the stacks of $(TSeT)_2Cl$ and $(TSeT)_2I$ respectively] and S...S 3.38 Å [between the stacks in $(TTT)_2I_3$]. Similarly, in the regular radical-cation stacks of TTF in TTF–halogen complexes with different stoichiometry, the average interplanar distance (3.55 to 3.61 Å) is less than twice the VR of sulphur. The conductivity of almost all the complexes with non-stoichiometric compositions is $\sim 300-550\ \Omega^{-1}\ cm^{-1}$ at room temperature.[126]

The discovery of the superconductivity of tetramethyltetraselenofulvalene hexafluorophosphate $(TMTSF)_2PF_6$,[130] and then of a whole series of related compounds $(TMTSF)_2A$, where A = ClO_4, AsF_6, SbF_6, etc.,[131,132] with superconducting transition temperature $T_c \simeq 1$ K, provided the starting point for a new stage in the study of organic conductors. These studies demonstrate the importance of VR in another field of the study of conductivity in organic conductors.

In the crystals of $(TMTSF)_2A$ the planar molecules form stacks extending along the *X* axis. For almost all pairs of Se atoms from neighbouring molecules along the *X* axis (within the stacks) and along the *Y* axis (between the stacks), the Se...Se distances (~ 3.9 Å)

are shorter than twice the VR of selenium. This suggests that the electrons can move fairly freely in the *XY* plane. This is confirmed by measurements of the anisotropy of the conductivity and the upper critical value of the magnetic field intensity.[128] The anions A are situated in the cavities formed by the packing of the zigzag conducting TMTSF chains. This quasi-one-dimensional metallic system is stabilised by pressure. If the VR of fluorine is taken as 1.4 Å, the diameter of the AsF_6 ion is close to 6.4 Å, and if the VR of oxygen is taken as 1.29 Å, the diameter of the ClO_4 ion is about 5.6 Å. The effect of the replacement of the AsF_6 ion in the $(TMTSF)_2AsF_6$ structure by the smaller ClO_4 ion is analogous to that of pressure; this 'chemical compression' gave the first organic superconductor at atmospheric pressure, $(TMTSF)_2ClO_4$.[131] The 'chemical compression' taking place when AsF_6 is replaced by PF_6 leads to equalisation of the lengths of the Se...Se contacts along the *X* and *Y* axes;[133] as a result, the difference in conductivity in these two directions is decreased. In the $(TMTSF)_2ClO_4$ crystals, the ratio of the dimensions of the cavities and the ClO_4 anions occupying them determines the types of ordering of the anions with decrease in temperature, and this has a significant influence on the change in properties.[127]

Superconductivity was later detected in a family of compounds, (BEDT-TTF)A. The molecule of BEDT-TTF (bis-ethylenedithiolotetrafulvalene) has eight S atoms in the conjugation chain. The change from TMTSF to BEDT-TTF made it possible to create organic conductors with even lower anisotropy. The crystalline salts of this family show a wide range of physical properties; they are capable of behaving as dielectrics, organic metals with a metal–dielectric transition, organic metals stable over a wide temperature range, and superconductors. In the investigation of the reasons for the difference in the conductivity of these substances, particular attention is paid to the intermolecular contacts S...S (of length ~3.7 Å or less) in and between the stacks.[134–139].

In the study of the conductivity of radical-ion salts, intermolecular (interionic) contacts S...S have been examined in other crystals, in particular in the structure of the tetraethylammonium salts of bis(1,3-dithiol-2-thione-4,5-dithiolato)gold(III).[140] Structures whose molecules contain both thio- and seleno-fulvalene rings, including the structure of bis-ethylenedithiodimethyldithiadiselenafulvalene tri-iodide,[141] in addition to S...S contacts, contain intermolecular Se...Se and S...Se contacts, close to the sums of the corresponding VR. Cation–anion contacts close to or shorter than the sums of the corresponding VR have also been analysed, for example S...I contacts with a length of 3.85 Å or less.[142]

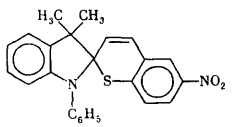
V. Chemical reactions

The reactivity of a substance is often influenced by steric factors. In this connection, steric effects of the following types will be examined: 1) steric hindrance leading to the elongation of covalent bonds or to the distortion of valence angles, 2) the shielding or complete blocking of the active centre of a molecule, 3) steric factors determining the angle of nucleophilic of electrophilic attack, and other forms of the influence of steric factors on chemical processes.

The elongation of a covalent bond as a result of crowding in the molecule facilitates the rupture of this bond in a chemical reaction. Thus in the molecule of fluorene-9-spiro-1-(3,4-di-t-butyl)-3,4-diphosphetane-2-spiro-9'-fluorene[88] (see section III), the increase in the length of the bond between the spiro-atoms to 1.626 Å leads to a considerable decrease in its strength, and when the compound is brought into solution, the cyclic structure breaks down with the rupture of this bond, as confirmed by the EPR spectra.[143]

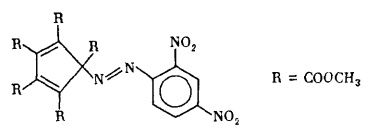
In the structure of 2,3-bis(trifluoromethyl)-2,3-bis(*p*-fluorophenyl)-hexafluorobutane,[90] the bonds in the central part of the molecule, in particular the central C–C bond (1.671 Å), are elongated considerably. Although in the opinion of the authors cited this cannot be due entirely to steric hindrance, the latter plays an important role, since the distances between the fluorine atoms of CF_3 groups in contact is 2.43–2.59 Å, which is much smaller than twice the VR of fluorine (2.80 Å). The authors cited[90] compared the properties of this compound with those of its analogue not containing F atoms (bicumyl), and noted the increased tendency of the fluoro-derivative to undergo dissociation to form radicals; for bicumyl this is not observed even at 200 °C. Similar easy rupture of an elongated single bond C–C 1.638 Å is also observed in the sterically crowded molecule of the thermally unstable 5,6-dibutyl-5,6-diphenyldecane (containing a number of short intramolecular contacts H...H of length 2.06–2.11 Å).[144]

Another example of a decrease in the strength of a bond elongated as a result of steric hindrance is provided by the molecule of 1'-phenyl-3',3'-dimethyl-6-nitrospiro(indoline-2,2'-[2H-1]-benzothiopyran).[145]



In this molecule, the length of the bond $C_{spiro}-S$ (1.866 Å) broken on photoexcitation is much greater than that of the corresponding bonds in six-membered heterocyclic compounds (1.80–1.83 Å [146]). The increase in length is due to the fact that the non-valence contact between the S atom of the benzothiopyran fragment and the C atom of one of the methyl groups of the indolene fragment (C...S 2.99 Å) according to Zefirov and Zorkii,[34] is 0.56 Å shorter than a normal S...C contact. In the opinion of the authors cited,[145] the photochemical properties of this molecule are explained by the vibrational mechanism of the rupture of the $C_{spiro}-S$ bond, which is elongated and weakened even in the ground state, and whose vibrations should be excited first.

Steric hindrance leading to the distortion of valence angles is also important, since under certain conditions it may initiate a chemical reaction at the corresponding site. An example is provided by an X-ray diffraction study[147] of 5-(2,4-dinitrophenylazo)-1,2,3,4,5-pentamethoxycarbonylcyclopentadiene.



As a result of steric hindrance (the shortest intramolecular distances C...N between valence-non-bonded atoms are 3.00 Å and 2.91 Å, whereas $2\sqrt{R_C R_N}$ = 3.20 Å), the valence angle CCN at the four-coordinate C atom is increased to 120°. The authors cited regard this feature as the factor responsible for the vigorous decomposition of the substance when heated to 100–110 °C. Moreover, the strain at this atom should facilitate the dissociation of the molecule in solution (at the C–N bond) to give an ion pair, whose recombination can take place at any of the carbon atoms of the cyclopentadiene ring.

The shielding of an active centre was dealt with by Bel'skii and co-workers,[148] who established by X-ray diffraction that in the molecule of 2,6-dicyano-3-trifluoromethyl-5-phenylaniline the distance between the H atom in position 4 of the aniline ring and one of the F atoms of a neighbouring trifluoromethyl group is 2.30 Å, and the distance from the H(4) atom to the nearest H atom of the phenyl substituent is 2.42 Å. Thus the hydrogen atom in position 4 is shielded by the trifluoromethyl and phenyl groups. As a result, electrophilic substitution cannot be carried out in position 4; in spite of numerous attempts, the authors cited could not obtain any 4-substituted aniline derivative of this type, whereas 3,5-dimethyl-2,6-dicyanoaniline readily undergoes electrophilic substitution.

It has been proposed[149] that the shielding of the metal atom in compounds MR_n can be estimated quantitatively using the solid angles, with vertices at the M atom, containing the inscribed R substituents, modelled by van der Waals spheres. The degree of shielding is characterised by the sum of these angles (the quantity Q), or more accurately by its approach to the total solid angle $4\pi \simeq 12.56$ rad. In the compounds $(R_3E)_2Hg$, where E = Si, Ge, Sn, the degree of shielding increases in the order R = Me, Ph, C_6F_5, which correlates with the decrease in reactivity, in particular the tendency to undergo oxidation. The fact that the value of Q is close to 4π indicates that the ligand environment of the metal is compact and hence stable. This explains, for example, the high thermal stability of $Ti(CH_2SiMe_3)_4$ and $V(CH_2SiMe_3)_4$, for which Q is 11.7 rad and 12.6 rad respectively, and the low stability of $TiMe_4$ (Q = 8.8 rad, decomposition temperature −40 °C) and $TiPh_4$ (Q = 9.3 rad, decomposition temperature −10 °C). It was suggested[149] that the value of Q can also be used to estimate the possible existence in principle of molecules of the type MR_n. A value in excess of 12.56 rad indicates steric strain, and a value which is much higher shows that the molecule cannot exist, for steric reasons. For example, in the hypothetical molecule $Ta(CH_2SiMe_3)_5$, the value of Q is 14.7 rad,[149] which is much greater than 4π. In fact, this compound has not yet been synthesised, despite repeated persistent attempts.[150] Another compound which has not been obtained is $(\pi\text{-Cp})_2CrCl_2$,[151] for which Q = 14.02 rad.

The VR of fluorine has been used[152] to illustrate that the ion NF_6^- cannot exist, in contrast to the PF_5 molecule and the PF_6^- ion. In the last two cases the overlap of the van der Waals spheres of the F atoms is extremely slight, whereas in the hypothetical NF_6^- ion it would be too great (summation of the covalent radii gives the distances P−F 1.74 Å and N−F 1.34 Å).

VR have also been used[153] for qualitative and quantitative estimates of the accessibility of the reaction centre in trityl ethers of sugars with the general formula Ph_3C-O-R, where R represents different sugars. A study of the spatial environment of the nucleophilic active centre—the ether oxygen atom—using Stuart–Briegleb models, based on X-ray diffraction data,[154,155] showed that in all the molecules studied the active centre is open only on the side of the vertex of the angle at the ether oxygen atom (the opposite side is completely shielded by one of the phenyl rings of the trityl group). Assuming that the glycosylating agent approaches the active centre chiefly along the bisector of the angle indicated on the side of its vertex, the authors cited[153] compared the degree of shielding of the ether oxygen atom in this direction in different molecules Ph_3C-O-R. For this purpose, three-dimensional models of the molecules were projected in the direction of the bisector of the $C-O-CPh_3$ angle. Analysis of the projections showed that in all cases the trityl group shields ~40% of the area of the active centre. In the molecule of 3-O-acetyl-4-O-trityl-1,2-O-[1-(*exo*-cyano)-ethylidene]-β–*L*-ramnopyranose, however, the active centre is shielded for the most part only by the trityl group (the shielding by H atoms is slight, and this shielding is easily removed by the conformational mobility). At the same time, in other molecules of this type, the active centre is more extensively shielded, both by the trityl group and by the O and C atoms of the sugar residue. To estimate quantitatively the degree of shielding of the active centre by the method proposed by Zakharov and co-workers,[149] three-dimensional models of the molecules were projected on a cylinder whose axis coincided with the bisector of the $C-O-CPh_3$ angle. According to the calculations, the above molecule allows practically free approach of the glycosylating agent to the active centre, whereas in the other cases, contact between the reagents is possible only for a definite relative orientation, so that the probability of effective collisions of the reacting molecules is lowered. This facilitates the competing reaction of isomerisation to give the glycosyl cation, which gives the 1,2-*cis*-bonded anomers.

An interesting example of the use of VR to analyse the chemical properties of molecules was described by Chernega and co-workers.[156] The sterically strained molecule of $(Me_3Si)_2N-P=N'-C_6H_2(t\text{-}Bu)_3$ (I) contains exclusively shortened contacts P...C (t-Bu) (3.26 Å and 3.37 Å; sum of the VR 3.60 Å [7]), and also a shortened Si...N contact (3.23 Å; sum of the VR 3.60 Å [7]). As a result the P=N′ (1.566 Å) is ~0.02 Å longer than the corresponding bonds P=N′ (1.544 Å and 1.545 Å) in the compounds $(Me_3Si)_2N-P=N'-SiMe_3$ (II) and $(Me_3Si, Me_3C)N-P=N'-CMe_3$ (III). Nevertheless, the reactivity of the first compound towards proton-donor reagents (alcohols, amines) is much lower than that of the last two compounds, and, moreover, compound I can be heated to 250 °C with no sign of dimerisation, in contrast to known λ^3-aminoiminophosphines, including compounds III and II, that is it has an exceptionally high thermal stability. This can be attributed to the fact that the atoms which elongate and weaken the P=N bond shield it at the same time. To investigate the magnitude of this shielding and how it changes when R′ = 2,4,6-$(t\text{-}Bu)_3C_6H_2$ is replaced by R″ = $SiMe_3$, the authors cited[156] used the program CRON [149] to calculate the projections of these substituents on a cylinder of unit radius with axis coinciding with the P=N′ bond. The calculations showed that the shielding of the P=N′ bond by R′ is ~1.5 times greater than that by R″. The greatest difference in the degree of shielding is observed in the region adjoining the P atom, that is on the side of the centre at which proton-donor reagent attack takes place. The sum Q of the solid angles with vertex at the P atom, calculated by the methods described,[149,157] is 4.4 rad for the substituent R′, and 2.4 rad for R″.

An analysis of the non-valence interatomic contacts has been used[158] to determine the angles of electrophilic and nucleophilic attack in reactions involving a divalent sulphur atom. The angular distribution of 169 S...X contacts smaller than the sum of the VR in organic, organometallic, and inorganic compounds of divalent sulphur (Y−S−Z) was studied. The authors cited suggested that when the attacking atom X is electrophilic, it approaches the S atom along a direction forming an angle of ~20° with the perpendicular to the Y−S−Z plane; if however, the X atom is nucleophilic, then with certain exceptions it approaches the S atom along the continuation of one of the valence bonds.

Another example of the influence of geometric characteristics, analysed using VR, on the chemical properties of molecules is provided by an X-ray structural study[159] of 2,10-diacetoxy-13-thia-bicyclo[7,3,1]-*cis*-tridec-5-ene sulphide and 2,9-dichloro-13-thia-bicyclo[8,2,1]-*cis*-tridec-5-ene sulphoxide (Fig. 3). In both molecules, the intramolecular distances between the S atom and the opposite C

atoms forming double bonds in the macrocyclic rings are only slightly greater than the value characteristic of the van der Waals contact C...S (3.55 Å), by 0.14 Å and 0.22 Å in the first case, and by 0.24 Å and 0.44 Å in the second. Moreover, in both cases the lone pairs of electrons of the S atoms are directed towards the C=C double bond. As a result of this conformation, the molecules being considered are 'prepared' for *trans*-annular transformations, which take place with these compounds under the influence of various reagents.

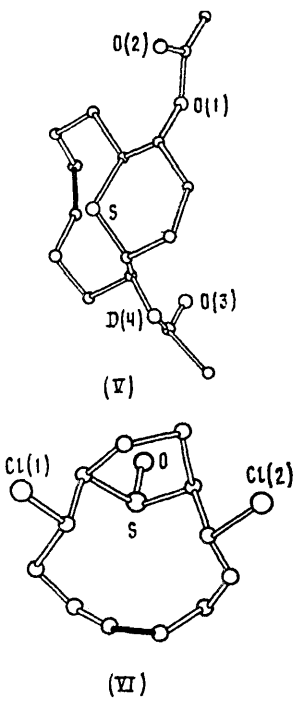
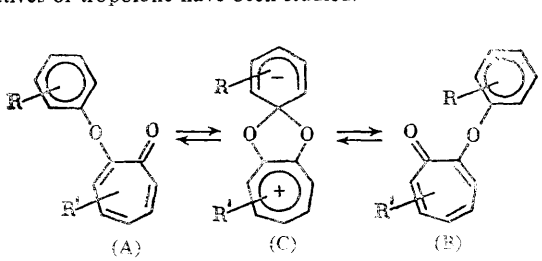


Figure 3. Conformations of the sulphide and sulphoxide molecules[159] (the double bonds are black).

In recent X-ray diffraction studies, the change in the geometry of molecules with similar compositions in an appropriately selected series of compounds is regarded as providing a model of the three-dimensional change in a molecule during a chemical reaction (mapping the course of chemical reactions). These studies have been described by Furmanova and Kompan.[160] The parameter used to follow the 'movement' of the system along the reaction path is often the distance between two atoms which initially are not bonded but which are joined by a valence bond as a result of the reaction.

In particular, the arylotropic rearrangements in O-nitroaryl derivatives of tropolone have been studied:[161,162]



By varying the number of positions of the substituents in the six- and seven-membered rings, a series of compounds was obtained, illustrating the course of the reaction (A) ⇄ (B), including the formation of the intermediate [the spiro-complex (C)]. In the molecule of S-(2′,4′,6′-trinitrophenyl)thiotropolone,[161] which has the *trans*-configuration, the torsional angle C(O)−C−S−C(Ar) (the angle φ) is 170°, the O...C(Ar) distance is greater than 4 Å, and the steric requirements for intramolecular *trans*-arylation are not satisfied. In O-(2′-nitro-4′-trifluoromethylsulphonylphenyl)-3,5,7-trimethyltropolone,[161] the aryl ring is rotated towards the carbonyl O atom (φ = 77°), and the distance O...C(Ar) 2.94 Å is practically equal to the normal van der Waals contact 2.97 Å, that is this structure is already prepared for the tautomeric transformation. The crystal of O-(2′,4′,6′-trinitrophenyl)tropolone,[161] contains two crystallographically independent molecules with similar geometric parameters; the O...C(Ar) distances in them (2.56 Å and 2.52 Å) are extensively shortened, indicating an attractive interaction between these atoms, that is the start of the formation of a new bond; the angle φ has the value 28.9° and 10.2° respectively. The O...C(Ar) distance is shortened to an even greater extent (to 2.45 Å) in the molecule of O-(2′,6′-dinitrophenyl)-3,5,7-trimethyltropolone,[162] where φ = 2°. The angle between the straight line O...C(Ar) and the plane of the aryl ring is 107.5°, and there is appreciable breakdown of the coplanarity of the covalent bonds at the C(Ar) atom, which is displaced from the plane of the atoms joined to it by 0.09 Å towards the carbonyl O atom. All this is characteristic of nucleophilic attack at an sp^2 carbon atom. Finally, the molecule of O-(2′,4′,6′-trinitrophenyl)-3,5,7-trimethyltropolone [162] has the structure of the spirocyclic intermediate of type (C) [in it, both O...C(Ar) distances are 1.47 Å].

Another example of the analysis of a reaction path using X-ray diffraction data is given by Sitkina and co-workers,[163] who regarded the molecule of 4-chlorophenylamino-3-acetoxy-1-methylindole-2-carboxaldehyde as a geometric model of the initial stage of the formation of the transition state of the inverse dark reaction of O → N transfer of the acyl group in O-acylated imines. In this molecule, the distance between the nucleophilic N atom and the migrating C atom is shortened to 3.02 Å (normal contact N...C 3.20 Å), indicating a weak attractive interaction.

Some of the above examples can be regarded as illustrating the influence of the three-dimensional structure of molecules, in particular the shielding of the reaction centres, on the rate of a chemical reaction.

The quantitative dependence of the reaction rate constant k on steric factors is given by the Taft equation[164] $\lg(k/k_0) = \Delta E_S(X)$, where $E_S(X)$ is a parameter characterising the steric effect of the substituent X. E_S is linearly dependent on the VR.[165] Subsequent studies[166] examined the parameter ν_X, the difference between the VR of the substituent X and the H atom: $\nu_X = R_X - R_H = R_X - 1.20$ Å. Using this parameter, the rate of esterification of substituted carboxylic acids by methanol or ethanol was described[167] by the modified Taft equation $\lg k = \psi\nu_X + h$, where ψ and h are empirical constants.

The changes in the reactivity of the chlorides of phosphoric and thiophosphoric acids $P(O)Cl_3$, $(RO)_nP(O)Cl_{3-n}$, and $(RO)_nP(S)Cl_{3-n}$, where n = 1, or 2, in the stepwise alcoholysis of aliphatic alcohols ROH (R = Me, Et, Pr, Iso-Pr, Bu, iso-But) have been analysed.[168] Assuming that the change in the reactivity of the reagents is due to steric factors, the authors cited took as a measure of the steric effects the values of ν given by Charton.[169] The relative reactivity in series with identical substituents in the two reagents is effectively described

by the equation $\lg k = av + b$, and in series with independent variation of the groups RO in the chlorides and R'O in the alcohols it is described by the equation

$$\lg k = av(\mathrm{OR}) + bv(\mathrm{OR}') + c,$$

where a, b, and c are constants.

The rate constants of bimolecular reactions have been calculated successfully[170] using the equation

$$k_{12} = \frac{(\sigma_1 + \sigma_2)^2}{4M^{1/2}} 0.1838 \cdot 10^{27} \exp(-B/T)T^{1/2}\left\{1 - \frac{C}{T}\left[1 + \frac{B}{T} - \frac{B^2}{T^2}\right]\right\},$$

where σ is the diameter of the species, calculated using the VR; M the reduced molecular mass $M_1M_2/(M_1 + M_2)$; and B and C are parameters calculated by the method described by Evdokimov.[170] The values of k were found (with a deviation of ~30% from the experimental values) over a wide temperature range up to 8000 K for the reactions

$$\mathrm{N} + \mathrm{O_2} = \mathrm{NO} + \mathrm{O},\ \mathrm{O} + \mathrm{O_3} = 2\mathrm{O_2},$$
$$\mathrm{Cl} + \mathrm{H_2} = \mathrm{HCl} + \mathrm{H},\ \mathrm{CO_2^{\cdot}} + \mathrm{N_2} = \mathrm{CO_2} + \mathrm{N_2^{\cdot}}$$

and other reactions. The results give correctly the temperature dependence of the rate constants.

VR are often used to determine the steric conditions under which solid-phase reactions of a particular type are possible. Thus in a study of the photo-isomerisation of naphthoquinone derivatives in the crystalline state[171] it was found that intramolecular transfer of the hydrogen atom takes place at distances comparable with the sum of the VR of the interacting atoms. According to data given by Shklover and co-workers,[172] solid-phase polymerisation in which a bond is formed between the atoms A and B of neighbouring molecules is possible if the distance R_{AB} does not exceed the quantity $(R_A + R_B + 0.5)$ Å.

An analysis of the intermolecular contacts in a hypothetical layer of molecules of 4,4'-diazidobiphenyl ($N_3-C_6H_4-C_6H_4-N_3$) (the structure of this layer was found by calculation using the method of flow trajectories and atom–atom potentials) made it possible to interpret the mechanism of the solid-phase polymerisation, accompanied by photolysis with the removal of two N_2 molecules and the formation of a nitrene radical.[173] The distance between the central N(1) atom of the azide group of one molecule and the N(2) atom joined to the aromatic ring of a neighbouring molecule is 3.0 Å, that is it is equal to the VR of the nitrogen atom. At the same time, the distance between N(2) and the nearest H atom of a neighbouring molecule (4.4 Å) is much greater than the length of the normal contact between these atoms (2.64 Å). This structure of the crystal should facilitate the reaction of the nitrene with the azide group of a neighbouring molecule and creates definite hindrance for the reaction with the removal of hydrogen; this is confirmed by analysis of the photolysis products.

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Van der Waals radii have been known for more than 50 years. They first appeared in crystal chemistry, and have subsequently found extensive application in the most varied branches of physical chemistry, in particular in the study of the mechanism of chemical reactions. The present review is the first attempt to present this topic systematically, and it naturally does not deal with all methods (and all conceivable methods) of using this simple and extremely effective concept. The material presented, however, demonstrates the variety of chemical applications of van der Waals radii.

References

1. F H Allen, O Kennard, D G Watson, et al. *J. Chem. Soc., Perkin Trans. 2*, 1987, S1
2. T V Timofeeva, N Yu Chernikova, P M Zorkii *Usp. Khim.*, 1980, **49**(6) 966 [English translation in *Russ. Chem. Rev.*, 1980(6)]; U Burkert, N L Allinger *Molecular Mechanics* (Translated into Russian), Izd. Mir, Moscow, 1986, 364 pp
3. A J Pertsin, A I Kitaigorodskii *The Atom–Atom Potential Method*, Springer Verlag, Berlin, Heidelberg, 1987, 397 pp
4. E Mack *J. Am. Chem. Soc.*, 1932, **54** 2141
5. N V Sidgewick *Annu. Rep. Prog. Chem.*, 1933, **29** 64
6. G Albrecht, R B Corey *J. Am. Chem. Soc.*, 1939, **61** 1087
7. L Pauling *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*, Cornell Univ. Press, London, 1939, 429 pp; 3rd Ed., 1960, 644 pp
8. A I Kitaigorodskii *Organicheskaya Kristallokhimiya* (Organic Crystal Chemistry), Izd. Akad. Nauk SSSR, Moscow, 1955, 558 pp
9. A I Kitaigorodskii *Molekulyarnye Kristally* (Molecular Crystals), Izd. Nauka, Moscow, 1971, 424 pp
10. R J Good, C J Hope *J. Chem. Phys.*, 1970, **53** 540
11. Yu V Zefirov, P M Zorkii *Zh. Strukt. Khim.*, 1974, **15** 118
12. P M Zorkii, M A Porai-Koshits, L M Prezman, G P Murave'eva *Zh. Strukt. Khim.*, 1969, **10** 633
13. Yu V Zefirov, M A Porai-Koshits *Zh. Strukt. Khim.*, 1980, **21**(4) 150
14. Yu V Zefirov, M A Porai-Koshits *Zh. Strukt. Khim.*, 1986, **27**(2) 74
15. Yu V Zefirov, P M Zorkii *Zh. Strukt. Khim.*, 1976, **17**(4) 745
16. A A Bondi *J. Phys. Chem.*, 1964, **68** 441
17. W Bolton *Acta Crystallogr.*, 1964, **17** 147
18. S C Nyburg, C H Faerman *Acta Crystallogr., Sect. B*, 1985, **41** 274
19. N A Ryabova, V I Ponomarev, V V Zelentsov, L O Atovmyan *Kristallografiya*, 1982, **27** 81
20. G V Romanenko, N V Podberezskaya, V V Bakakin *Zh. Strukt. Khim.*, 1985, **26**(5) 103
21. Yu A Simonov, M A Yampol'skaya, G S Matuzenko, et al. *Zh. Neorg. Khim.*, 1986, **31**(4) 941 [English translation in *Russ. J. Inorg. Chem.*, 1986(4)]
22. P M Zorkii, Yu V Zefirov *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1972, (5) 590
23. Yu V Zefirov, P M Zorkii *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1978, **19** 554, 678
24. V K Bel'skii, P M Zorkii *Zh. Strukt. Khim.*, 1970, **11** 75
25. Yu V Zefirov, P M Zorkii *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1979, **20** 104
26. L D Arutyunyan, V I Ponomarev, L O Atovmyan, et al. *Koord. Khim.*, 1979, **5** 943
27. C Roemming, P E Hansen *Acta Chem. Scand.*, Ser. A, 1979, **33**(4) 251
28. P M Zorkii, Ya M Nesterova *Zh. Strukt. Khim.*, 1986, **27**(1) 115
29. A S Batsanov, Yu T Struchkov *Zh. Strukt. Khim.*, 1984, **25**(4) 150
30. T S Kuntsevich, T N Tarkhova, I V Khoroshun *Zh. Strukt. Khim.*, 1982, **23**(1) 111
31. L Pauling, R B Corey, *Proc. Natl. Acad. Sci. USA*, 1951, **37** 235; *Proc. R. Soc. London B*, 1953, **141** 21
32. J D Watson, F H C Crick *Nature (London)*, 1953, (171) 738

33. V P Chuprina, V I Poltev *Nucl. Acid. Res.*, 1983, **11** 5205
34. Yu V Zefirov, P M Zorkii *Zh. Strukt. Khim.*, 1976, **17** 994
35. T Atabaev, Yu V Gatilov, N V Podberezskaya, et al. *Zh. Strukt. Khim.*, 1982, **23** 179
36. G C Pimentel, A L McClellan *The Hydrogen Bond* (Translated into Russian), Izd. Mir, Moscow, 1964, 462 pp
37. W C Hamilton, J A Ibers *Hydrogen Bonding in Solids*, Benjamin, New York, 1968, 284 pp
38. Yu V Zefirov *Zh. Obshch. Khim.*, 1976, **46** 2636
39. Z Rahim, B N Barman *Acta Crystallogr., Sect. B*, 1978, **34** 761
40. J A Kanters, J Kroon, A F Peerdeman, C A Vliegenthart *Nature (London)*, 1969, (222) 370
41. C E Nordman, A S Weldon, A L Patterson *Acta Crystallogr.*, 1960, **13** 418
42. H M Berman, S H Kim *Acta Crystallogr., Sect. B*, 1968, **24** 897
43. J Hvoslef *Acta Crystallogr.*, 1968, **24** 23
44. B P van Eijck, J A Kanters, J Kroon *Acta Crystallogr.*, 1965, **19** 435
45. V I Poltev, Doctoral Thesis, Institute of Biological Physics, Academy of Sciences of the USSR, Pushchino, 1985, 360 pp
46. V I Poltev, N V Shulyupina *Mol. Biol.*, 1984, **18** 1549
47. L Kh Minacheva, V G Sakharova, G G Sadikov, et al. *Koord. Khim.*, 1986, **12** 266
48. M Yu Antipin, Yu T Struchkov *Zh. Struct. Khim.*, 1984, **25**(1) 122
49. N G Furmanova, V I Naddaka, V P Krasnov *Zh. Strukt. Khim.*, 1981, **22**(4) 188
50. Yu V Zefirov *Zap. Vses. Miner. Obshch.*, 1985, **114**(3) 384
51. Yu V Zefirov *Zh. Strukt. Khim.*, 1981, **22**(2) 194
52. E D Stevens *Mol. Phys.*, 1979, **37** 27
53. B Vonnegut, B E Warren *J. Am. Chem. Soc.*, 1936, **58** 2459
54. A I Kitaigorodskii, T L Khotsyanova, Yu T Struchkov *Zh. Fiz. Khim.*, 1953, **27** 780
55. V K Bel'skii, L A Chetkina, P M Zorkii, G A Gold'er *Kristallografiya*, 1970, **15** 262
56. A I Kitaigorodskii, P M Zorkii, V K Bel'skii *Stroenie Organicheskogo Veshchestva* (The Structure of Organic Substances), Izd. Nauka, Moscow, 1980, Vol. 1, 646 pp; 1982, Vol.2, 509 pp
57. G N Tishchenko, P M Zorkii, M A Porai-Koshits *Zh. Strukt. Khim.*, 1961, **2** 434
58. D Grdenic *Quart. Rev.*, 1965, **19** 303
59. O G Matyukhina, A N Sobolev, L Ya Pech, et al. *Zh. Strukt. Khim.*, 1985, **26**(2) 113
60. A J Canty, G B Deacon *Inorg. Chim. Acta*, 1980, **45** L225
61. N G Bokii, Yu T Struchkov, D N Kravtsov, E M Rokhlin *Zh. Strukt. Khim.*, 1973, **14** 502
62. P M Zorkii, M A Porai-Koshits in Ya I Gerasimov, P A Akishin (Editors) *Sovremennye Problemy Fizicheskoi Khimii* (Current Problems in Physical Chemistry), Izd. Mosk. Gos. Univ., Moscow, 1968, Vol. 1, p. 98
63. C Stora, N Poyer *Bull. Soc. Chim. Fr.*, 1966, (3) 841
64. O G Matyukhina, A N Sobolev, Ya E Leeis, et al. *Koord. Khim.*, 1985, **11** 264
65. T N Tarkhova, E V Chuprunova, M A Simonov, N V Belov *Kristallografiya*, 1977, **22** 1004
66. M Yu Antipin, A M Ellern, V F Sukhoverkhov, et al. *Dokl. Akad. Nauk SSSR*, 1984, **279** 892
67. P M Zorkii in Ya M Kolotyrkin (Editor) *Fizicheskaya Khimiya. Sovremennye Problemy* (Physical Chemistry. Current Problems), Izd. Khimiya, Moscow, 1982, p. 134
68. P M Zorkii, M A Porai-Koshits *Kristallografiya*, 1961, **6** 655
69. P M Zorkii, M A Porai-Koshits *Kristallografiya*, 1967, **12** 989
70. L M Prezman, P M Zorkii *Zh. Strukt. Khim.*, 1971, **12** 1044
71. A V Dzyabchenko *Zh. Strukt. Khim.*, 1987, **28**(6) 59
72. P M Zorkii, V K Bel'skii in Ya I Gerasimov, P A Akishin (Editors) *Sovremennye Problemy Fizicheskoi Khimii* (Current Problems in Physical Chemistry), Izd. Mosk. Gos. Univ., Moscow, 1970, Vol. 4, p. 379
73. V G Dashevskii *Konformatsii Organicheskikh Molekul* (The Conformations of Organic Molecules), Izd. Khimiya, Moscow, 1974, 432 pp
74. W J Orville-Thomas in W J Orville-Thomas (Editor) *Internal Rotation in Molecules* (Translated into Russian), Izd. Mir, Moscow, 1977, 510 pp
75. R P Shibaeva, L P Rozenberg *Kristallografiya*, 1980, **25** 268
76. M I Matsaberidze, A S Batsanov, R G Gerr, et al. *Koord. Khim.*, 1985, **11** 411
77. C W Bunn, E R Howells *Nature (London)*, 1954, (174) 549
78. G Natta, P Corradini *Nouv. J. Chim.*, 1960, **15** (1) 40
79. G G Aleksandrov, Z T Struchkov, V N Knyazev, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, (8) 1802
80. G Bunick, D Voet *Acta Crystallogr., Sect. B*, 1974, **30** 1651
81. S B Bulgarevich, E G Amarskii, A A Shvets, O A Osipov *Zhur. Org. Khim.*, 1976, **46** 1708
82. V I Sokol, Yu V Zefirov, M A Porai-Koshits *Koord. Khim.*, 1979, **5** 1249
83. L G Kuz'mina, Yu T Struchkov, A I Nekhaev *Zh. Strukt. Khim.*, 1972, **13** 1115
84. N G Bokii, Yu T Struchkov, B Ya Simkin, et al. *Zhur. Strukt. Khim.*, 1978, **19** 866
85. D S Yufit, Yu T Struchkov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, (2) 2724
86. N B Kaz'mina, B A Kvasov, M Yu Antipin, et al. *Zh. Org. Khim.*, 1986, **22** 1678
87. M Yu Antipin, Yu T Struchkov, E G Ter-Gabrielyan, N P Gambaryan *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, (3) 588
88. A N Chernega, M Yu Antipin, Yu T Struchkov, et al. *Zh. Strukt. Khim.*, 1984, **25**(2) 122
89. N G Bokii, Yu T Struchkov, A E Kalinin, et al. *Itogi Nauki i Tekhniki. Kristallokhimiya* (Progress in Science and Technology. Crystal Chemistry), Izd. VINITI, Moscow, 1977, Vol. 12, p. 52
90. V R Polishchuk, M Yu Antipin, V I Bakhmutov *Dokl. Akad. Nauk SSSR*, 1979, **249** 1125
91. B A Arbuzov, O A Erastov, G N Nikonov, et al. *Dokl. Akad. Nauk SSSR*, 1982, **267** 650
92. L M Dikareva, M A Porai-Koshits, G G Sadikov, et al. *Zh. Neorg. Khim.*, 1978, **23**(4) 1044 [English translation in *Russ. J. Inorg. Chem.*, 1978(4)]
93. F A Cotton, B G DeBoer, M D LaPrade, et al. *J. Am. Chem. Soc.*, 1970, **92** 2926
94. A S Sadykov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, (11) 2432
95. A A Pasynskii, A S Antsyshkina, Yu V Skripkin, et al. *Zh. Neorg. Khim.*, 1981, **26**(9) 2435 [English translation in *Russ. J. Inorg. Chem.*, 1981(9)]
96. M Kurahashi *Bull. Chem. Soc. Jpn.*, 1974, **47** 2067
97. V M Kozhin *Zh. Strukt. Khim.*, 1968, **9** 671
98. M Yu Antipin, Yu T Struchkov, N I Delyagina, I L Knunyants *Kristallografiya*, 1983, **28** 280

99. A T Hutton, H M N Irving, K R Koch, et al. *J. Chem. Soc., Chem. Commun.*, 1979, (2) 57
100. S Aleby *Acta Crystallogr., Sect. B*, 1974, **30** 2877
101. A I Kitaigorodskii *Smeshannye Kristally* (Mixed Crystals), Izd. Nauka, Moscow, 1983, p. 29
102. G S Belikova, L M Belyaev in A V Shubnikov, N N Sheftal' (Editors) *Rost Kristallov* (The Growth of Crystals), Izd. Akad. Nauk SSSR, Moscow, 1961, Vol. 3, p. 316
103. E V Shpol'skii *Usp. Fiz. Nauk*, 1963, **80** 255
104. A A Askadskii *Usp. Khim.*, 1977, **46**(6) 1122 [English translation in *Russ. Chem. Rev.*, 1977(6)]
105. A A Askadskii, Yu I Matveev *Khimicheskoe Stroenie i Fizicheskie Svoistva Polimerov* (The Chemical Structure and Physical Properties of Polymers), Izd. Khimiya, Moscow, 1983, 248 pp
106. A A Askadskii, E G Gal'pern, T P Matveeva, et al. *Vysokomol. Soedin., Ser. A*, 1987, **29** 2433
107. D W van Krevelen *Properties of Polymers*, Elsevier, Amsterdam, 1972, 427 pp
108. A A Askadskii *Deformatsiya Polimerov* (The Deformation of Polymers), Izd. Khimiya, Moscow, 1973, p. 53
109. S L Sosin, Yu V Shevchenko, A A Askadskii *Vysokomol. Soedin., Ser. A*, 1977, **19** 1088
110. A A Askadskii, O A Mel'nik, G L Slonimskii, et al. *Vyoskomol. Soedin., Ser. A*, 1985, **27** 151
111. A A Abramzon, S I Goloudina *Izv. Vys. Ucheb. Zaved. SSSR, Khim. Khim. Tekhnol.*, 1985, **28**(10) 28
112. V I Troitskii *Kristallografiya*, 1986, **31** 997
113. V I Troitskii, Yu M L'vov, L A Feigin *Dokl. Akad. Nauk SSSR*, 1987, **295** 373
114. A K Lyashchenko, A S Lileev *Koord. Khim.*, 1984, **10** 1607
115. T V Lesnichaya *Ukr. Khim. Zh. (Russ. Ed.)*, 1987, **53** 1277
116. Yu I Dolzhenko, T Inabe, Yu Maruyama, Bull. Chem. Soc. Jpn., 1986, **59** 563
117. Yu V Isaev, Yu N Novikov, M E Vol'pin, Synthetic Metals, 1982, **5** 23
118. G V Tsitsishvili, T G Andronikashvili, G N Kirov, L D Filizova *Prirodnye Tseolity* (Natural Zeolites), Izd. Khimiya, Moscow, 1985, p. 16
119. F D Cramer *Einschlussverbindungen* (Translated into Russian), Izd. Inostr. Lit., Moscow, 1958, 169 pp
120. G N Chekhova, Yu A Dyadin *Izv. Sib. Otd. Akad. Nauk SSSR, Ser Khim. Nauk*, 1986, (2) 66
121. V R Melik-Adamyan, V V Barynin, A A Vagin, et al. *Kristallografiya*, 1987, **32** 638
122. V I Klassen, V A Mokrousov *Vvedenie v Teoriyu Flotatsii* (Introduction to the Theory of Flotation), Gosgortekhizdat, Moscow, 1959, p. 309
123. M Yu Antipin, Yu T Struchkov, E S Kozlov *Zh. Strukt. Khim.*, 1985, **26**(4) 96
124. N G Bolii, G N Zakharova, Yu T Struchkov *Zh. Strukt. Khim.*, 1967, **8** 501
125. Yu N Gachegov, G B Soifer *Zh. Strukt. Khim.*, 1984, **25**(8) 158
126. R P Shibaeva *Itogi Nauki i Tekniki. Kristallokhimiya* (Progress in Science and Technology. Crystal Chemistry), 1981, Vol. 15, p. 189
127. L P Gor'kov *Usp. Fiz. Nauk*, 1984, **144** 381
128. A I Buzdin, L N Bulaevskii *Usp. Fiz. Nauk*, 1984, **144** 415
129. I Shirotani, H Kobayashi *Bull. Chem. Soc. Jpn.*, 1973, **46** 2595
130. D Jerome, A Mazaud, M Ribault, K Bechgaard *J. Phys. Lett. (Fr.)*, 1980, **41** L-49
131. K Bechgaard, K Carneiro, M Olsen, et al. *Phys. Rev. Lett.*, 1981, **46** 852
132. S S P Parkin, M Ribault, D Jerome, K Bechgaard *J. Phys., Ser. C*, 1981, **14** 5305
133. F Wudl *J. Am. Chem. Soc.*, 1981, **103** 7064
134. R N Lyubovskaya, R B Lyuboskii, R B Shibaeva, et al. *Pis'ma Zh. Eksp. Teor. Fiz.*, 1985, **42** 380
135. R P Shibaeva, R M Lobkovskaya, E B Yagubskii, E E Kostyuchenko *Kristallografiya*, 1986, **31** 455
136. V F Kaminskii, V N Laukhin, V A Merzhanov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, (2) 342
137. T G Takhirov, O N Krasochka, O A D'yachenko, et al. *Khim. Fiz.*, 1988, **7**(2) 151
138. S S Nagapetyan, E R Arakelova, L V Belousova *Zh. Neorg. Khim.*, 1988 **33**(1) 160 [English translation in *Russ. J. Inorg. Chem.*, 1988(1)]
139. R Kato, H Kobayashi, A Kobayashi, Y Sasaki *Chem. Phys. Lett.*, 1985, 131
140. E B Yagubskii, L Yu Ukhin, V E Shklover, et al. *Dokl. Akad. Nauk SSSR*, 1986, **290** 115
141. M Z Aldoshina, L O Atovmyan, L M Gol'denberg, et al. *Dokl. Akad. Nauk SSSR*, 1986, **289** 1140
142. R P Shibaeva, R M Lobkovskaya, V F Kaminskii, et al. *Kristallografiya*, 1986, **31** 920
143. O I Kolodyazhnyi, I V Shevchenko, V P Kukhar' *Zh. Org. Khim.*, 1983, **53** 1233
144. W Littke, U Drueck *Angew. Chem.*, 1979, **91** 434
145. S M Aldoshin, A S Kholmanskii, L O Atovmyan *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 576
146. B P Biryukov, B V Unkovskii *Itogi Nauki i Tekhniki. Kristallokhimiya* (Progress in Science and Technology. Crystal Chemistry), 1974, Vol. 9, p. 110; 1976, Vol. 11, p. 132
147. O E Kompan, M Yu Antipin, Yu T Struchkov, et al. *Zh. Org. Khim.*, 1985, **21** 2032
148. V K Bel'skii, I I Zviedre, S V Belyakov, et al. *Izv. Akad. Nauk Latv. SSR, Ser. Khim.*, 1985, 246
149. L N Zakharov, G A Domrachev, Yu T Struchkov *Zh. Strukt. Khim.*, 1983, **24**(3) 75
150. R R Schrock *Acc. Chem. Res.*, 1979, **12** 98
151. M L H Green *Organometallic Compounds. Vol. 2. The Transition Metals* (Translated into Russian), Izd. Mir, Moscow, 1972, 175 pp
152. D A Bochvar, N P Gambaryan, L M Epshtein *Usp. Khim.*, 1976, **45**(5) 1316 [English translation in *Russ. Chem. Rev.*, 1976(5)]
153. L G Vorontsova, M O Dekaprilevich, O S Chizhov *Bioorg. Khim.*, 1986, **12**(2) 257
154. L G Vorontsova, M O Dekaprilevich, O S Chizhov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, (3) 604; 1985, (7) 1563
155. M O Dekaprilevich, L G Vorontsova, O S Chizhov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, (1) 72
156. A I Chernega, M Yu Antipin, Yu T Struchkov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, (6) 1304
157. C A Tolman *Chem. Rev.*, 1977, **77** 313
158. R E Rosenfield, R Parthasarathy, J D Dunitz *J. Am. Chem. Soc.*, 1977, **99** 4860
159. L A Aslanov, V M Ionov, V I Andrianov, et al. *Khim. Geterotsikl. Soedin.*, 1977, 1628
160. N G Furmanova, O E Kompan in M A Porai-Koshits (Editor) *Problemy Kristallokhimii* (Problems of Crystal Chemistry), Izd. Nauka, Moscow, 1985, p. 122

161. N G Furmanova, L P Olekhnovich, V I Minkin, et al. *Zh. Org. Khim.*, 1982, **18** 474
162. N G Furmanova, Yu T Struchkov, O E Kompan, et al. *Zh. Strukt. Khim.*, 1980, **21**(2) 83
163. L M Sitkina, A D Dubonosov, V A Bren' *Zh. Org. Khim.*, 1987, **23** 803
164. R W Taft *Steric Effects in Organic Chemistry*, Wiley, New York, 1956, p. 556
165. M Charton *J. Am. Chem. Soc.*, 1969, **91** 615
166. M Charton *Prog. Phys. Org. Chem.*, 1973, **10** 81
167. M Charton *J. Am. Chem. Soc.*, 1975, **97** 1552
168. L F Kasukhin, V P Kukhar' *Zh. Org. Khim.*, 1986, **56** 970
169. M Charton *J. Org. Chem.*, 1977, **42** 3531
170. V B Evdokimov *Zh. Fiz. Khim.*, 1986, **60**(11) 2702 [English translation in *Russ. J. Phys. Chem.*, 1986(11)]
171. J R Scheffer *Acc. Chem. Res.*, 1980, **13** 283
172. V E Shklover, N G Bokii, Yu T Struchkov *Usp. Khim.*, 1977, **46**(8) 1368 [English translation in *Russ. Chem. Rev.*, 1977(8)]
173. S V Zelentsov, A V Oleinik, L N Karyakina *Khim. Vys. Energ.*, 1986, **20** 339

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The separation of uranium isotopes by chemical isotopic exchange

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ABSTRACT. Data on the separation of uranium isotopes by chemical isotopic exchange have been reviewed. Promising methods for enriching uranium have been compared.

The bibliography contains 120 references.

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I. Introduction

The industrial production of enriched uranium is based on gas diffusion (GD).[1] In many countries, however, an intensive search is being carried out to find other methods of enrichment making it possible not only to lower the cost per separative work unit (kg S. W. U.) but also to decrease considerably the consumption of raw material and energy.[1–3] As alternatives to GD, methods based on the use of the centrifuge, lasers, effusion phenomena, a rotating plasma, and chemical isotopic exchange (CIE) are being examined.[2,3] Their theoretical principles and the possibility of their practical application have been examined in a number of reviews,[2–12] and there is an extensive patent literature. The greatest interest in CIE is being shown in Japan and France,[5,6] but published systematic reviews of this topic are inadequate. Some publications[3,5,12–18] deal only with individual aspects of the use of CIE to separate uranium isotopes, and ten years have passed since the publication of the review by Filippov and co-workers,[6] which deals most fully with this problem. In this period, many new and interesting publications have appeared, which not only develop the ideas presented in earlier work but also propose various fundamentally new approaches to the solution of the problem of separating uranium isotopes by chemical methods.

Of all the methods used to separate uranium isotopes, only CIE does not require the use of gaseous compounds or the atomic vapour of uranium. The regular features observed in the isotopic enrichment of uranium by CIE may be useful in the development of methods for separating the isotopes of heavy elements which for any reason do not form stable volatile compounds.

The aim of the present review is to analyse published data on the separation of uranium isotopes by chemical isotopic exchange and to compare promising methods for enriching uranium.

II. Theoretical principles of the separation of uranium isotopes by chemical isotopic exchange

In principle, chemical methods for separating isotopes may be based on kinetic or thermodynamic isotope effects arising in chemical transformations. In both cases the magnitude of the isotope effects is determined by the differences in the zero-point energies of the vibrations of the bonds in the isotopic molecules involved in the reactions.[1,19] Since the difference in the masses of the isotopic forms of molecules or ions is small, the interatomic distances and force constants of the bonds can with good accuracy be regarded as invariant.[19]

The CIE methods used at present are mainly based on thermodynamic isotope effects, since a single separation step is reversible. In this case the separation of isotopes can easily be made a multi-stage process by using counter-current separating systems. Moreover, the expenditure of energy in these processes is determined chiefly by the organisation of the phase reversal.[19]

In schemes for enriching uranium by CIE, the most widely encountered systems are those in which the isotopic exchange takes place between forms which do not react chemically and which are selectively distributed between two phases. The equilibrium constant of the isotopic exchange reaction (K) and hence the isotope separation coefficient (α) can be calculated by statistical thermodynamics.[1,19] In particular, for the heavy hydrogen isotopes, use is made of the approximate Bigeleisen–Mayer equation,[19] from which it follows that the values of $\ln\alpha$ are proportional to the square of the reciprocal of the mass of the isotope. Thus for CIE reactions in uranium compounds, very low values of α can be expected. The observed isotopic effects can be increased, however, by making use of complex processes in which the values of α for the elementary reactions act in the same direction and increase the overall effect. To determine the regular features of the change in the values of α in CIE processes, it has been proposed that isotopic exchange reactions be classified using three factors: the oxidation state of the element, the nature of the coordinated ligand, and the configuration of the coordination sphere.[20–22] The highest values of α should be achieved in systems in which the compounds being compared differ from one another to the greatest extent in terms of all three factors. The element in the

higher oxidation state should be combined with σ,π-donor ligands (N, O, F), and should form an unsaturated coordination sphere. For the element in the lower oxidation state, the coordinated ligands should have σ,π-donor and weak π-acceptor properties (Cl, Br, I, S, Se), and the coordination sphere should be close to saturation. Under real conditions, only a certain approximation to the optimum systems is possible, since the selection principles are contrary to the requirements for thermodynamic stability. Systems containing elements in different oxidation states are most promising, systems containing complexes with different configurations occupy second place, and systems differing only in the ligands are least promising.

A theoretical analysis of the values of α in isotopic fractionation in $U^{IV}-U^{VI}$ systems has been carried out.[23-26] The values of K have been calculated for the reactions:[23]

$$[^{235}U(H_2O)_8]^{4+} + [^{238}UO_2]^{2+} \rightleftarrows [^{238}U(H_2O)_8]^{4+} + [^{235}UO_2]^{2+},$$
$$^{235}U(H_2O)_4Cl_4 + [^{238}UO_2]^{2+} \rightleftarrows {}^{238}U(H_2O)_4Cl_4 + [^{235}UO_2]^{2+}.$$

At 20 °C, ^{235}U should be concentrated as UO_2^{2+} if the distances $U-H_2O$ in $[U(H_2O)_8]^{4+}$ and $U(H_2O)_4Cl_4$ are shorter than 2.26 Å and 2.30 Å respectively. X-Ray diffraction data indicate that these conditions are satisfied. The wavenumbers of the doubly degenerate (ν_2) and antisymmetric (ν_3) vibrations of the U−O bonds have been used to calculate the ratios of the reduced partition functions (RPF) of the UO_2^{2+} ion in its compounds with ClO_4^-, Cl^-, NO_3^-, and SO_4^{2-}.[24] The contribution of ν_3 to the RPF is 85% at 25 °C, and increases with increase in temperature. The equilibrium constants of the CIE reactions involving UO_2^{2+} are sensitive to changes in ν_2 resulting from complex formation. The separation coefficient for the isotopes ^{235}U and ^{238}U in U^{IV}–U^{VI} systems in the presence of cation exchangers is given by the expression[25,26]

$$\ln\alpha = \ln\alpha' + \ln[1 + (K-1)/(1+\bar{\rho})] + \ln[1 + (K^{-1}-1)/(1+\rho)], \quad (1)$$

where α' is the separation coefficient for the system containing only uranyl ions, K the equilibrium constant of the CIE reaction between U^{IV} and U^{VI} in solution, and ρ and $\bar{\rho}$ the molar ratios of U^{VI} and U^{IV} in solution and in the ion exchanger respectively.

It follows from Eqn. (1) that the influence of K on α is greater, the greater the difference between ρ and $\bar{\rho}$, that is the higher the selectivity of the sorption of the ionic forms of uranium. The concentration profiles of the elution curves, and equations relating the concentrations of the ith isotope to the position of the band in the column have been obtained, and the way in which the overall separation coefficient is related to the local values of α and the time taken to establish the steady state has been determined.[26,27]

To select the best method for separating uranium isotopes, it is also necessary to take account of economic factors. It has been suggested[5] that to be competitive, CIE methods must satisfy the following requirements:

1) the values of α should be not less than 10^{-3};

2) the chemical forms taking part in the exchange should be stable and should be distributed selectively between the phases;

3) the time for which uranium is involved in an elementary step should not exceed 1 min;

4) an effective means of phase reversal must be available.

The average consumption of energy should be about 5 eV per atom for reflux streams of high intensity.

III. The separation of uranium isotopes by ion exchange

1. Reactions involving U^{VI}

The results of experiments on the separation of uranium isotopes in a system formed by a uranyl salt solution and a sulphonic acid cation exchanger were published in 1954.[28] UO_2^{2+} was eluted through a column of Dowex 50 × 8 resin (50–100 mesh) in the Cu-form using a 5×10^{-3} M solution of $(NH_4)_2MgA$, where H_4A = EDTA. For a UO_2^{2+} band length of 28 cm and a migration distance of 90 cm, the specimen was enriched in the ^{235}U isotope from 4% to 5% at the front of the band. The isotopic fractionation took place as a result of the isotopic exchange reaction

$$[^{238}UO_2A]_s^{2-} + [^{235}UO_2]_r^{2+} \rightleftarrows [^{235}UO_2A]_s^{2-} + [^{238}UO_2]_r^{2+},$$

where the subscripts 's' and 'r' refer to the solution and resin phases respectively. In this system, phase reversal is described by the following equations:

$$[UO_2A]_s^{2-} + Cu_r^{2+} \rightarrow [UO_2]_r^{2+} + CuA^{2-} \text{ (sorption)}, \quad (2)$$
$$[UO_2]_r^{2+} + (NH_4)_2MgA \rightarrow [UO_2A]_s^{2-} \text{ (desorption)}. \quad (3)$$

Equilibria (2) and (3) are displaced to the right, so that both band fronts remain sharp during the elution, and no change in the band length takes place. This method of elution was called the Spedding method, after one of the authors.[28] In the process studied, the value of α for $^{235}U/^{238}U$ reached 1.002. It was later established[29] that in fact, $\alpha = 1.00006 \pm 0.00005$. The Spedding method has also been used to study isotopic replacement reactions in a cation exchanger–solution system using a column of length 1–2 m filled with Amberlite IR-120 or Dowex 50 × 8 resin in the H^+-form.[30] The sorption was carried out from $UO_2(NO_3)_2$, UO_2Cl_2, $UO_2(ClO_4)_2$, and $UO_2(SO_4)$ solutions. Solutions of ammonium acetate, citrate, and tartrate were used as eluants. The values of α obtained varied in the range 1.0001–1.0004. The values of α obtained using Dowex 50 × 8 resin were higher than those obtained using Amberlite IR-120.

Table 1. Isotopic enrichment in UO_2^{2+}–cation exchanger systems.[31-34]

Eluant	pH	Rate of elution, ml h^{-1}	Length of migration, cm	Rate of movement of the band, cm h^{-1}	$10^4\,\varepsilon$
Perchlorate	—	—	—	—	0.0±0.1
Chloride	7	9.5	197	1.85	0.25±0.1
Tricarballylate	—	—	—	—	0.66±0.1
Acetate	5	6.9	197	0.51	0.88±0.1
Glycollate	7	7.8	198	0.83	1.03±0.1
Lactate	7	7.0	203	0.80	1.42±0.15
Citrate	—	—	—	—	1.80±0.15
Malonate	7.5	6.3	200	1.4	2.18±0.2

Note. LS-6 cation exchanger (H^+-form, 100–200 mesh), 25 °C, column diameter 1 cm, eluant concentration 0.1 M; $\varepsilon = \alpha - 1$.

The Spedding method has been used to study the isotopic fractionation of uranium in a uranyl–cation exchanger system with elution by solutions of ammonium carboxylates or $NiCl_2$.[31-34] The results are given in Table 1. Enrichment in ^{235}U takes place at the

elution front, that is the carboxylate form of the uranyl complexes is enriched. The correlation between $\varepsilon = \alpha - 1$ and the wavenumbers ν_3 (cm^{-1}) of the antisymmetric vibrations of the UO_2^{2+} group in the complexes is given by the equation

$$\varepsilon = 4.62 \cdot 10^{-6}(960 - \nu_3),$$

where 960 cm^{-1} is the value of ν_3 in the resin phase. The data in Table 1 show good agreement with the results of a study[35] in which the eluant used for UO_2^{2+} sorbed on Dowex 50 resin was 0.07–0.22 M ammonium α-hydroxyisobutyrate solution (pH 2–6). The enrichment in ^{235}U took place in the solution phase, and the value of ε, $(1.9–0.6) \times 10^{-4}$, depended on the pH of the eluant.

The isotopic fractionation of uranium in UO_2^{2+}–cation exchanger systems with desorption by complex-forming reagents is also being studied in China.[36] It has been found[37] that the isotopic effects in UO_2^{2+}–anion exchanger systems are lower than those in cation-exchange chromatography.

Table 2. Isotopic fractionation of uranium in U^{IV}–cation exchanger systems.[38–41]

Eluant solution	Temperature, °C	Percentage cross-linking of resin	Length of column, m	Enrichment in $^{235}U^*$ relative to natural uranium, %
0.3 M NH_4Cl, HCl	30	10	12	4.9
0.45 M NH_4Cl, HCl	60	12	12	5.5
0.4 M NH_4Cl, HCl	—	15	12	6.2
0.15 M Na_2SO_4	40	20	10	3.3
0.2 M Na_2SO_4	30	16	10	2.9
0.2 M NaCl, 0.28 M HCl	—	20	8	2.8
0.2 M NaCl, 0.27 M HCl	—	10	5	1.4
0.28 M HCl	—	16	12	2.4
0.18 M H_2SO_4	35	16	10	2.0
1 M H_2SO_4	—	5	10	1.5
0.01 M NaF, 0.5 M H_2SO_4	—	—	4	1.1
Lactic acid 0.6 M	30	10	10	4.2
Sulphosalicylic acid 0.4 M	75	15	10	5.1
Citric acid				
0.1 M	60	12	10	4.6
0.5 M	—	—	4	0.8

*The enrichment takes place in the 'trailing' part of the elution curve.

2. Reactions involving U^{IV}

Japanese workers[38–41] have developed methods for separating uranium isotopes in U^{IV}–cation exchanger systems with elution by various complex-forming reagents (Table 2). Strongly acidic styrene–divinylbenzene cation exchange resins with different degrees of cross-linking have been used. In contrast to the systems containing UO_2^{2+}, with U^{IV} the enrichment in ^{235}U takes place in the resin phase, and the values of ε are lower for U^{IV} than for the uranyl ion. If U^{IV} is desorbed using pure H_2SO_4 solutions, marked spreading of the uranium zone is observed, so that solutions of $MgSO_4$ or an $H_2SO_4 + MgSO_4$ mixture have been proposed as eluants.[39,40] The value of ε when an $MgSO_4 + H_2SO_4$ mixture was used was 5×10^{-5}.[39]

In the elution of U^{IV} with solutions of citric,[41] malonic, and lactic[42] acids, the elementary separation coefficient decreases with increase in temperature. The values of ε are approximately the same for all three acids. The value for citric acid is 6×10^{-5} at 50°C.[41]

A method for separating uranium isotopes in a U^{IV}–anion exchanger system has been patented.[43] Uranium(IV) was sorbed on a chloromethylated or aminated styrene–divinylbenzene anion exchange resin from a solution containing NH_4HSO_4. The uranium was desorbed using an $NH_4HSO_4 + H_2SO_4$ mixture. In a column of length 10 m, enrichment in the ^{235}U isotope by 10% relative to the original concentration took place at the front of the elution curve.

Thus the single-stage separation coefficients of uranium isotopes in ion-exchange systems containing different ionic forms of the metal in the same oxidation state are too low for these systems to be used on the industrial scale. Recently, however, systems in which the enrichment coefficient ε reaches 10^{-3} have been found. Thus in the isotopic exchange reaction between U^{VI} extracted by a 0.1 M solution of the macrocyclic polyether dicyclohexyl-18-crown-6 in 1,2-dichloroethane and U^{VI} in an aqueous solution containing 3.1–3.9 M HCl, enrichment of the organic phase in the ^{235}U isotope was observed, and the calculated value of α was 1.002 ± 0.004.[44] In the corresponding system containing U^{IV}, enrichment of the organic phase in the light isotope was again observed, and the coefficient α was 1.001 ± 0.0003.[45] An interesting feature is that the separation coefficients for $^{235}U/^{238}U$ and $^{40}Ca/^{42}Ca$ in the systems containing the crown ether were found to be close to one another ($\alpha = 1.0010 \pm 0.0002$ for $^{40}Ca/^{42}Ca$).[46] The reasons for these high isotopic effects in the uranium systems are not yet clear.

IV. The isotopic fractionation of uranium in electron exchange processes

1. The U^{IV}–U^{III} system

The values of α can be increased considerably by using systems in which uranium is present in different oxidation states in the compounds undergoing exchange. The U^{IV}–U^{III} system has been proposed as one such system.[47–51] The different oxidation states are separated using ion exchange resins[47] or various extracting agents.[47–51]

In the ion exchange method, U^{IV} is sorbed from 8 M HCl solution, and U^{III} remains in the aqueous phase. When a cation exchanger is used, U^{III} is sorbed, and U^{IV} remains in the aqueous solution containing 0.25 M H_2SO_4. In both cases, U^{IV} is enriched in the ^{235}U isotope. The values obtained for α were 1.0024 and 1.0020 for the anion exchanger and the cation exchanger respectively. In practice, it is difficult to use ion exchangers, because of the instability of U^{III}.

It is recommended that in extraction systems, U^{IV} be transferred to the organic phase as its complexes with alkyl phosphates, phosphine oxides, phosphonates, or phosphinates. The organic diluents used are benzene, toluene, dodecane, or kerosene. The results of the experiments are given in Table 3. The isotopic fractionation involves the reaction

$$^{235}U^{III}_{aq} + {}^{238}U^{IV}_{org} \rightleftarrows {}^{235}U^{IV}_{org} + {}^{238}U^{III}_{aq}.$$

Since appreciable rearrangement of the structure of the species involved in the exchange is not required, this reaction is rapid, and its kinetic charactersitics are determined by the inter-phase transfer time. Irrespective of the extracting agent, the U^{IV} compound is enriched in the light isotope ^{235}U.

It is desirable that the separation of uranium isotopes in extraction systems be carried out by the counter-current method; the aqueous phase should contain 0.1–2.5 M UCl_3 and 4–9 M HCl, and the organic phase 0.1–1 M U^{IV}. To prevent the oxidation of U^{III}, the process must be carried out in a nitrogen atmosphere, and the reagents should be free from ions which catalyse the oxidation of U^{III}. It has also been suggested that reagents combining with oxygen should be introduced into the system.

It is recommended that phase reversal be carried out electrochemically.[51] Zinc amalgam (1.1–1.8% Zn) can be used as the cathode to reduce U^{IV} in the aqueous phase. The solution used for the electrolysis should contain 4–5 M $ZnCl_2$. Under these conditions, liberation of gas does not take place in the reduction of U^{IV}. The anode for oxidising U^{III} may consist of lead, lead amalgam, graphite, mercury, or tantalum; the best characteristics are shown by lead.

2. The CHEMEX process

In 1977 it was reported that an industrial method had been developed in France for obtaining uranium with a low degree of enrichment (up to 3.5% ^{235}U) from natural raw material by isotopic exchange in an extraction system (the CHEMEX process).[52] Later, various characteristics of this process were described in more detail.[18,53–56] The isotopic exchange between U^{IV} in the organic phase and U^{III} in the aqueous phase is carried out in plastic pulsation counter-current columns with a diameter of 1.2 m and a height of 30 m. Organophosphorus compounds are used as the extracting agents. The rate of the overall process is determined by the kinetics of inter-phase transfer. The kinetic charactersitics give an efficiency of up to 200 kg S. W. U. per year for a column volume of 1 m^3. The value of the single-stage separation coefficient reaches 1.0025. Phase reversal is achieved electrochemically in a cell with a graphite anode and a dropping mercury cathode. U^{IV} is reduced in the aqueous phase. The self-oxidation of U^{III} is prevented using a patented method.[50] The overall scheme of the CHEMEX process is shown in Fig. 1.

The cascade for the production from natural uranium of 250 000 kg S. W. U. per year of product with an enrichment of 3.5% in ^{235}U includes 20 identical extraction columns. The production of 50 tons of uranium with an enrichment of 3.5% requires 250 tons of natural uranium. 200 tons of depleted uranium (0.2% ^{235}U) are produced. The output is doubled by combining two identical cascades in a module (Fig. 2). The expected energy consumption is 300 kW per kg S. W. U.

The French Atomic Energy Commission proposes in 1990 to begin the construction of a plant with a capacity of 10^6 kg S. W. U. per year, consisting of two parallel modules and containing 80 exchange columns. The contruction will cost 25–30 million dollars. To develop the method, a model assembly was constructed in 1970, and in March 1985 a pilot plant consisting of a module with dimensions one tenth of those of the industrial assembly was brought into operation in Pierrelatte.[51] The main disadvantages of the method are in the loss of uranium in the technological cycle, and the low rate of the process, which requires the use of large-scale equipment and large quantities of uranium. The time required for the equilibrium state to be established is several months.

3. The $U^{IV}-U^{VI}$ system

a) The kinetics of electron transfer between U^{IV} and U^{VI}

In the development of the Manhattan project, it was established[58] that the equilibrium constant (K) of the exchange reaction

$$[^{238}UO_2]^{2+} + {}^{235}U\,(IV) \rightleftarrows [^{235}UO_2]^{2+} + {}^{238}U\,(IV) \qquad (4)$$

differs from 1 and is equal to 1.0012–1.0013. At that time, however, this reaction could not be used to obtain enriched uranium, because of the low values of the enrichment coefficient and the very long equilibration time.

Table 3. Separation of uranium isotopes by extraction in the $U^{IV}-U^{III}$ system.[50]

Extracting agent*	Diluent	Concentration of U^{IV} in the organic phase, M	Composition of the aqueous phase	Temperature, °C	Phase contact time, s	α
TBP	benzene	0.4	0.4 M U(III), 7 M HCl	21	15	1.0030
TBP (50%)	dodecane	0.2	0.2 M U(III), 7 M HCl	—	49—132	1.0026
TBP (40%)	kerosene	0.4	0.4 M U(III), 7 M HCl	21	15	1.0025
TBP (42%)	xylene	0.42	2.35 M U(III), 0.13 M U(IV), 1.55 M HCl	35	30	1.0028
TBP (50%)	toluene	0.42	0.4 M U(III), 8 M HCl	—	30	1.0026
n-Butyl di-isobutylphosphonate (40%)	dodecane	0.55	1 M U(III), ** 0.125 M U(IV), 4.6 M HCl	20	60	1.0025
TOPO (10%)	toluene	0.12	0.11 M U(III), 0.01 M U(IV), 5 M HCl	25	60	1.0024
Di-n-pentyl sulphoxide (2 M)	tetrachloroethane	0.44	0.43 M U(III), 0.16 M U(IV)	25	60	1.0020
Di-2-EHHP (30%)	toluene	0.08	0.08 M U(III), 4.5 M HCl, 6 M HBr	20	300	1.0020
Tri-2-methylbutyl phosphate	dodecane	0.67	0.7 M U(III), 8.2 M HCl	30	60	1.0027

*TBP = tributyl phosphate, TOPO = trioctylphosphine oxide, di-2-EHHP = di-2-ethylhexyl hydrogen phosphate.
**The given ratio between the organic and aqueous phases is 0.5.

The kinetics of the isotopic exchange reaction (4) in homogeneous solutions have been studied in considerable detail.[6] Only the main conclusions about the kinetics and mechanism of reaction (4) will be examined in the present review.

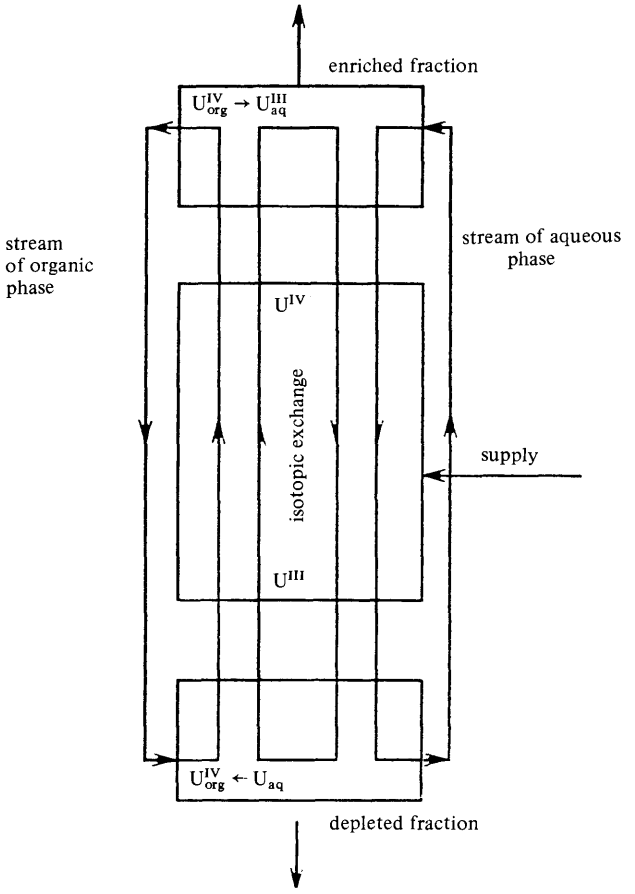


Figure 1. Diagram of the streams in the extraction column of the CHEMEX process.[18]

The order of the reaction between U^{IV} and U^{VI} with respect to the concentration of the reagents is usually fractional. In solutions with a relatively low acidity (2 M acid), its rate (R) is inversely proportional to the cube of the H^+ concentration. It has been suggested that in this acidity range the isotopic exchange mechanism includes the hydrolysis of U^{IV}. In hydrochloric acid solutions with an HCl concentration greater than 3 M, R increases with increase in the acid concentration. It has been suggested that under these conditions the exchange involves chloro-complexes of U^{IV} and U^{VI}. In H_2SO_4 and $(NH_4)_2C_2O_4$ solutions, isotopic exchange takes place between U^{IV} and U^{VI} sulphate and oxalate complexes respectively. In water–acetone and water–ethylene glycol mixtures, the orders of the reaction with respect to U^{IV}, U^{VI}, and H^+ show a complex dependence on the concentration of the organic solvent; the highest values of R are observed for a concentration of the organic component of 30–40%. The rate of reaction (4) increases considerably on ultraviolet irradiation of the solution.

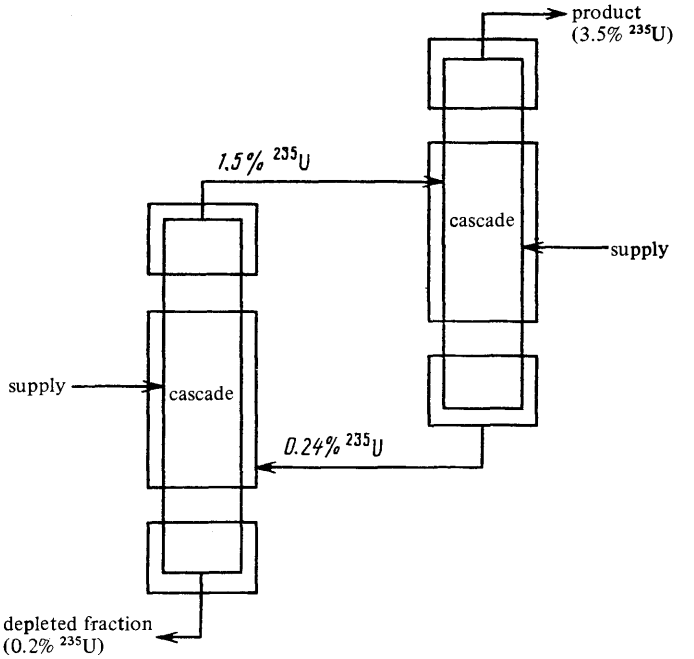


Figure 2. Industrial module of the CHEMEX process.[5]

Most authors consider that electron transfer between U^{IV} and U^{VI} involves the formation and subsequent disproportionation of U^{V}.[6]

Japanese workers studied the kinetics of isotopic exchange between U^{IV} and U^{VI} in the presence of Dowex 5 × 4 cation exchange resin[59] and Dowex 2 × 8 anion exchange resin.[60] The isotopic exchange process in the cation exchange resin involves two stages: exchange in the resin phase between U^{IV} and U^{VI}, and exchange between U^{IV} in the resin and U^{VI} in the solution. The rate of exchange in the resin phase is 10^3–10^4 times that of the corresponding reaction in the solution. The rate of exchange in the resin depends markedly on the acidity of the solution, but a corresponding relationship is not observed for the exchange in the solution. The apparent activation energies of these stages are 24.5 kJ mol^{-1} and 58.4 kJ mol^{-1} respectively.

The reaction in the anion exchange resin is described by the scheme:

$$\begin{aligned} &^{238}U(IV)_r + {}^{235}U(VI)_r \rightleftarrows {}^{235}U(IV)_r + {}^{238}U(VI)_r, \\ &^{238}U(IV)_s + {}^{235}U(IV)_r \rightleftarrows {}^{235}U(IV)_s + {}^{238}U(IV)_r, \\ &^{235}U(VI)_r + {}^{238}U(IV)_s \rightleftarrows {}^{235}U(IV)_s + {}^{238}U(VI)_r. \end{aligned} \quad (5)$$

The rate constant of reaction (5) at 30 °C is 7.3×10^{-4} litre mol^{-1} min^{-1}, which is much lower than the rate constant of the exchange in a homogeneous solution under analogous conditions. The explanation given for this phenomenon is that the concentration of acid in the resin phase is lower than that in the solution.[60] The activation

energy of reaction (5) is 96.2 kJ mol^{-1}, which is close to that in solution (101–105 kJ mol^{-1}). It has been suggested that the mechanisms of isotopic exchange in the solution and in the anion exchange resin are similar.

Isotopic exchange between U^{IV} and U^{VI} in systems containing AV-17-10P anion exchange resin in 6 M HCl solution, KU-8-2P cation exchange resin in 0.5 M HCl solution, and titanium phosphate in 0.7 M H_2SO_4 solution has been studied under static conditions.[61–63] In hydrochloric acid solutions at 25 °C in the absence of catalysts, practically no exchange takes place, but in the presence of titanium phosphate and sulphuric acid the rate of exchange is fairly high ($k = 1.5 \times 10^{-3}$ litre mol^{-1} s^{-1}). It is suggested that the limiting stage of the exchange is the reaction between U^{IV} sorbed on titanium phosphate and U^{VI} in the aqueous phase. In 6 M HCl solutions the rate of isotopic exchange increases considerably in the presence of Fe^{II} salts, but this effect is not observed in 0.5 M HCl solutions.

Table 4. Influence of catalysts on the rate of isotopic exchange in the $U^{IV}-U^{III}$ system.

Catalyst	Concentration of catalyst, M	Concentration of HCl, M	Temperature, °C	k, litre mol^{-1} min^{-1}	k/k_0^*	Refs.
$FeCl_2$	2.5	1	55	9.5	179	[65, 66]
	0.1	2	50	0.082	58	
$CuCl_2$	0.1	4	70	1.4	175	[68]
VCl_3	0.05	4	70	0.17	21	[68]
$CrCl_3$	0.1	4	70	0.01	1.25	[66—68]
p-Benzoquinone	0.05	1.7	90	2.0	1.2	[67]
Hydroquinone	0.1	4	90	0.53	4.8	[69]
Alloxan	0.1	2	50	0.37	65	[67, 69]
$VCl_3 + CrCl_3$	0.05+0.1	4	70	0.38	48	[66]
$FeCl_2$ + alloxan	0.1+0.02	2	50	0.24	170	[66, 69]
$FeCl_2 + CrCl_3$	0.07+0.2	2	50	0.18	129	[66, 67]
$FeCl_2$ + LiCl + γ-picoline	0.7+2.5+0.3	1.5	55	14.0	264	[67]
$FeCl_2$ + LiCl + piperidine	0.7+2.5+0.3	1.5	55	14.8	279	[67, 68]
$FeCl_2$ + ethanol (40%)	1.0	4	55	42.4	820	[67, 69]

* k_0 is the exchange rate constant under corresponding conditions in the absence of a catalyst.

The rate of electron exchange between U^{IV} and U^{VI} can be increased considerably using various catalysts. Thus the reaction between U^{IV} sorbed by a cation exchange resin and U^{VI} in solution is catalysed by the nitrate ion.[64] Detailed studies have shown that the reaction is catalysed by various metal cations, for example Cu^{II}, In^{III}, Tl^{I}, Sn^{IV}, V^{III}, Nb^{V}, As^{III}, Cr^{III}, Mo^{V}, Mn^{II}, Pd^{II}, Hg^{II}, Sb^{III}, Bi^{III}, Zr^{IV}, Re^{V}, Ru^{III}, and Fe^{II},[65–67] and by various organic compounds, such as dicarboxylic or sulphonic acids, hydroxyacids, acids containing N,S-donor atoms and salts of these acids, furans,[68,69] derivatives of quinone and hydroquinone, catechols, and alloxans.[67,69] The concentration of catalyst varies in the range 0.05–3 M.[70] The use of a mixture of catalysts often gives a synergic effect, the magnitude of which depends markedly on the catalysts.[66,67] The catalystic systems are chosen so that the difference in the potentials for the U^{IV}/U^{VI} couple and the redox couple of the catalyst is 0–0.05 V.[67,71] The data in Table 4 show that in a number of cases the rate of the isotopic exchange between U^{IV} and U^{VI} can be increased by a factor of almost 1000. Since the mechanism of isotopic exchange in the $U^{IV}-U^{VI}$ system has not been reliably established, the nature of the action of the catalysts is not yet fully understood. Thus the search for the best catalytic systems is carried out mainly by trial and error.

b) Isotopic effects in the $U^{IV}-U^{VI}$ system

A method for separating uranium isotopes by CIE, in which equimolar quantities of the original U^{IV} and U^{VI} salts are mixed in the light at 25–75 °C and pH 1.5–1.9 has been described.[72] After 1 h, exchange is stopped by adding 3 M HCl solution. The oxidation states of uranium are separated by precipitating U^{IV} with a 5% excess of oxalic acid. In nine separation steps the ^{235}U concentration increases from 0.7052% to 0.7090%.

The exchange reaction was also carried out in 0.207 M H_2SO_4 for 20 h at 35 °C in the dark in a nitrogen atmosphere.[72] Uranium(IV) was precipitated using hydrofluoric acid. For the separation of ^{235}U and ^{238}U, $\alpha = 1.0013 \pm 0.0004$. Similar experiments were carried out in perchloric acid solutions,[74] where the value of α was 1.0012.

Isotope fractionation in the $U^{IV}-U^{VI}$ system in the presence of 0.05 M $CuBr_2$ as catalyst has been studied.[70] The experimental scheme is shown in Fig. 3. Dowex 50W × 4 was used as sorbent. After eight-fold repetition, the ^{235}U enrichment factor was 1.0042. It is suggested[73] that the value of α in the $U^{IV}-U^{VI}$ system is independent of the ligands coordinated to uranium.

Gonda and Kakihana[75] passed 0.05 M solutions of trioctylamine (TOA) or TBP in benzene, saturated with U^{IV} and U^{VI}, through ion-exchange columns with a length of 100 cm and a diameter of 1.2 cm, filled with Dowex 21K anion exchange resin, at a rate of 25 ml h^{-1}. In the system containing TBP, the solution at the outlet from the column was enriched in ^{235}U by a factor of 1.017 compared with the original solution. When TOA was used, the filtrate was depleted in the light isotope ($\alpha = 0.987$). Since in the system containing TBP the anion exchange resin sorbs mainly U^{VI}, in the TOA – U^{IV} system ^{235}U is apparently concentated as $[UO_2]^{2+}$.

When a solution containing 0.5 M H_2SO_4, 0.03 M NaF, and equimolar quantities of U^{IV} and U^{VI} was passed at a rate of 0.5 ml min^{-1} through a column of length 100 cm filled with a cation exchange resin, the resin sorbed mainly U^{IV}.[76] At the outlet from the column, the ^{235}U enrichment factor was 1.009. With increase in the rate of elution to 2 ml min^{-1}, the enrichment factor decreased to 1.000333.

In the counter-current method for separating the isotopes,[77] uranium(IV) sorbed by a strongly acidic cation exchanger moves downwards, and an aqueous solution of U^{VI} moves upwards. In the upper part of the column, U^{VI} slightly enriched in ^{235}U is removed, reduced to U^{IV}, and sorbed on the cation exchanger used in the second column. Uranium(IV) depleted in ^{235}U is removed from the lower part of the first column, oxidised to U^{VI}, and passed to the second column.

A slightly different counter-current method for separating uranium isotopes has been proposed.[78] In this method, the cation exchanger with U^{IV} sorbed on it again moves downwards, but an oxidising agent containing 1% H_2O_2 moves upwards. U^{IV} is oxidised to U^{VI}, desorbed from the resin, and moves upwards with the eluant. Uranium(VI) in the upper part of the column is enriched in the light isotope.

The isotopic fractionation of uranium in counter-current columns makes it possible to carry out a multi-stage process. In the U^{IV}–U^{VI} system, however, this cannot be achieved by using a stationary layer of ion exchanger. For example, Fujii and

co-workers[79] sorbed U^{VI} on a strongly basic macroporous ion exchanger placed in a column with a length of 100 cm and a diameter of 1 cm. Uranium was eluted with a solution containing 0.1–0.12 M $TiCl_3$ and 4–5 M HCl at a rate of elution in the range 3.75–12.3 ml h^{-1}. When the eluant comes in contact with the resin, U^{VI} is reduced to U^{IV}. Since U^{IV} is weakly sorbed by the anion exchanger under the conditions of the experiments, most of it is transferred to the aqueous phase and moves with the eluant. The movement of U^{IV} is accompanied by isotopic exchange between U^{IV} in the aqueous phase and U^{VI} in the exchanger phase. If the rate of attainment of isotopic equilibrium is sufficiently high, isotopic fractionation takes place repeatedly during the passage of the front,[70] as a result of which U^{IV} is enriched in the ^{235}U isotope in the tail of the elution curve. The values of ε obtained at 70 °C and 87 °C were 7.3×10^{-4} and 7.0×10^{-4} respectively. The number of theoretical plates in the experiments varied from 570 to 990, depending on the rate of elution and temperature.

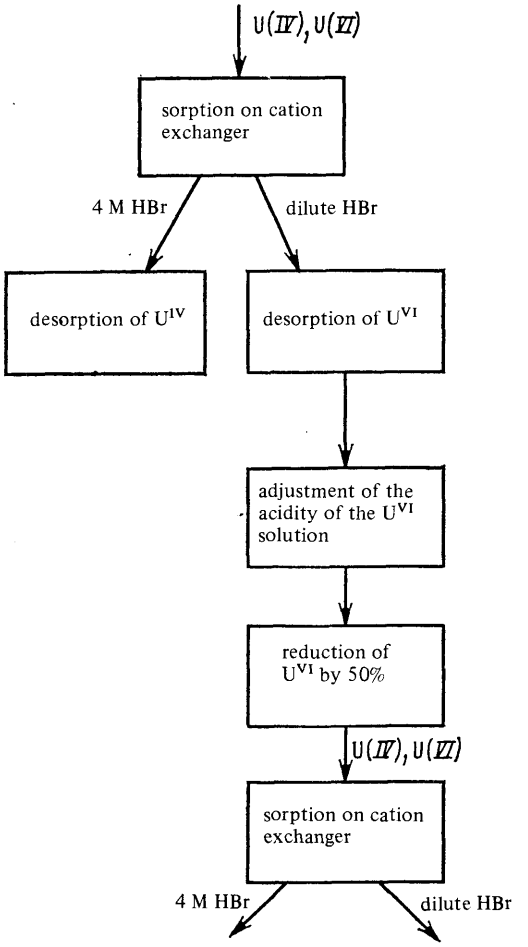


Figure 3. Diagram of the experiment to study isotopic effects in the $U^{IV}-U^{VI}$ system.[70]

Similar experiments were carried out with a cation exchanger in the U^{IV}-form.[64] 0.1 M $Fe(NO_3)_3$ solution was used as eluant. During the elution, U^{IV} was oxidised to U^{VI}, and was washed from the column. Enrichment in ^{235}U took place at the front of the elution curve.

Ponta and Calusaru[80] passed a solution of a U^{VI} salt through a column filled with a cation exchanger in the Ti^{III}-form. U^{VI} was reduced to U^{IV} and sorbed on the resin, and Ti^{III} was converted into TiO^{2+} and washed from the column. The observed isotopic effect is determined by the superposition of the relatively large isotopic effect of the electron exchange between U^{IV} in the resin and U^{VI} in the solution on the weaker isotopic effect of opposite sign due to the reduction of U^{VI} by Ti^{III}.

The methods of separation described above have proved unsuitable for industrial application, however. A method for separating uranium isotopes based on the continuous movement of a uranium zone along a column[81] filled with Dowex 50W-X8 cation exchange resin in the Ti^{III}-form was patented in 1972. When a solution of U^{VI} is passed through the column, the U^{VI} is reduced to U^{IV}, which is sorbed by the resin. As a result, a U^{IV} zone is produced in the upper part of the column. A solution of $FeCl_3$, which oxidises the sorbed uranium, is then passed through the column. The U^{VI} formed is transferred to the solution, and moves with the eluant to the boundary between the zones of uranium and the reducing agent Ti^{III}, where U^{VI} is again reduced to U^{IV} and sorbed by the cation exchanger. The uranium zone moves continuously along the column, and selective distribution of the uranium isotopes takes place at its boundaries as a result of isotopic exchange between U^{IV} from the resin and U^{VI} from the solution. Enrichment in ^{235}U takes place at the boundary between the zones of uranium and the reducing agent. The results of similar experiments carried out by other workers,[82–84] show good agreement with these data.[81]

The chromatographic separation of uranium isotopes according to the above scheme[81] has also been carried out using anion exchange resins.[85–88] In the experiments of Fukuda and co-workers,[88] the zone of uranium, present as anionic complexes of U^{VI}, moved along a column filled with a strongly basic anion exchanger in the Fe^{III}-form. A Ti^{III} solution was used as eluant. The HCl concentration lay in the range 9–4 M, and the temperature in the range 15–83 °C. $FeCl_2$ solution was used to catalyse the isotopic exchange. Enrichment in the light isotope took place in the 'trailing' part of the zone. The values of ε obtained at 30, 50, and 87 °C were 7.8×10^{-4}, 6.8×10^{-4}, and 7.0×10^{-4} respectively. Fe^{III}, Tl^{III}, Mo^{VI}, Sb^{V}, Cr^{VI}, Ce^{IV}, and Hg^{II} were proposed as oxidising agents, and Ti^{III}, V^{II}, V^{III}, Nb^{III}, Cr^{II}, and Cu^{I} as reducing agents.[89] The eluted mixture is treated with oxygen to regenerate the oxidising agent. The reducing agent is regenerated by hydrogen in the presence of catalysts (Pt, Ru, Rh, Pd, Os, or Ir).[89]

4. The ACE process

In 1972, the Japanese firm Asahi Chemical Industry began to develop an industrial method for obtaining uranium with a low degree of enrichment.[14] This method has been called the ACE process.[14] The method is based on isotopic exchange between U^{IV} and U^{VI}. Both cation exchangers and anion exchangers are used to separate the ionic forms of uranium. The firm has developed new highly effective resins giving the process improved kinetic characteristics, which make it economic.

A pilot plant for enriching uranium by CIE (one tenth of the size of the industrial assembly) was brought into operation in Japan in 1985.[90] The capacity of the assembly is 1–2 thousand kg S. W. U. per year. The cost of construction was about 15.8 million dollars.[91] The cascade consists of four columns with a height of 3 m and a diameter of 8 m (Fig. 4), filled with anion exchange resin. The sphericity and dimensions of the particles are varied along the length of the column.[92] Fe^{III} is used as oxidising agent, and Ti^{III} as eluant. The time required to establish the steady state to obtain uranium with an enrichment of 3% is 20–90 d, and the expenditure of energy is 105–180 kW.h per kg S. W. U.[93] To obtain uranium with an enrichment of 93%, the time taken to establish the steady state is 9–10 years.[13]

V. The separation of uranium isotopes in the UF_6-NOUF_6 system

Nugent[94] and Ogle[95] found that in the isotopic exchange between UF_6 and $NOUF_6$, relatively high isotopic fractionation of uranium takes place, and the light isotope is concentrated in the UF_6. Nugent[94] carried out the experiments in a column with a small diameter, filled with $NOUF_6$ in anhydrous HF. A solution of UF_6 in Freon-114, which is denser than the solution in the column, was dispersed in the upper part of the column. Isotopic exchange takes place as the drops fall. The value found for α was 1.0016. Similar results were obtained using the complexes $NOUF_7$ and NO_2UF_7 instead of $NOUF_6$. Ogle[95] used solutions of UF_6 in trichlorotrifluoroethane, dichlorotetrafluoroethane, or perfluorotributylamine. The data obtained by Ogle show good agreement with those obtained by Nugent.[94] A scheme for an assembly for separating uranium isotopes, based on the above method, has been proposed.[96] The values of α in the UF_6(gas)$-NOUF_6$(solid) system at 25 °C and 70 °C are 1.0016 and 1.0011 respectively.[73] The rate of exchange increases in the presence of HF. The main obstacle to the practical utilisation of the exchange between UF_6 and $NOUF_6$ is the high stability of $NOUF_6$ in anhydrous HF solutions towards oxidising agents.[94,98] The oxidation of $NOUF_6$ is necessary to organise phase reversal. F_2, ClF_3, ClF_5, BrF_3, and BrF_5 have been proposed as oxidising agents.[98] The problem of the repeated utilisation of NO has not yet been solved.[98] Moreover, the time taken to establish isotopic equilibrium is fairly long (~2 h), even in the presence of HF. These difficulties make it unlikely that an economic industrial method for separating uranium isotopes based on the reaction between UF_6 and $NOUF_6$ will be developed in the near future.

VI. Other methods

Many workers have used a combination of ion exchange and various electrochemical processes to increase isotopic effects. Thus a method in which isotopic exchange between U^{IV} and U^{VI} is combined with counter-current electromigration has been described.[99] After the electrochemical cell had operated for 1400 h, the ^{235}U concentration in the anode compartment increased by a factor of 1.0007. The method is uneconomic, compared with gas diffusion. Uranium isotopes have also been separated by electromigration using cation exchange membranes.[100] The authors cited suggested that the use of ion exchange membranes should increase the efficiency of isotopic fractionation, since the solvation of uranium ions in the membrane is less extensive than in solution, so that the differences in the masses of the isotope-containing forms should be greater for separation in the membrane. For the fractionation of ^{235}U and ^{238}U by this method α = 1.00006.

The theory of the separation of isotopes by electromigration in an ion exchanger–solution system has been developed, with allowance for the association of the ions and the formation of ion pairs, and also for isotopic exchange between ionic forms in solution and in the exchanger phase.[101]

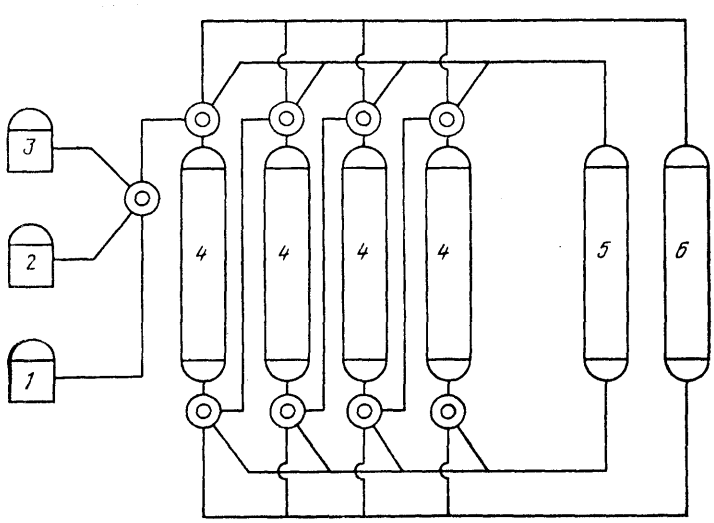


Figure 4. Diagram of the cascade of the ACE process:[2] *1*, vessel for depleted uranium; *2*, vessel for enriched uranium;, *3*, vessel for natural uranium; *4*, separating columns; *5,6*, columns for regenerating the oxidising agent and the reducing agent.

A combination of ion exchange and electrophoresis has been used.[102] Natural U^{IV} chloride was sorbed on the cation exchanger, and then eluted with a mixture of glycine and $CaCl_2$. A voltage was applied to the ends of the chromatographic column (current density 2–3 mA cm^{-2}); the cathode was situated in the upper part. The concentration of ^{235}U at the cathode after 3, 10, and 20 h was 0.736, 0.744, and 0.750 mol% respectively.

A cyclic process involving electro-adsorption and electro-desorption on porous electrodes having a highly developed surface and ion-exchange properties has been proposed for separating uranium isotopes.[103] The sorption–desorption cycles are synchronised with the periodic change in the direction of the flow of liquid, so that a concentration gradient is created along the column.

A kinetic isotopic effect has been detected in the sorption of $[UO_2]^{2+}$ on ion exchange resins under static conditions.[104,105] The sorbents used were the strongly acidic cation exchange resin Amberlite IR-120 in the H^+-form and the strongly basic anion exchange resin Amberlite IRA-400 and the weakly basic anion exchange resin Amberlite IRA-93 in the OH^-, Cl^-, or SO_4^{2-} forms. The ratio of the concentrations of ^{235}U and ^{238}U changed during the sorption. The time dependence of the separation coefficient α shows an extremal point, whose position depends on many factors. When the cation exchange resin was used, the maximum values of α were observed 2 min after contact with the solution, and with the anion exchange resins the smallest value of α was observed after 5–10 min. After passing the extremal point, the ratio $^{235}U/^{238}U$ returned to the original value. The values of α at the extremal points when Amberlite IR-120, IRA-93, and IRA-400 were used were 1.02, 1.03, and 0.99 respectively. The same authors patented similar methods for separating uranium isotopes, based on the kinetic isotopic effect in the sorption of $[UO_2]^{2+}$ on a carboxylic acid cation exchanger on an acrylic base[106] and on an anion exchanger consisting of a structured copolymer of glycyl methacrylate and amines.[107]

The values of α obtained in the works cited[104–107] are more than 10–100 times the uranium isotope enrichment coefficients in equilibrium processes with electron transfer. The nature of the observed phenomenon is not yet clear.

It has been found[108] that the rate of formation of uranyl hydroxide acetate as a result of the irradiation of $UO_2(CH_3COO)_2$ solution with visible light is different for ^{235}U and ^{238}U. The observed phenomenon was attributed to the magnetic isotope effect.

The lack of data on the magnitude and sign of this effect, however, does not make it possible to relate it directly to magnetic phenomena. Moreover, U^{VI} is reduced to U^{IV} when uranyl acetate solutions are irradiated with light. The authors cited[108] did not take account of this process. It follows from the theory of magnetic isotope effects[109] that their highest values are achieved when various conditions are observed. Firstly, the constants of the hyperfine interaction (HFI) with the magnetic nuclei of different isotopes in intermediate radical pairs should differ considerably from one another. Secondly, the HFI constants for one of the isotopes should have high values. Thirdly, the generation of triplet radical pairs is necessary, since their recombination is always preceded by a singlet–triplet interconversion, which leads to the most effective selection of the isotopes.

Until recently, there was lack of agreement on the electronic state of the excited uranyl group.[110] In particular, it was stated that as a consequence of strong spin–orbit coupling, the existence of a characteristic spin in the many-electron uranium atom was impossible. It has been shown,[111] however, that the application of an external magnetic field under certain conditions leads to a decrease in the yield of U^{IV} in the photoreduction of the uranyl group under the influence of N,N-diallyl-N,N-dimethylammonium chloride. The sign of the magnetic effect proves unambiguously the existence of a triplet state of the excited uranyl ion, which on photoreduction gives a triplet radical pair. Thus the appearance of magnetic isotope effects is probably possible in principle in the photoreduction of UO_2^{2+}. The search for specific systems in which these effects are greatest is obviously necessary.

VII. Comparison of the methods

According to the estimates of various specialists, even at the low rates of development of nuclear energy, the annual requirements of the capitalist countries for enriched uranium will be 30 million kg S. W. U. by 1990, and 60 million kg S. W. U. by the year 2000.[12] The production of enriched uranium will be increased both by modernising existing gas-diffusion (GD) plants and by introducing assemblies based on new principles. At the present time, three gas-diffusion plants are operating in the USA (Oak Ridge, Paducah, Portsmouth), and three in Western Europe, of which two are in France (Pierrelatte, Tricastin), and one in Britain (Capenhurst). The production of enriched uranium by GD in the EEC countries is controlled by the international organisation Eurodiff.

In 1970, Britain, West Germany, and the Netherlands established the firm Urenco to develop the ultracentrifuge (UC) method for separating uranium isotopes. In 1979, this firm began to operate two demonstration assemblies in Capenhurst (Britain) and Almelo (The Netherlands), which by 1987 had produced approximately 2 million kg S. W. U. of enriched uranium.[42] A pilot plant with an output of 75 000 kg S. W. U. per year using the UC method is operating in Nintyo-Toge, Japan. In 1985, the Japanese firm PNC began the construction of a similar plant with a planned output of 200 000 kg S. W. U. per year.[113] It is planned to provide 30% of Japan's requirements for enriched uranium from plants using the UC method.

In the USA, approximately 2.6 million dollars have been spent in the construction of a UC plant in Portsmouth.[114] It was planned to bring the first cascade of the plant with an output of 13.2 million kg S. W. U. per year into operation in 1988. The Department of Energy of the USA, however, decided to halt the development of the UC method.[114,115] A method based on the selective photo-ionisation of the atomic vapour of uranium under the influence of laser radiation (AVLIS) was chosen for industrial application in the nineteen-nineties.[115] The main advantages of the AVLIS method over UC is the lower capital expenditure and the lower cost of production per kg S. W. U., and also the greater flexibility for improvement of the method and a gradual increase in output.[115] The very high values of α (see Table 5) make it possible to use depleted uranium from GD plants as the starting material for the AVLIS process.[116] In the USA it is planned to begin in 1988 the construction of a plant using the AVLIS method with a planned output of 10 million kg S. W. U. per year.[115] A similar programme for separating plutonium isotopes is also being developed.[12] It is proposed to begin work on this in 1990. In 1984, 71.9 million dollars were spent on the development of this program. The AVLIS process is also being studied in France,[115] Japan,[117] and Britain.[118]

Representatives of Urenco state, however, that by the late nineteen-eighties the new generation of centrifuges will make it possible to achieve the same economic characteristics as the AVLIS process.[119]

Table 5. Comparison of methods for separating uranium isotopes.[2,5,7,116]

Method*	Level of development	α	Energy consumption, kW per kg S.W.U.	Capital expenditure, dollars per kg S.W.U.	Cost of product, dollars per kg S.W.U.
GD	principal method	1.003	2400—2500	250	95
UC	large-scale plants being brought into production	1.005	100—135	400	90
SJ	construction of large-scale plants being planned	1.015	3000—3600	350	125
SSJ	ditto	1.025	4000	—	—
AVLIS	demonstration assembly being constructed	~100**	50—150	60—70	25—30
MLIS	laboratory studies	2—4	235	—	—
CHEMEX	demonstration assembly in operation	1.002	300	325	60—65
ACE	ditto	1.001	105—180	—	—
PM	laboratory studies	1.1	330	—	—

*GD = gas diffusion, UC = ultracentrifuge, SJ = separating jet method, SSJ = supersonic jet method, AVLIS = selective laser photo-ionisation, MLIS = selective laser photo-dissociation, PM = plasma method; ** separation coefficient without allowance for losses 10^3-10^4.

In addition to AVLIS, the selective laser photo-dissociation of UF_6 vapour (the MLIS process) is also being developed. This method has certain advantages over AVLIS, since UF_6 is extremely volatile.[5] The MLIS process does not give such high values of α as the AVLIS process, however (see Table 5), so that it is necessary to increase the number of stages. The MLIS process is being studied in the Institute of Physical and Chemical Studies in Japan.[120] It is proposed to develop the MLIS method to the AVLIS level.

The separating jet (SJ) method has been developed in West Germany since the mid nineteen-fifties. In 1975, Brazil and West Germany agreed to construct a demonstration plant for enriching uranium by this method.[3] Table 5 shows that the SJ method is the most expensive of the alternative methods.

The supersonic jet (SSJ) method is being developed in the United Arab Republic, where a pilot plant with a planned output of about 300 thousand kg S.W.U. per year has been constructed. Insufficient technical information has been published on this process.

Attempts have been made to separate uranium isotopes in a strongly ionised rotating column of uranium plasma or in the plasma of a low-pressure arc with a hollow cathode (PM).[3] The details of the mechanism of the separation of the isotopes in the plasma are not yet clear, because of the complexity of its structure. The technical problems associated with the use of uranium compounds in a plasma have not been solved.

Comparison of different methods for separating uranium isotopes shows that the chief advantages of CIE methods are the simplicity of the equipment, the use of traditional technology and non-aggressive reagents, and the economic features.[3] Their disadvantages are the low values of α, the long times taken to establish equilibrium, and the complexity of the methods for phase reversal. The developers of the CHEMEX and ACE processes, however, have managed to overcome the difficulties and to develop competitive methods for enriching uranium (see Table 5). The CHEMEX process gives the cost of 1 kg S.W.U. at the level of 60% of the cost of 1 kg S.W.U. in the Eurodiff plants.[115] An advantage of the ACE process over the CHEMEX process is the simplicity of phase reversal, since the latter process requires the use of additional equipment to carry out the redox reactions (electrolyser, etc.).[90] Table 5 shows that the energy used in the ACE process is much lower than that in the CHEMEX process. At the same time, the value of ε for the CHEMEX process is twice that for the ACE process.

Because of these disadvantages, it cannot be said that CIE methods occupy a leading place in the technology of uranium enrichment. These simple and economic methods may prove useful, however, in countries where the requirements for uranium with a low degree of enrichment are low and where there is no need to develop a large-tonnage capital-intensive technology such as GD or UC. Moreover, CIE methods may possibly find application when combined with other promising methods such as laser methods in the early stages of the production of uranium with a low degree of enrichment, when it is necessary to process very large volumes of the starting material.

The possibilities provided by chemical methods for separating uranium isotopes have not been exhausted. In particular, much can still be achieved using processes based on kinetic isotopic effects.

References

1. M Semla, J Perrier *The Separation of Isotopes* (Translated into Russian), Atomizdat, Moscow, 1980, p. 168
2. M M Miller *Energy*, 1984, **9** 829
3. S Villani (Editor) *Uranium Enrichment* (Translated into Russian), Energoatomizdat, Moscow, 1983, 320 pp
4. S S Alimpiev, N V Karlov, B B Krynetskii, Yu N Petrov *Itogi Nauki i Tekhniki, Radiotekhnika* (Progress in Science and Technology, Radio Technology), Vol. 22, Izd. VINITI, Moscow, 1980, Parts 1 and 2
5. M V Veselova, I D Sokolova *Metody Razdeleniya Isotopov Urana s Pomoshch'yu Lazera i Khimicheskogo Ionnogo Obmena za Rubezhom* (Methods Used in Other Countries for Separating Uranium Isotopes Using Lasers and Chemical Ion Exchange), Izd. TsNIIatominform, Moscow, 1979, 32 pp
6. E A Filippov, M R Agevnin, L D Efimova, et al. *Sovremennye Metody Razdeleniya Izotopov Urana* (Present-Day Methods for Separating Uranium Isotopes), Moscow, 1979, 76 pp
7. *Tekhnologiya i Ekonomika Abogashcheniya Urana, Atomnaya Tekhnika za Rubezhom* (The Technology and Economics of Uranium Enrichment, Atomic Technology in Other Countries), No. 8, 1983, p. 27
8. S Villani *Naturwissenschaften*, 1984, **71** 115
9. *Nucl. Eng. Int.*, 1985, **30**(7) Ref. No. 36
10. *Nucl. Energy*, 1984, **23**(4) 194
11. H Lee *Proceedings of the 3rd Pacific Chemical Engineering Congress, Seoul, 1983*, Vol. 3, p. 326
12. G A Kotel'nikov, L N Nefedova *Atomnaya Tekhnika za Rubezhom* (Atomic Technology in Other Countries), No. 3, 1986, p. 8
13. S Fujine, Y Naruse, K Shiba *Nucl. Technol.*, 1983, **62** 317

14. T Miyake, K Takeda, K Imamura, H Obanawa *Nucl. Technol.*, 1984, **64** 237
15. J Kahovec *Chem. Listy*, 1980, **74** 398
16. K Stamberg, J Cabicar *Jad. Energ.*, 1981, **27** 338
17. K Stamberg, J Cabicar *Jad. Energ.*, 1982, **28** 32
18. J M Lerat, C Lorrain *Uranium Enrichment by Solvent Extraction: Solvent Extraction and Ion Exchange Nuclear Fuel Cycle*, Paris, 1985, p. 53
19. B M Andreev, Ya D Zel'venskii, S G Katal'nikov *Razdelenie Stabil'nykh Izotopov Fiziko-khimicheskimi Metodami* (The Separation of Stable Isotopes by Physicochemical Methods), Energoatomizdat, Moscow, 1982, 202 pp
20. N M Zhavoronkov, D A Knyazev, A A Ivlev, G D Klinskii *Zh. Fiz. Khim.*, 1977, **51**(1) 1 [English translation in *Russ. J. Phys. Chem.*, 1977(1)]
21. N M Zhavoronkov, D A Knyazev, A A Ivlev, G D Klinskii *Zh. Fiz. Khim.*, 1978, **52**(4) 897 [English translation in *Russ. J. Phys. Chem.*, 1978(4)]
22. D A Knyazev, G D Klinskii *Isotopenpraxis*, 1978, **14** 41
23. Y Yato, H Kakihana *Bull. Tokyo Inst. Technol.*, 1975, **127** 63
24. T Oi, T Watanabe, H Kakihana *J. Nucl. Sci. Technol.*, 1986, **23** 86
25. Y Fujii, M Aida, M Okamoto, T Oi *Sep. Sci. Technol.*, 1985, **20** 377
26. H Kakihana *Proceedings of the European Nuclear Conference, Nuclear Energy Authority*, 1975, Vol. 12, p. 37
27. R Jacques *Sep. Sci. Technol.*, 1980, **15** 533
28. F H Spedding, J E Powell, H J Svec, et al., US AEC, 1954, Ref. ISC-475
29. A C Rutenberg, J S Drury *J. Inorg. Nucl. Chem.*, 1969, **31** 2289
30. M Ciric *Energ. Nucl.*, 1968, **10** 376
31. M Okamoto, R Goda, A Nakagawa, et al. *Isotopenpraxis*, 1980, **16** 293
32. A Nakagawa, Y Sakuma, M Okamoto, M Maeda *J. Chromatogr.*, 1983, **265** 231
33. Y Tanaka, J Fukuda, M Okamoto, M Maeda *J. Inorg. Nucl. Chem.*, 1981, **43** 3291
34. H Y Kim, M Kaikhana, M Aida, et al. *J. Chem. Phys.*, 1984, **81** 6266
35. J Aaltonen, K G Heumann, P Pietila *Z. Naturforsch., B*, 1974, **29** 190
36. S Li, Q Chen, D Su, et al. *Huazue Yu Fangshe Huazue*, 1982, **4** 126
37. R Goda, Y Sakuma, Y Fujii, M Okamoto *Isotopenpraxis*, 1982, **18** 293
38. US P. 3 953 569; *Chem. Abs.*, 1977, **84** 118 300
39. Y Sakuma, M Okamoto, H Kakihana *J. Nucl. Sci. Technol.*, 1981, **18** 793
40. Japan P. 7 573 092; *Chem. Abs.*, 1976, **81** 167 286
41. T Oi, Y Sakuma, M Maeda, M Okamoto *Isotopenpraxis*, 1983, **19** 261
42. T Oi, Y Sakuma, M Okamoto, M Maeda *J. Chromatogr.*, 1982, **242** 281
43. BRD P. 2 235 603; *Chem. Abs.*, 1973, **78** 118 300
44. Y Han, S Xu, J Qian, S Gao *J. Nucl. Radiochem.*, 1986, **8** 177
45. X Wen, W Luo, D Wang *J. Nucl. Radiochem.*, 1986, **8** 118
46. M Hiraoka *Crown Compounds, Their Characteristics and Applications* (Translated into Russian), Izd. Mir, Moscow, 1986, 363 pp
47. French P. 2282928; *Ref. Zh. Khim.*, 1977, 13L5P
48. US P. 4 012 480; *Chem. Abs.*, 1978, **87** 26 570
49. B. P. 1 467 174; *Chem. Abs.*, 1978, **87** 94 418
50. B. P. 1 541 805; *Chem. Abs.*, 1980, **91** 99 955
51. BRD P. 2 705 895; *Chem. Abs.*, 1978, **87** 191 073
52. M Giraud *Proceedings of the International IAEA Conference, Salzburg, 1977*, p. 24
53. J C Guais *Rep. Gen. Nucl.*, 1982, (1) 68
54. J H Coates *Proceedings of the International IAEA Conference, Amsterdam, 1980*, p. 3
55. C Bernaud, J H Coates, M Gelee, et al. *Rev. Gen. Nucl.*, 1983, (1) 49
56. J H Coates, C Bernaud, P L Plurien *Proceedings of the International IAEA Conference, Vienna, 1983*, p. 893
57. *Nucl. Europe*, 1985, **5**(6) 39
58. R W Woodard *Chemical Separation of the Isotopes of Uranium*, Union Carbide Corp., Oak Ridge, 1948, Y-185
59. J Shimokawa, G Nishio, T Komori *J. Nucl. Sci. Technol.*, 1964, **1** 51
60. H Kakihana *Proceedings of the IIIrd International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1963*, p. 1439
61. M V Ryzhinskii, P A Bronzov, M Yu Vitinskii *III Vsesoyuznaya Konferentsiya po Khimii Urana: Tezisy Dokladov* (Summaries of Papers Presented at the Third All Union Conference on the Chemistry of Uranium), Izd. Nauka, Moscow, 1985, p. 124
62. M V Ryzhinskii, M Yu Vitinskii *Radiokhimiya*, 1986, **28** 742
63. M V Ryzhinskii, P A Bronzov, M Yu Vitinskii *Radiokhimiya*, 1986, **28** 748
64. N Paunescu, A Calusaru *Isotopenpraxis*, 1978, **14** 160
65. Japan P. 8 227 730; *Ref. Zh. Khim.*, 1983, 15L6P
66. Japan P. 8 239 813; *Ref. Zh. Khim.*, 1982, 15L7P
67. B. P. 1 565 392; *Chem. Abs.*, 1980, **93** 247 278
68. Japan P. 8 252 853; *Ref. Zh. Khim.*, 1984, 15L4P
69. Japan P. 8 241 974; *Ref. Zh. Khim.*, 1983, 20L23
70. Netherlands P. 7 609 046; *Chem. Abs.*, **88** 160 497
71. Japan P. 5 805 690; *Chem. Abs.*, 1983, **98** 214 026
72. US P. 2 787 587; *Chem. Abs.*, 1958, **51** 9368
73. T M Florence, G E Batley, A Ekstrom, et al. *J. Inorg. Nucl. Chem.*, 1975, **37** 1961
74. K Takeda, H Onitsuka, T Watanabe *J. At. Energy Jpn.*, 1986, **28** 82
75. K Gonda, H Kakihana *Nucl. Sci. Abs. Jpn.*, 1986, (1) 5221
76. P J Daloisi, M J Orlett, J W Tracy, A J Saraceno, Goodyear At. Corp., Piketon, Ohio, 1976, p. 22, Ref. GAT-865
77. French P. 1 480 129; *Chem. Abs.*, 1968, **68** 8602
78. B. P. 1 120 208; *Ref. Zh. Khim.*, 1969, 14L26
79. Y Fujii, J Fukuda, H Kakihana *J. Nucl. Sci. Technol.*, 1978, **15** 745
80. A Ponta, A Calusaru *Isotopenpraxis*, 1975, **11** 422
81. BRD P. 2 155 895; *Chem. Abs.*, 1972, **77** 55 268
82. Rumanian P. 62 074; *Chem. Abs.*, 1978, **88** 66 771
83. A Calusaru, S Murgulescu *Naturwissenschaften*, 1976, **63** 578
84. Japan P. 8 014 700; Chem. Abs., 1980, **93** 157 613
85. Japan P. 7 978 069; *Ref. Zh. Khim.*, 1981, 1L7P
86. BRD P. 3 022 237; *Chem. Abs.*, 1981, **94** 92 395
87. Netherlands P. 8 003 506; *Chem. Abs.*, 1980, **92** 205 251
88. J Fukuda, Y Fujii, M Okamoto *Z. Naturforsch., A*, 1983, **38** 1072
89. Japan P. 5 727 733; *Ref. Zh. Khim.*, 1984, 15L8P
90. *Ekspress-informatsiya TsNIIatominform* (Express Information, Central Scientific Research Institute for Atomic Information), 1986, (2) (1447), p. 11

91. *Ekspress-informatsiya TsNIIatominform* (Express Information, Central Scientific Research Institute for Atomic Information), 1985, (38) (1441), p. 13
92. Japan P. 8 258 982; *Ref. Zh. Khim.*, 1984, 17L13P
93. M Seko, T Miyake, H Takeda *AIChE Symp. Ser.*, 1982, **78** (221), p. 41
94. B P Nugent, Goodyear At. Corp., Piketon, Ohio, 1972, p. 22, Ref. GAT-675
95. P R Ogle, US AEC, 1972, Ref. GAT-674
96. French P. 2 331 369; *Ref. Zh. Khim.*, 1978, 9L14P
97. A J Saraceno, C F Trivisonno, Goodyear At. Corp., Piketon, Ohio, 1972, p. 11, Ref. GAT-674
98. J Chatelet, M Luce, P Plurien, P Rigny, *International Conference on Uranium Isotope Separation*, 1975, Vol. 30, p. 5
99. US P. 2 813 064; *Chem. Abs.*, 1958, **52** 16 075
100. T Fujii, H Kakihana, M Okamoto *Isotopenpraxis*, 1979, **15** 203
101. I A Tikhomirov, E R Gofman, G S Tikhonov *Zh. Fiz. Khim.*, 1978, **52**(9) 2337 [English translation in *Russ. J. Phys. Chem.*, 1978(9)]
102. Japan P. 7 652 194; *Ref. Zh. Khim.*, 1976, 15L18P
103. Y Oren, A Soffer *Sep. Sci. Technol.*, 1984, **19** 575
104. J Cacibar, K Stamberg *React. Pol.*, 1983, **1** 309
105. Czech. P. 214 904; *Ref. Zh. Khim.*, 1985, 14L9P
106. Czech. P. 225 464; *Ref. Zh. Khim.*, 1986, 5L31P
107. Czech. P. 7686; *Ref. Zh. Khim.*, 1988, 1L10P
108. US P. 4 567 025; *Ref. Zh. Khim.*, 18L4P
109. A L Buchachenko, R Z Sagdeev, K M Salikhov *Magnitnye i Spinovye Effekty v Khimicheskikh Reaktsiakh* (Magnetic and Spin Effects in Chemical Reactions), Nauka, Novosibirsk, 1978, 293 pp
110. M D Marcantonatos *J. Chem. Soc., Faraday Trans.*, 1980, **76** 1093
111. N A Golubkova, I V Khudyakov, D A Topchiev, A L Buchachenko *Dokl. Akad. Nauk SSSR*, 1988, **300** 147
112. *Atomnaya Tekhnika za Rubezhom* (Atomic Technology in Other Countries), Vol. 5, 1988, p. 40
113. *Atoms in Japan*, 1988, **32**(5) 9
114. *Energy Daily*, 1985, **13** 2, Ref. No. 119
115. *Energy Daily*, 1985, **13** 6, Ref. No. 112
116. *Nucl. Eng. Int.*, 1985, **30** 776, Ref. No. 377
117. *Gensienerugi*, 1985, (8) 5; cited in *Ekspress-informatisya TsNIIatominform* (Express Information, Central Scientific and Research Institute of Atomic Information), 1985, (19) (1422), p. 9
118. *Nucl. Fuel*, 1984, **9**(15) 13
119. J Davis *J. Am. Inst. Chem. Eng.*, 1982, **78**(221) 71
120. *Atoms in Japan*, 1985, **29**(8) 22

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The vapour phase heterogeneous-catalytic hydrogenation of carbonyl compounds and carbon monoxide

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ABSTRACT. A systematic account is given of data on the mechanisms and kinetics of processes involving the vapour phase hydrogenation of carbonyl compounds and carbon monoxide to hydrocarbon on transition metals. The activity and selectivity series in relation to the reduction of the carbonyl group and CO are determined mainly by the energies of the bonds formed by the compounds hydrogenated and hydrogen with the metal. The bond energy depends in its turn both on the chemical nature of the metal and on the degree of its dispersion. The role of the geometrical factor, which influences the concentration of the active centres, is also examined.

Rules for the selection of catalysts for the hydrogenation of carbonyl compounds and CO on transition metals have been formulated on the basis of the relations discovered between the physicochemical and catalytic properties.

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I. Introduction

Processes involving the heterogeneous-catalytic hydrogenation of carbonyl compounds (aldehydes, ketones, etc.) include a large number of reactions of practical interest, especially when it is possible to achieve them at low temperatures and atmospheric pressure. At the same time, these reactions have been little investigated and only recently has there been a greater interest in them.

Carbon monoxide may be regarded as the simplest representative of carbonyl compounds and syntheses based on it make it possible to obtain a large number of products of practical value.

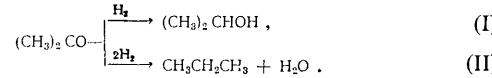
Despite the large variety of the hydrogenation reactions of carbonyl compounds, they have many features in common, whose discovery should promote the development of theoretical principles for the prediction and selection of catalysts.

The present review will consider mainly studies carried out in recent years on the mechanisms, kinetics, and catalyst selection rules for processes involving the gas-phase hydrogenation of carbonyl compounds as well as CO to hydrocarbons. The liquid-phase hydrogenation of aldehydes, ketones, and unsaturated oxo-compounds in solutions at an elevated pressure has been described in detail in other reviews and monographs.[1–4]

II. Thermodynamics of processes involving the hydrogenation of carbonyl compounds and carbon monoxide

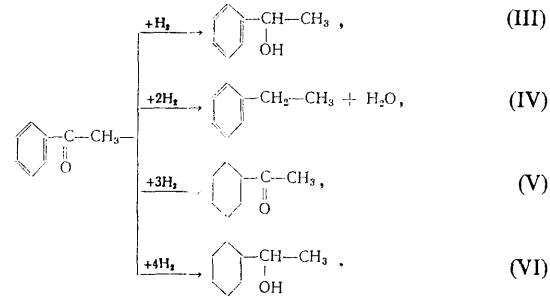
Depending on the reaction conditions and the catalyst used, the hydrogenation of carbonyl compounds can result in the formation of alcohols, hydrocarbons, and also reduction products with retention of the carbonyl group.

The reduction of acetone in the presence of metal catalysts takes place mainly with formation of isopropyl alcohol and propane:[5]



(I)
(II)

The interaction of acetophenone with hydrogen leads to a more complex composition of the product, because in this case there is a possibility of both the hydrogenation of the aromatic rings and of the complete or partial reduction of the carbonyl group:[5]



(III)
(IV)
(V)
(VI)

The standard Gibbs free energies ΔG_r° of the hydrogenation of acetone (in the range 300–450 K) and acetophenone (at 300–600 K) and the corresponding equilibrium constants K_e, found at a pressure

of 0.1 MPa, are listed in Table 1. Evidently in the temperature range from 300 to 600 K the equilibrium constants of reactions (II) and (IV) are several orders of magnitude higher than the K_{ei} of reactions (I) and (III). Consequently at the above temperatures the complete reduction of acetone to propane and of acetophenone to ethylbenzene is thermodynamically more favourable.

The similarity of the K_{ei} for reactions (I) and (III) and also for reactions (II) and (IV) indicates a comparatively small influence of the nature of the substituent at the carbonyl group on the thermodynamic probability of its reduction. The hydrogenation of the aromatic ring of acetophenone is easier than the reduction of the carbonyl group.

With increase in temperature (in the range 300–600 K), the equilibrium constants of the reactions involving the reduction of the carbonyl group and the hydrogenation of the aromatic ring of acetophenone diminish. Analysis of the constants K_{ei} shows that, in the experimental temperature range, reactions (II) and (IV)–(VI) are almost irreversible in contrast to reactions (I) and (III). An increase in the overall pressure of the systems to 1–10 MPa makes it possible to raise the equilibrium yield of isopropyl alcohol and methylphenylmethanol to 75–100 mol %.[5]

A thermodynamic analysis of the principal acetone hydrocondensation reactions involving the formation of higher (C_6-C_9) alcohols, ketones, and hydrocarbons and oxygen-containing compounds from CO and H_2 has been considered.[7,8] The temperature dependence of the equilibrium constants of the reactions involving the formation of methane and its homologues, i.e.

$$CO+3H_2=CH_4+H_2O, \qquad \text{(VII)}$$

$$nCO+(2n+1)H_2=C_nH_{2n+2}+nH_2O \ (n\geqslant 2), \qquad \text{(VIII)}$$

from the synthesis gas is presented in Table 2.[8] Evidently, with increase in temperature, the thermodynamic probability of the synthesis of methane homologues falls. However, it remains high for all hydrocarbons (up to ~700 K). The differences between the thermodynamic probabilities of the formation of hydrocarbons of different types are unimportant, since the process selectivity is determined by kinetic and not thermodynamic factors. The available data[8] make it possible to calculate the equilibrium compositions of products with a specified number of carbon atoms in the molecule.

Table 2. Temperature dependence of the equilibrium constants of the CO + H_2 reactions.[8]

Hydrocarbon formed	$\lg K_e$			
	300 K	500 K	700 K	900 K
CH_4	24.7	10.1	3.6	—0.1
C_2H_6	37.4	12.7	1.8	—4.4
C_6H_{14}	94.9	27.4	—2.4	—12.1
$C_{10}H_{22}$	152.3	41.8	—6.9	—34.2
$C_{20}H_{42}$	295.6	77.8	—18.0	—71.9
cyclo-C_6H_{12}	89.5	24.9	—3.6	—19.7
cyclo-$C_6H_{11}-CH_3$	106.1	30.0	—3.5	—22.3

III. Characteristics of the adsorption of reactants on the surfaces of metal catalysts

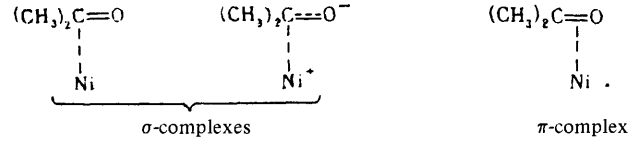
1. Adsorption of carbonyl compounds

The structure and nature of the surface species formed in the adsorption of carbonyl compounds on metal catalysts have been investigated mainly by IR spectroscopy. It has been found[9] that at 298 K acetone on the iron surface forms the π-complex $(CH_3)_2C{=}O$ (Fe). At the same time, the spectrum contains absorption bands characterising the alkoxy-groups $(CH_3)_2CO-Fe$. On nickel and cobalt, extensive decomposition of the acetone molecule to carbon monoxide has been observed. The presence in the IR spectra of

Table 1. Temperature dependence of the standard Gibbs free energies (in kJ mol^{-1}) and equilibrium constants (in kPa^{-1}) in reactions (I)–(VI).[5]

T, K	Reactions											
	(I)		(II)		(III)		(IV)		(V)		(VI)	
	$-\Delta G_r^0$	K_e	$-\Delta G_r^0$	K_e	$-\Delta G_r^0$	K_e	$-\Delta G_r^0$	K_e	$-\Delta G_r^0$	K_e	$-\Delta G_r^0$	K_e
300	20.31	$3.55\cdot10^5$	98.82	$1.778\cdot10^{19}$	20.31	$3.55\cdot10^5$	99.53	$1.995\cdot10^{19}$	151.4	$3.162\cdot10^{28}$	169.58	$3.981\cdot10^{31}$
325	17.97	$9.1\cdot10^4$	96.14	$3.2\cdot10^{17}$	—	—	—	—	—	—	—	—
350	14.63	$1.5\cdot10^4$	93.26	$8\cdot10^{15}$	14.13	$1.3\cdot10^4$	94.01	$1.21\cdot10^{16}$	163.15	$2.512\cdot10^{26}$	174.43	$1.120\cdot10^{28}$
375	10.87	$3.3\cdot10^3$	88.62	$4\cdot10^{14}$	—	—	—	—	—	—	—	—
400	8.57	$1.3\cdot10^3$	87.78	$4\cdot10^{13}$	7.98	$1.1\cdot10^3$	89.54	$5\cdot10^{13}$	174.43	$6.31\cdot10^{24}$	179.32	$2.512\cdot10^{25}$
425	3.34	$3.0\cdot10^2$	81.76	$3\cdot10^{12}$	—	—	—	—	—	—	—	—
450	—	—	80.34	$4\cdot10^{11}$	1.80	$1.6\cdot10^2$	81.97	$3\cdot10^{11}$	180.5	$5.01\cdot10^{23}$	184.17	$2.51\cdot10^{22}$
500	—	—	—	—	—4.35	40	77.54	$0.13\cdot10^{10}$	198.3	$5.01\cdot10^{23}$	189.06	$5.6\cdot10^{21}$
550	—	—	—	—	—	—	70.39	$0.5\cdot10^9$	210.05	$7.9\cdot10^{21}$	193.91	$3\cdot10^{20}$
600	—	—	—	—	—	—	59.94	$0.2\cdot10^7$	217.57	$7.9\cdot10^{20}$	194.62	$9\cdot10^{18}$

absorption bands in the range 1570–1700 cm^{-1} indicates the presence of π-complexes on the nickel and cobalt surfaces. In a study of the adsorption of acetone and of its deuteriated derivatives on Ni/SiO_2 in the temperature range 298–473 K, Young and Sheppard[10] suggested the possibility of forming two types of complexes between nickel and the ketone:



The adsorption of acetone on the 5% Ru/Al_2O_3 catalysts, differing in the content of preadsorbed hydrogen, has been investigated by IR spectroscopy. The authors[11] believe that, regardless of the presence or absence of H_2 on the ruthenium surface, acetone is hydrogenated on platinum group metals[12] via the formation of only alkoxy-groups and that π-complexes are not produced.

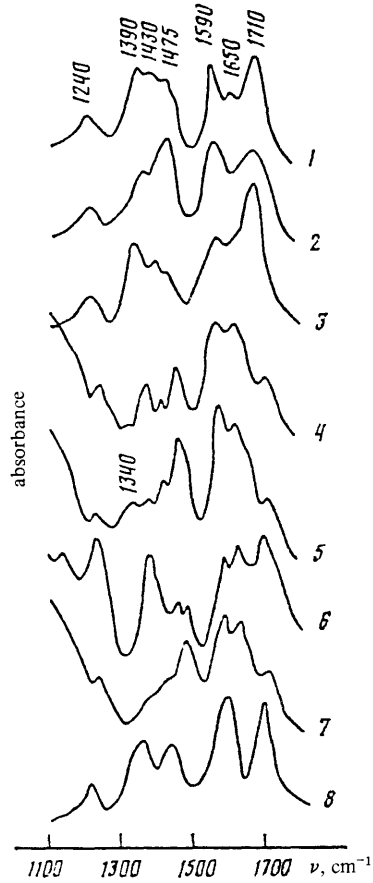


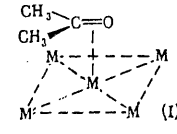
Figure 1. IR spectra of acetone adsorbed on deposited metals: *1*, Fe; *2*, Co; *3*, Ni; *4*, Ru; *5*, Rh; *6* Ir; *7*, Pt; *8*, Cu.

The IR spectra of acetone adsorbed on deposited transition metals, obtained under conditions close to those in the catalytic reaction (I), are presented in Fig. 1.[13–15] Acetone is hardly adsorbed on the surface of the Pd/Al_2O_3 catalyst—the corresponding absorption band could not be detected in the IR spectrum. The observed shift ($\Delta\nu \simeq 20$ cm^{-1}) of the maximum of the band corresponding to the vibration of the carbonyl group [$\nu(CO) = 1740$ cm^{-1}] has been explained by the presence of a weak chemisorption bond between the CO groups of acetone and the OH groups on the γ-Al_2O_3 surface, which corresponds to the formation of complexes with the $(CH_3)_2C=O...H-O-Al\langle^{O-}_{O-}$ hydrogen bond.[16] A new absorption band in the range 1590–1605 cm^{-1} appears in the spectrum of acetone adsorbed on metal catalysts. In addition, an absorption band in the range 1640–1650 cm^{-1} has been detected after adsorption on Fe, Ru, Rh, Ir, and Pt. When $(CH_3)_2CO$ is adsorbed on deposited transition metals (M), there is a possibility of the formation of a donor–acceptor complex when π-electrons are transferred from the ketone molecule to the unoccupied *d* orbitals of the metal or a dative interaction may take place, in which the *d* electrons of the metal are localised in the antibonding π* orbitals of the carbonyl group.[17]

The direction of the shift of the electron density in the adsorption complex depends on the ratio of the electronegativities of the metal atom and the ketone molecule. The electronegativity of the $(CH_3)_2CO$ molecule is determined by the electronegativities of the carbon and oxygen atoms of the carbonyl groups, which are respectively 2.55 and 3.44 on the Pauling scale.[18] The electronegativities of metals on this scale decrease in the sequence

$$\mathrm{Pt}(2.28),\ \mathrm{Ru}(2.28) > \mathrm{Ir}(2.2),\ \mathrm{Rh}(2.2) > \mathrm{Ni}(1.91) > \mathrm{Cu}(1.90) > \mathrm{Co}(1.88) > \mathrm{Fe}(1.8). \qquad \text{(IX)}$$

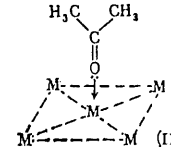
Taking into account the greater electronegativity of the acetone molecule compared with that of the metal atoms, it has been suggested[13–15] that in the system considered the dative interaction predominates over the donor–acceptor interaction, so that the appearance of the absorption band in the range 1590–1605 cm^{-1} characterises the formation of a planarly oriented π-complex (I) on the surfaces of the catalysts investigated:



(I).

The energy of the dative interaction increases with decrease in the electronegativity of metals, so that acetone should be adsorbed most strongly on the catalyst located at the end of the series (IX), which agrees with experimental data.[13]

In conformity with the work of Blyholder and co-workers,[9,19] the absorption band in the range 1640–1650 cm^{-1} has been assigned[13,15] to the formation of a donor–acceptor complex:



(II)

in which the molecular orbital of the CO group overlaps the unoccupied *d* orbital of the metal.

The conclusions concerning the structure of the adsorption complexes were confirmed by our quantum-chemical calculations on the interaction of acetone with Ni and Cu clusters, carried out by

the INDO method.[20] It follows from the results that the formation of a "parallel" π-complex (I) with an acetone molecule is more likely for the Cu cluster, whereas for the Ni cluster the probabilities of the formation of the complexes (I) and (II) are approximately the same. Regardless of the nature of the metal (Ni, Cu), the loosening of the C=O bond in the π-complex (I) is greater than in the donor–acceptor complex (II). This permits the conclusion that the π-complex (I) is the most probable intermediate in the catalytic hydrogenation of acetone.

Acetone and other carbonyl compounds form type (II) complexes with the surface of simple and mixed oxides used as carriers for metal catalysts, while hydrogen-bonded complexes are produced on coordination to surface OH groups.[16,39,40] The adsorption of acetone on the surfaces of oxides may be accompanied by aldol and crotonic condensations, whose mechanisms (for γ-Al_2O_3) were investigated in our previous studies.[16,41]

2. The adsorption of carbon monoxide

The experimental and calculated data for the adsorption of CO on transition metals has been described systematically in monographs[21–24] and reviews.[25–28] Depending on the nature of the metal and the adsorption conditions, the CO molecule initially forms a weak one-electron bond, which is rapidly converted into stronger bonds: a linear bond with one metal atom and a bridge bond with two or more M atoms:[26]

$$M + CO \rightleftarrows M^- \ldots CO^+ \rightleftarrows M{-}C{\equiv}O \overset{M}{\rightleftarrows} \begin{matrix} M \\ M \end{matrix}\!\!>\!C{=}O. \qquad (X)$$

Quantum-chemical calculations[29] on the interaction of CO with iron, cobalt, nickel, and copper atoms with formation of the linear form of the M–CO bond have shown that the M–C bond strength diminishes in the sequence Fe > Co, Ni > Cu, whilst the energy of the M–O bond increases in the sequence Ni < Co < Cu < Fe. The calculated data agree well with the IR spectroscopic results,[30,31] on the basis of which it has been concluded that there is a dative bond between the above metals and the CO molecule involving the formation of the π-complex (the alkoxy-complex is hardly formed). The following sequence based on decreasing M–C bond strengths has been established for platinum group metals on the basis of absorption spectra:[32–34]

$$Ir > Ru > Pt > Rh > Pd.$$

According to quantum-chemical calculations,[35] the average M–CO bond energy diminishes with increase in electronegativity in series (IX), while the strength of the C–O bond in the adsorbed molecule increases, so that the presence of metals with the lowest electronegativity (Fe, Co) should promote to the greatest extent the rupture of the CO bond and the formation of hydrocarbons via the reaction between CO and H_2. This conclusion has been confirmed by numerous experimental data.[36–38]

The adsorption of CO on simple and mixed oxides of non-transition metals results in the formation of carboxylate and carbonate structures of different types.[22,24]

3. The adsorption of hydrogen

The adsorption properties of massive and dispersed metal catalysts in relation to hydrogen have been investigated in fair detail.[2,22,23,25,42] Analysis of the available and experimental calculated data shows that the dissociative form of the adsorption of H_2 predominates on Group VIII metals; on copper, hydrogen is adsorbed in the form of molecules,[43] whilst on ruthenium both molecular[15] and dissociative[23] forms of adsorption of H_2 are observed (depending on the adsorption conditions and the degree of dispersion of the metal).

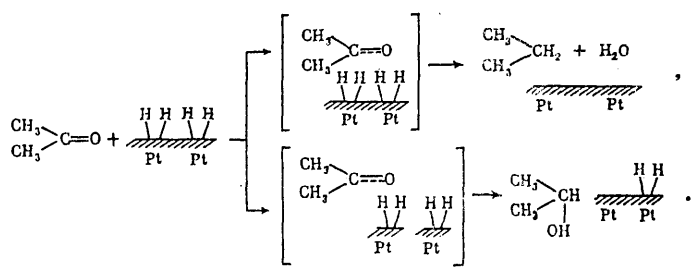
IV. The mechanism and kinetics of the hydrogenation of ketones and CO

1. Hydrogenation of acetone

When reaction (I) was carried out on sputtered metal films, it was shown[44] that the rate of the process r is independent of the partial pressure of acetone P_A, depends in a complex manner on the partial pressure of hydrogen P_{H_2}, and is inhibited as the concentration of the reaction product (isopropyl alcohol) increases. The kinetic equation $r = kP_A^{1.2}P_{H_2}^{1.5}$, where k is the reaction rate constant, has been proposed[45] for the reaction on Raney nickel.

The kinetic orders of reaction (I) have been determined[46,47] and a kinetic equation, describing the process on an inhomogeneous surface in the region of reversibility, has been devised in addition.[47] It has been suggested[44,47] that the rate of the reaction is determined by the stage involving the surface interaction of the adsorbed acetone molecules with the hydrogen atoms or molecules.

The following parallel mechanism of the hydrogenation of acetone to propane and alcohol on a diatomic active centre of the catalyst has been proposed[48] in the case of platinum black:



The kinetics of the vapour-phase hydrogenation of acetone on massive nickel, cobalt, copper, and their alloys have been studied in detail by Avetisov and Gel'bshtein and co-workers.[49–52] It has been shown[49] that the rate of reaction increases appreciably with increase in P_A, depends to a lesser extent on P_{H_2}, and is inhibited by the isopropyl alcohol formed. The observed reaction orders with respect to the components are variable and depend on their concentrations and temperature. It has been suggested[49] that hydrogen atoms adsorbed on nickel in the H^+-form enter into the reaction and that the rate of this process is limited by the surface interaction of the adsorbed ketone molecules and H atoms. It has been assumed[49] that acetone and hydrogen are adsorbed on different active centres of the catalyst surface. The non-planar acetone molecules do not then occupy all the adsorption centres on the metal surface even when the latter is fully saturated. On these grounds, it has been postulated[49] that hydrogen atoms are adsorbed on the metal surface in the gaps between the ketone molecules. An adsorption mechanism of reaction (I) has been put forward on the basis of kinetic data and the corresponding equation, which describes satisfactorily the experimental relations, has been derived.[49]

The kinetic relations and the reaction mechanism characteristic of the reactions on nickel are retained on the cobalt catalyst and nickel–cobalt alloys containing between zero and approximately 50 at.% of cobalt.[52]

It has been established[50] that, in the presence of massive copper, the rate of reaction hardly depends on P_A, increases with increasing P_{H_2}, and diminishes with increasing partial pressure of isopropyl alcohol P_{al}. On the basis of the results of studies[53,54] in which it had been shown that at temperatures below 573 K hydrogen is not adsorbed on copper, Babkova et al.[50] examined different versions of the impact (with respect to H_2) mechanism of the hydrogenation of acetone.

The hypothesis[50] that the hydrogenation of acetone on copper can be described with the aid of the mechanism proposed by Twigg[55] for the hydrogenation of ethylene on nickel as applied by Temkin[56] to the hydrogenation of ethylene on a palladium membrane is interesting. This mechanism can be represented schematically as follows:

Scheme 1

1) $(CH_3)_2CO + Z \rightleftarrows Z(CH_3)_2CO$,
2) $Z(CH_3)_2CO + Z_1 + H_2 \rightleftarrows Z(CH_3)_2COH + Z_1H$,
3) $Z(CH_3)_2COH + Z_1H \rightarrow Z(CH_3)_2CHOH + Z_1$,
4) $Z(CH_3)_2CHOH \rightleftarrows (CH_3)_2CHOH + Z$,

where Z and Z_1 are adsorption centres on the catalyst surface.

Hydrogen from the gas phase interacts with an adsorbed acetone molecule (on the adsorption centre Z), which results in the formation of a partly hydrogenated form of acetone and a hydrogen atom adsorbed on a free centre (Z_1) on the copper surface. The ability of copper to adsorb atomic hydrogen has been reliably established.[57] On the basis of the scheme described above, equations describing the experimental data in the experimental temperature and reactant concentration ranges have been proposed.[50]

The similarity of the kinetics of the acetone hydrogenation reaction catalysed by nickel and nickel–copper alloys with a copper content up to 60 at.% suggested[51] that the mechanism proposed[50] for the hydrogenation of acetone on the nickel catalyst is valid also for the nickel–copper alloy having the composition indicated above. For a higher copper content in the alloy (> 60 at.%), acetone is hydrogenated in conformity with Twigg's mechanism describing the reaction on the copper catalyst.

The kinetics of the reversible hydrogenation of acetone on the nickel catalyst have been investigated.[47,58] The hydrogenation reaction proceeds via two pathways: the adsorbed ketone molecule reacts with adsorbed hydrogen atoms and a partly hydrogenated acetone molecule reacts either with gas-phase hydrogen or with a second adsorbed hydrogen atom. The dehydrogenation of isopropyl alcohol includes a stage in which the gas-phase alcohol interacts with the dissociatively adsorbed hydrogen.[47,58]

The kinetics of the hydrogenation of acetone in a differential flow reactor at 423 K in the presence of Cu, Pt, Pd, and Rh deposited on kieselguhr have been studied.[59] 29 kinetic equations, corresponding to the Langmuir–Hinshelwood mechanism, have been analysed by the ECV method. The activity of the platinum group metal diminishes in the following sequence according to the reaction rate constants (k expressed in mol/h kg of catalyst): Pt > Rh > Pd. The activities of the catalysts investigated lie in the following sequence in terms of the initial rate of hydrogenation: Cu > Rh > Pt > Pd. The series presented must be regarded as arbitrary, since the concentrations of the metals deposited on kieselguhr were different and the specific surfaces of the metals were therefore also different. Furthermore, at temperatures above 737 K it is essential to take into account the reversibility of the acetone hydrogenation reaction,[5] which was not done in the above study.[59]

The experimental relations obtained in the presence of the copper catalyst were described[59] by a kinetic model according to which the molecularly adsorbed hydrogen reacts with a dissociatively adsorbed acetone molecule, but the authors do not explain what they mean by the dissociative adsorption of acetone on copper and what is the mechanism of this process. The kinetic equations proposed[59] for the description of the processes occurring on platinum group metals (Pt, Rh, Pd) are consistent with the mechanism according to which the rate is determined by the interaction between the adsorbed hydrogen and acetone molecules. However, these conclusions conflict with numerous literature data, according to which the atomic form of the adsorption of hydrogen predominates on the surface of platinum metals.

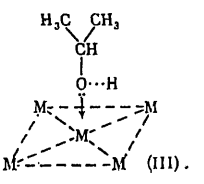
We carried out a systematic study of the vapour-phase hydrogenation of acetone on deposited and massive transition metals.[13–15,60–65] Detailed investigation of the kinetics of reaction (I) at different temperatures showed that the following picture is observed in all cases: the rate of the process increases with increasing concentrations of the reactants, reaching saturation. The reaction product (isopropyl alcohol) does not inhibit the hydrogenation of acetone on all catalysts other than the copper and ruthenium catalysts, where a decrease in rate with increase in P_{Al} was observed.[14,15]

The study of the mechanism and kinetics of the reverse reaction—the dehydrogenation of isopropyl alcohol on the Pt/Al_2O_3 catalyst, i.e.

$$(CH_3)_2CHOH \rightarrow (CH_3)_2CO + H_2, \qquad \text{(XI)}$$

demonstrated the following features: with increase in P_{Al} and for low values of P_{H_2}, the rate of reaction (XI) increases, reaching saturation. In the presence of an excess of hydrogen, the order of the reaction with respect to the alcohol increases, approaching unity. The reaction products (acetone and hydrogen) then inhibit reaction (XI).

These results made it possible, in the first place, to account for the influence of the alcohol concentration on the kinetics of reaction (I). The character of this influence depends significantly on the degree of coverage of the metal surface by hydrogen θ_H, which affects the adsorption of isopropyl alcohol on the metal surface. The isopropyl alcohol molecule, which has no unsaturated bonds, is adsorbed (perpendicularly) on the metal surface as a result of the dissociation of the OH group. This leads to the formation of the alkoxy-structure[64]



(III).

In the joint adsorption of $(CH_3)_2CHOH$ and H_2 molecules, competition is observed:[64] the atomically adsorbed hydrogen prevents the dissociation of the OH group of the isopropyl alcohol molecule and the adsorption of the latter on the metal. This is manifested clearly in the dehydrogenation of isopropyl alcohol, where an increase in P_{H_2} in the reaction mixture leads to the inhibition of reaction (XI) and an increase in the reaction order with respect to the alcohol.

The following mechanism for the reversible addition of hydrogen to the carbonyl group has been proposed[64,65] on the basis of the entire set of adsorption and kinetic data obtained:

Scheme 2

1) $H_2 + 2Z_H = 2Z_HH$,
2) $(CH_3)_2CO + Z_A = Z_A(CH_3)_2CO$,
3) $Z_A(CH_3)_2CO + Z_HH \rightleftarrows Z_A(CH_3)_2COH + Z_H$,
4) $Z_A(CH_3)_2COH + Z_HH \rightleftarrows Z_H(CH_3)_2CHOH + Z_A$,
5) $Z_H(CH_3)_2CHOH = (CH_3)_2CHOH + Z_H$,

where Z_A and Z_H are the centres for the adsorption of acetone and hydrogen respectively.

The equilibrium adsorption of the initial reactants takes place in the first two stages: acetone forms the π-complex (I) on the polyatomic centre Z_A, while the dissociative adsorption of hydrogen takes place on single M-centres Z_H.

Our data make it possible to justify and specify in detail the physical significance of the active centres (Z_A and Z_H) postulated by Babkova et al.[49]

The study of the IR spectra of the acetone adsorbed on metals[13–15] (Fig. 1) led to the conclusion that at the temperatures of the catalytic reaction (~330–370 K) the ketone molecule is oriented "parallel" to the metal plane [the complex (I)]. For this orientation, acetone is adsorbed only on specific groups of M atoms with a suitable geometry (of the type of Balandin's multiplets). The fraction λ of such complex centres Z_A is small, so that acetone hardly affects the adsorption of H_2 on single centres Z_H (on the rest of the surface), whose fraction is close to unity. Since the transition state (the rate-limiting stage of the process) is formed on a pair of centres $Z_A + Z_H$, the number of active centres (n_a) for the catalytic reaction should be small. The quantity n_a enters into the expression for the pre-exponential factor k_L^0 in the expression for the rate constant for the rate-limiting stage:[66]

$$k_L^0 = \kappa(k_BT/h)n_a \exp(\Delta S_L^*/R),$$

where k_BT/h is the frequency factor, κ the transmission coefficient, usually equal to unity, ΔS^*_L the entropy of activation, and R the gas constant. Since ΔS^*_L for stages of the type $A_{ads} + B_{ads} = C_{ads}$ is usually small in absolute magnitude,[67] we have $k_L^0 \simeq (k_BT/h)_a$, so that an increase in k_L^0 with decrease in the degree of dispersion of the metal, up to a certain limit corresponding to the $(n_a)_{max}$, is to be expected. This corresponds to a situation such that the probability of the existence of the complex groups Z_A on the planes of the microcrystals increases as the metal particles grow (with This corresponds to a situation such that the probability of the existence of the complex groups Z_A on the planes of the microcrystals increases as the metal particles grow (with increase in $\bar{d}$) and the fraction of the active surface also increases, reaching saturation, whereupon the fraction of the planar M atoms becomes virtually unity. Fig. 2 confirms this, catalysts of different chemical composition, characterised by different activation energies E_L, fitting on a single straight line. Comparison of the experimental maximum values of $k_L^0 \simeq 10^6$ (Table 3) with the "normal" value $k_L^0 = 10^7$–10^8 mol m^{-2} × s^{-1}, corresponding to $\gamma = 1$, shows that the fraction of the working surface λ is only a few per cent even on large crystals.

The ideas described are also confirmed by the results of a study[68] in which it has been established that the adsorption of acetone and hydrogen in the presence of the Pt/Al_2O_3 catalyst with different degrees of dispersion takes place without competition. The activity of the catalyst increases with increase in the size of the Pt system from 5 to 20 nm and then remains constant.

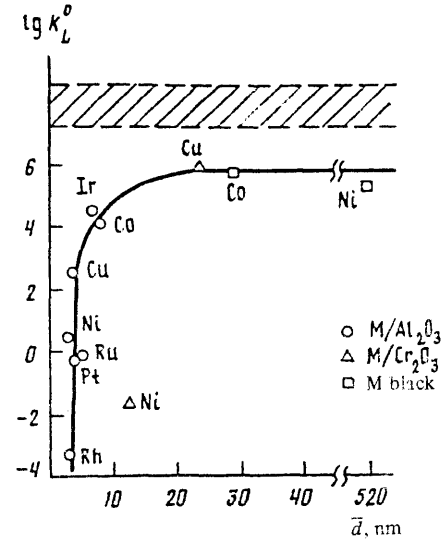


Figure 2. Dependence of the pre-exponential factor of the rate constant for the rate-limiting stage on the hydrogenation of acetone on the degree of dispersion of the metal. The dashed lines represent the values of k_L^0 corresponding to the entire working surface ($\lambda = 1$) for $\Delta S_L^* \simeq 0$–20 J mol^{-1} K^{-1}.

Table 3. Kinetic and thermodynamic characteristics of the acetone hydrogenation reaction on metals.

Catalyst	$\bar{d}$ for metal, nm	$10^7 r^*$, mol m^{-2} s^{-1}	E_L, kJ mol^{-1}	$10^7 k_L^{**}$, mol m^{-2} s^{-1}	k_L^0, mol m^{-2} s^{-1}	$10^{-5} b_A^{**}$, Pa^{-1}	q_A, kJ mol^{-1}	ΔS_A^*, J mol^{-1} K^{-1}	q_C, kJ mol^{-1}
Pt/Al_2O_3	3.9	44	31	65.4	0.38	7	12.5	—21	—
Ir/Al_2O_3	6.8	11.7	71	2.5	$3 \cdot 10^4$	73.5	83	—191	—
Rh/Al_2O_3	2.5	7.7	17	16	$6 \cdot 10^{-4}$	12	14	—22	—
Ni/Al_2O_3	2.4	7.5	43	6.6	3.0	58.5	83	—214	—
Ru/Al_2O_3	4.4	7.0	39	20	0.8	35	34	—72	40
Cu/Al_2O_3	3.0	5.0	58	3.3	$3 \cdot 10^2$	120	80	—197	86
Co/Al_2O_3	7.5	4.6	68	2.5	$9 \cdot 10^2$	150	81	—197	—
Pd/Al_2O_3	5.0	inactive							
Fe/Al_2O_3	4.2	»							
Cu/Cr_2O_3	23	30	70	132	$9.8 \cdot 10^5$	80	39	—77	92
Ni/Cr_2O_3	11.5	15.3	26	21	$2.1 \cdot 10^{-2}$	10	24	—53	—
Ni black	520	15.8	72	16.6	$2.5 \cdot 10^5$	12	32	—83	—
Co black	28.4	3.0	80	2.2	$5.8 \cdot 10^5$	15	42	—112	—
Cu black	1170	inactive							
Au ***		$2 \cdot 10^{-4}$							

Note. Mixture composition; $P_A = 10$, kPa, $P_{H_2} = 50$ kPa.

*Calculated for 364 K.

**Calculated for 337 K.

***The data of Stoddart and Kemball[44] are quoted.

It follows from the competing adsorption of hydrogen and isopropyl alcohol that these substances are bound to the same centres (Z_H) and that the alcohol forms the complex (III). The equilibrium desorption of the product takes place in stage 5. Stages 3 and 4 are reversible but non-equilibrium. At low temperatures stage 3 is slowest.[64]

The observed rate of reaction of acetone under stationary conditions is

$$r = r_3 - r_{-3} = r_4 - r_{-4}, \quad (1)$$

where $\gamma \pm i$ are the rates of the stages in the forward and reverse directions. When account is taken of Eqn. (1), the overall kinetic equation for the reversible hydrogenation of acetone, corresponding to Scheme 2, is

$$r = r_3 - r_{-3} = k_3 \frac{b_A P_A}{1 + b_A P_A + l} \frac{\sqrt{b_{H_2} P_{H_2}}}{1 + \sqrt{b_{H_2} P_{H_2}} + b_a P_a} - k_{-3} \frac{l}{1 + b_A P_A + l} \frac{1}{1 + \sqrt{b_{H_2} P_{H_2}} + b_a P_a}, \quad (2)$$

in which $k_{\pm i}$ are the rate constants for the stages in the forward and reverse directions and b_A, b_{H_2}, and b_a are the adsorption coefficients of acetone, hydrogen, and the alcohol respectively, and

$$l = (k_3 b_A P_A + k_{-4} b_a P_a)/(k_4 \sqrt{b_{H_2} P_{H_2}} + k_{-3}).$$

The quantity l represents the "degree of reversibility of the reaction"[64,65] and is equal to the fraction of the centres Z_A occupied by the same hydrogenated form of acetone. Eqn. (2) agrees quantitatively with experimental data for the kinetics of reaction (I) in both the forward and reverse directions: the inhibiting effect of hydrogen on the adsorption of the alcohol is then clearly manifested.[64]

Under conditions remote from equilibrium (at low temperatures where $l \to 0$), acetone is hydrogenated by the mechanism presented in Scheme 3:

Scheme 3

1) $H_2 + 2Z_H = 2Z_HH$,
2) $(CH_3)_2CO + Z_A = Z_A(CH_3)_2CO$,
3) $Z_A(CH_3)_2CO + Z_HH \rightarrow Z_A(CH_3)_2COH + Z_H$,
4) $Z_A(CH_3)_2COH + Z_HH \xrightarrow{fast} Z_H(CH_3)_2CHOH + Z_A$,
5) $Z_H(CH_3)_2CHOH \xrightarrow{fast} (CH_3)_2CHCH + Z_H$.

In this case Eqn. (2) assumes a simpler form[13,15] (the term characterising the reverse reaction is missing) and describes satisfactorily the kinetic data for the forward process in the presence of all the catalysts investigated (Table 3) with the exception of copper and ruthenium. When the copper and ruthenium catalysts are used, account must be taken of the observed inhibition of reaction (I) by the isopropyl alcohol formed and of the involvement in the reaction of the hydrogen adsorbed in the molecular form, which we have established by the programmed thermal desorption method.[15,43] Scheme 3 must therefore be modified somewhat:

Scheme 4

1) $H_2 + Z_H = Z_HH_2$,
2) $(CH_3)_2CO + Z_A = Z_A(CH_3)_2CO$,
3) $Z_A(CH_3)_2CO + Z_HH_2 \rightleftarrows Z_H(CH_3)_2CHOH$,
4) $Z_H(CH_3)_2CHOH = (CH_3)_2CHOH + Z_H$.

Here too the rate-limiting stage is the interaction of the adsorbed starting materials, while in the remaining stages equilibrium is established. The kinetic equation

$$r = k_3 \frac{b_A P_A}{1 + b_A P_A} \frac{b_{H_2} P_{H_2}}{1 + b_{H_2} P_{H_2} + b_a P_a},$$

which describes satisfactorily the experimental data for the Cu and Ru catalysts,[14,15] corresponds to this mechanism (Scheme 4).

The study of the individual stages of the mechanism of the hydrogenation of acetone on transition metals has shown[65] that, if the reactive π-complex (I) is formed on adsorption of the ketone, then partial reduction of the complex leads only to isopropyl alcohol. When acetone is adsorbed as the donor–acceptor complex (II), the carbonyl group of the ketone is fully reduced with elimination of the oxygen atom. Bearing in mind that acetone and other ketones are weak Lewis bases, we achieve such alteration in the form of adsorption and in the mode of reaction[69] by using bifunctional catalysts containing, apart from the transition metals, also strong Lewis acid centres L to which the oxygen of the carbonyl group is bound via the unshared electron pair. Hydrogen is activated on the metal. We propose[70] the following two pathway mechanism (Scheme 5) of the complete reduction of the carbonyl group of acetone [reaction (II)]:

Scheme 5

1) $H_2 + 2Z_H = 2Z_HH$,
2) $(CH_3)_2CO + Z_L = Z_L(CH_3)_2CO$,
3) $Z_L(CH_3)_2CO + Z_HH = Z_L(CH_3)_2COH + Z_H$,
4) $Z_L(CH_3)_2COH + Z_HH = Z_L(CH_3)_2CHOH + Z_H$,
5) $Z_L(CH_3)_2CHOH = (CH_3)_2CHOH + Z_L$,
6) $Z_L(CH_3)_2COH + Z_HH \rightarrow Z_LC_3H_6 + H_2O + Z_H$,
7) $Z_LC_3H_6 + Z_HH \rightarrow Z_LC_3H_7 \xrightarrow{Z_HH} C_3H_8 + Z_L + 2Z_H$.

Equilibrium is established in stages 1–5 which determine the rate of formation of isopropyl alcohol. Stage 3 is common to the synthesis of the alcohol and the hydrocarbon. The rate of the total hydrogenation of acetone is limited by Stage 6, in which the addition of a H atom to the adsorbed semihydrogenated form of the acetone is accompanied by dehydration and the formation of adsorbed propene $Z_LC_3H_6$ in the form of a π-allyl complex,[71] which is then rapidly hydrogenated to propane in a single stage.

The following kinetic equation corresponds to Scheme 5:

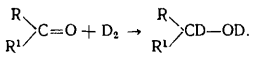
$$r = k_6 \frac{K_3 b_A P_A \sqrt{b_{H_2} P_{H_2}}}{1 + b_A P_A \left(1 + K_3 \sqrt{b_{H_2} P_{H_2}}\right) b_a P_a} \frac{\sqrt{b_{H_2} P_{H_2}}}{1 + \sqrt{b_{H_2} P_{H_2}}}, \quad (3)$$

where k_6 is the rate constant for the rate-limiting stage and K_3 the equilibrium constant for the third stage. Eqn. (3) describes satisfactorily[70] the experimental and kinetic data for the complete hydrogenation of acetone in the presence of the bifunctional catalyst.

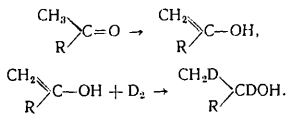
As a result, the kinetic and thermodynamic characteristics of the different stages in the mechanisms of the acetone hydrogenation reactions occurring via Schemes 2–5 were calculated from experimental data for the catalysts listed in Table 3: the rate constants, the adsorption coefficients, the activation energies, the heats (q_i) and entropies (ΔS_i^0) of adsorption, and the pre-exponential factors of the rate constants. Analysis of the data obtained yielded new arguments in support of the proposed mechanisms and made it possible to find relations between the physicochemical and catalytic properties of the substances which can be used in the selection and improvement of catalysts for the hydrogenation of carbonyl compounds. These relations will be examined below.

The mechanism of the hydrogenation of acetone and other ketones has been investigated with the aid of deuterium–hydrogen

exchange.[2,72–74] In order to describe the interaction of deuterium with carbonyl compounds, two limiting mechanisms are usually employed:[2,72] the "ketone" and "enol" mechanisms. According to the ketone mechanism, deuterium adds directly to the carbonyl group:



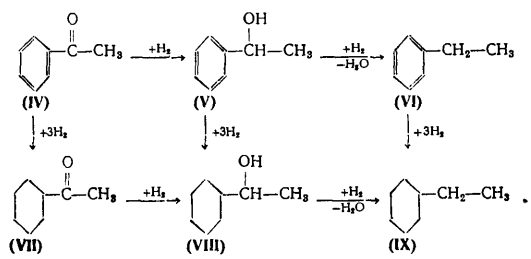
The "enol" mechanism presupposes the preliminary enolisation of the ketone and the subsequent addition of deuterium to the C=C bond:



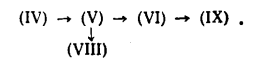
According to data[73,74] obtained in the study of the interaction of deuterium with alicyclic ketones in the presence of a prefused iron catalyst (in the temperature range from 323 to 483 K), the relative contributions of the "ketone" and "enol" mechanisms are in the proportions 1 : 1.5.

2. Hydrogenation of acetophenone

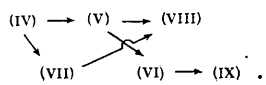
The hydrogenation of acetophenone is a complex process whose detailed mechanism has not been investigated:



Schemes for the conversion of acetophenone in the presence of nickel, platinum, and palladium have been proposed by Balandin and co-workers[75] on the basis of calculations of the adsorption energies of the index groups. On nickel, the hydrogenation process takes place in accordance with the following scheme:



For the palladium catalyst, the scheme remains the same but, as a consequence of the greater difference between the adsorption energies of the CO group and the aromatic rings, the addition of hydrogen to the ring on palladium is fairly difficult. On platinum as well as on nickel and palladium, the keto-group is most readily hydrogenated. At the same time, the reactivity of the aromatic rings in the presence of the platinum catalyst becomes higher than that of the alcoholic group, which was not observed[75] on nickel and palladium. It has therefore been suggested[75] that the hydrogenation of acetophenone proceeds according to the scheme



In terms of activity in the acetophenone hydrogenation reaction, the metals considered can be arranged in the following sequence: Ni > Pd > Pt. The hydrogenolysis on the metals indicated should proceed with much difficulty.[75]

In the hydrogenation of acetophenone on industrial catalysts (Cu–Cr–Ba; Ni–Ti–Al), it has been shown[76] that the copper–chromium–barium specimen is more selective in relation to the formation of methylphenylmethanol, while the nickel–titanium–aluminium specimen is more active in relation to the overall conversion of acetophenone. In the presence of the catalysts indicated, the process proceeds via the consecutive scheme (IV) → (V) → (VI). An empirical kinetic equation has been obtained and a mathematical model has been proposed for the process.[76]

3. Hydrogenation of aliphatic and cyclic ketones

The kinetics of the hydrogenation of aliphatic and alicyclic ketones in the presence of a premelted iron catalyst are described by the power equation[77]

$$r = kP_{\text{k}}P_{\text{H}_2}^{0.5}. \qquad (4)$$

The following mechanism, presupposing the adsorption of the reactants on the same centres (Z) of the iron catalyst, has been put forward on the basis of kinetic data for the hydrogenation of 2-octanone:[78]

Scheme 6

1) $H_2 + 2Z = 2ZH$,
2) $R^1COR^2 + Z = ZR^1COR^2$
3) $ZR^1COR^2 + ZH \rightarrow ZR^1C(OH)R^2$,
4) $ZR^1C(OH)R^2 + ZH = ZR^1CH(OH)R^2$,
5) $ZR^1CH(OH)R^2 = R^1CH(OH)R^2 + Z$.

The rate of the process is limited by the addition of the first hydrogen atom to the adsorbed ketone molecule; equilibrium is established in the remaining stages. Eqn. (4) has been used[77] to optimise the hydrogenation of alicyclic ketones (C_5, C_6) formed in the synthesis of alcohols by the oxidation of higher paraffins.

In order to optimise the phenol hydrogenation process in the manufacture of caprolactam, the kinetics of the addition of hydrogen to phenol and cyclohexanone molecules have been studied.[79] The following mechanism has been proposed for the reversible hydrogenation of cyclohexanone to cyclohexanol on nickel catalysts on the basis of kinetic measurements:[80]

Scheme 7

1) $H_2 + 2Z_H = 2Z_HH$,
2) $C_6H_{10}O + Z_c = Z_cC_6H_{10}O$,
3) $Z_cC_6H_{10}O + 2Z_HH \rightleftarrows Z_cC_6H_{11}OH + 2Z_H$,
4) $Z_cC_6H_{11}OH = C_6H_{11}OH + Z_c$,

where Z_c and Z_H are the centres for the adsorption of the ketone and hydrogen respectively. It is assumed that the two hydrogen atoms add simultaneously to the adsorbed ketone molecule. Cyclohexanone and hydrogen are adsorbed on different centres (Z_c and Z_H), of the catalyst, whose surface is regarded as effectively uniform. The kinetic equation proposed on the basis of this mechanism (Scheme 7) describes satisfactorily the experimental relations. These relations served as the basis of the mathematical model used to optimise the synthesis of cyclohexanol.[81]

The mechanisms of the hydrogenation of aliphatic and cyclic ketones (Schemes 6 and 7) are in general similar to the mechanism of the incomplete hydrogenation of acetone (Scheme 2), which we have established, while the kinetic equation (2), which we proposed for the description of the experimental relations obtained in the hydrogenation of acetone, is applicable also to the description of the

kinetics of the hydrogenation of 2-octanone established by Glebov et al.[78]

4. Hydrogenation of carbon monoxide

Numerous studies have been devoted to the hydrogenation of CO on metals, which leads mainly to the formation of methane and higher hydrocarbons.[36–38, 82–85] The proposed mechanisms[86–88] refer solely to the conversion of CO into methane and do not take into account the simultaneous formation of methane homologues. The mechanism of the formation of methane homologues has stages in common with the mechanism of the synthesis of methane itself and these common stages affect the rate of formation of CH_4.

The study of reactions (VII) and (VIII) on deposited metallic catalysts of different types (Table 4) enabled us to put forward[89–92] the following CO hydrogenation mechanism:

Scheme 8

1) $H_2 + 2Z = 2ZH$,
2) $CO + Z = ZCO$,
3) $ZCO + ZH = ZCOH + Z$,
4) $ZCOH + ZH \rightarrow ZX_0 + Z$,
5) $ZX_0 + ZH \rightarrow ZX_0' \xrightarrow{ZH} CH_4 + H_2O + Z$,
6) $ZX_0 + ZCO \rightarrow ZX_1 + Z$,
6') $ZX_1 + ZH \rightarrow ZX_1' \xrightarrow{ZH} C_2H_6 + H_2O + Z$,
7) $ZX_1 + ZCO \rightarrow ZX_2 + Z \ldots$,

where the adsorbed AX_0 species is the common intermediate in the formation of all the products. Its interaction with ZH affords methane (chain termination), while the reaction of ZX_0 with a carbon-containing species leads to a new adsorbed species ZX_1,, leading to the synthesis of higher hydrocarbons (chain propagation).

Table 4. Specific catalytic activities and selectivities of metal catalysts in the hydrogenation of CO.

Catalyst	$\bar{d}$ for metal, nm	$10^7 r^*$, mol m^{-2} s^{-1}	Selectivity w.r.t. methane S_{CH_4}
Ru/Al_2O_3	4.4	6.7	0.872
Rh/Al_2O_3	2.5	5.5	0.943
Co/Al_2O_3	7.5	5.04	0.940
Ni/Al_2O_3	2.4	4.7	0.957
Ni/Cr_2O_3	11.5	4.7	1.0
Pt/Al_2O_3	3.9	0.4	0.99
Ir/Al_2O_3	6.8	0.2	1.0
Pd/Al_2O_3	5.0	0.1	1.0
Fe/Al_2O_3	4.2	inactive	—
Cu/Al_2O_3	3.4	inactive	—

Note. Mixture composition: P_{CO} = 20 kPa, P_{H_2} = 50 kPa.

*Calculated for 548 K.

The first four stages in Scheme 8 determine the activity of the catalyst and the others determine its selectivity. It is assumed that adsorption equilibrium is established in stages 1–3, while the rate of the overall process is then determined by stage 4. The way in which ZCOH interacts with ZH, via the intermediate formation of the "enolic" form of formaldehyde ZCOH or via the formation of the surface carbide ZC with liberation of water, is immaterial for the process kinetics.

The question of the composition and structure of the carbon-containing species interacting with ZX_i is obscure. The IR spectra obtained under the conditions of the catalysis[84] usually manifest only the absorption bands of the adsorbed CO molecules which form complexes with the deposited metals [see Eqn. (X)]. Consequently, the surface concentrations of other carbon-containing intermediate compounds can be regarded as negligible.

The kinetic equation for the overall conversion of CO (in conformity with Scheme 8) can be written in the form

$$r = r_4 = k_4 \frac{K_3 b_{CO} P_{CO} b_{H_2} P_{H_2}}{\left[1 + b_{CO} P_{CO} + \sqrt{b_{H_2} P_{H_2}}(1 + K_3 b_{CO} P_{CO})\right]^2}, \quad (5)$$

where k_4 is the rate constant for the rate-limiting stage 4, K_3 the equilibrium constant for stage 3, and $b_i P_i$ are the products of the adsorption coefficients and the partial pressures of the reactants. Eqn. (5) describes quantitatively the experimental relations for all the catalysts which we have investigated and agrees with the kinetic results obtained in other studies.[86,87,93] The heats of adsorption q_{CO} of CO on metals, agreeing with the values of q_{CO} found by other procedures,[23] were calculated from the temperature variation of b_{CO}.[90,91]

The following expression for the process selectivity with respect to methane S_{CH_4} can be written on the basis of Scheme 8:[89,91,92]

$$S_{CH_4} = r_5/(r_5 + r_6) = [1 + (k_6 b_{CO} P_{CO}/k_5 \sqrt{b_{H_2} P_{H_2}})]^{-1}, \quad (6)$$

where r_i and k_i are the rates of stages 5 and 6 and the corresponding rate constants.

The selectivity with respect to higher hydrocarbons S_{C_n} is $1-S_{CH_4}$. Consequently

$$S_{C_n} = \frac{k_6 b_{CO} P_{CO}/k_5 \sqrt{b_{H_2} P_{H_2}}}{1 + (k_6 b_{CO} P_{CO}/k_5 \sqrt{b_{H_2} P_{H_2}})}. \quad (7)$$

Eqns. (6) and (7) lead to kinetic equations describing the processes involving the hydrogenation of CO to methane and higher hydrocarbons (the Fischer-Tropsch synthesis):

$$r_{CH_4} = rS_{CH_4}, \quad r_{C_n} = rS_{C_n}. \quad (8)$$

These expressions describe the experimental data satisfactorily.[89,91]

The rate of formation of individual hydrocarbons can be calculated from Eqn. (8) and the Schultz–Flory equation:[84]

$$c_n = n(1-\alpha)^2\alpha^{n-1}, \quad (9)$$

where c_n is the concentration of the hydrocarbon in which the number of carbon atoms is n. The coefficient α, which is usually found empirically from the proportions of the products,[84] is the probability of the formation of the higher hydrocarbon, i.e. the ratio of the rate of chain propagation (r_p) to the sum of the rates of chain propagation and termination (r_t):

$$\alpha = r_p/(r_p + r_t) = r_6/(r_6 + r_5). \quad (10)$$

The physical significance of the coefficient α follows from Eqn. (10). It consists in the fact that $\alpha = S_{C_n}$ in Eqn. (9):

$$\alpha = [1 + \beta(\sqrt{P_{H_2}}/P_{CO})]^{-1}, \quad (11)$$

where

$$\beta = k_5 \sqrt{b_{H_2}}/k_6 b_{CO}.$$

Thus the mechanism proposed for the hydrogenation of CO (Scheme 8) and the corresponding kinetic equation (5) make it possible to elucidate the significance of the coefficient α in terms of the rate (equilibrium) constants for the elementary stages.

V. The rules for the selection of ketone hydrogenation catalysts

1. Catalytic activity

The available data on the empirical selection of catalysts for the hydrogenation of carbonyl compounds are presented in a model review.[1] The mechanisms which we have established for the acetone hydrogenation reactions permit an approach to a rational selection and improvement of catalysts for the selective hydrogenation of carbonyl compounds.

It can be seen from the data in Table 3 that the specific catalytic activity r [the rate of reaction (I)] decreases in the sequence

$$\begin{aligned} &Pt/Al_2O_3 > Cu/Cr_2O_3 > Ni\ black > Ni/Cr_2O_3 > \\ &> Ir/Al_2O_3 > Rh/Al_2O_3 > Ni/Al_2O_3 > Ru/Al_2O_3 > \\ &> Cu/Al_2O_3 > Co/Al_2O_3 > Co\ black \gg Fe/Al_2O_3, Pd/Al_2O_3, Cu\ black. \end{aligned} \quad (XII)$$

The last three members of this series did not exhibit an activity in reaction (I); the causes of this have already been examined.[13,14]

The series (XII) agrees qualitatively with the activity series of metallic films found by Stoddart and Kemball:[44]

$$Pt > Ni > Fe,\ W > Pd > Au. \quad (XIII)$$

However, it is essential to note that the following problem arises when the metal activity series in low-temperature hydrogenation (and similar processes) are compared and interpreted. During these processes, there is no appreciable influence of the reaction medium on the catalyst, levelling out the differences between specimens of the same chemical composition but with different degrees of dispersion, as happens, for example, in many oxidation reactions[67] occurring at higher temperatures. The smaller the crystal size, the higher the coordinative unsaturation of the surface M centres and the greater their affinity for the reactants. This is indicated, in particular, by the increase in the heat of adsorption of acetone q_A with decrease in the average metal particle size $\bar{d}$ (Fig. 3). The latter agrees with the results of numerous quantum-chemical calculations,[94] showing that, on passing from small clusters to large crystals, the metal–metal cohesion bond is strengthened and the metal–adsorbate adhesion bond is weakened, saturation being attained in the region of approximately 10–20 nm. Relations of this kind are apparently characteristic of low-temperature "structure-sensitive" (in Boudart's terminology[95]) hydrogenation processes and other reactions.

With increase in the heat of adsorption of acetone, q_A, the adsorption entropy falls—the thermodynamic compensation effect occurs:[15,62] the higher the heat of adsorption, the more negative the entropy (ΔS^0_H) (the smaller the mobility of the adsorbed species). However, even in the presence of such an effect, the influence of the degree of dispersion of the metal on the acetone adsorption coefficient b_A is considerable (it vanishes only on passing to large crystals). The position of the metal in the activity series therefore depends both on its chemical nature and on the degree of its dispersion.

For "structure-sensitive" reactions such as the hydrogenation of the carbonyl group of ketones, the role of the degree of the dispersion of the metal may not be manifested solely in its influence on the energy of the bonds between the reactants and the surface. The probability of the multipoint adsorption of complex molecules of the compound hydrogenated and of the activated complexes may depend on the dimensions of the microcrystal (Fig. 2). Furthermore, account must be taken of the influence of the chemical nature of the crarier on the activity both as a consequence of the interaction of the metal with the carrier and of the activation of the substrate on the sections of the carrier adjoining the metal. The ability of the hydrogen adsorbed on the metal to migrate to neighbouring sections of the oxide carrier is well known.[96] This can explain the finding that the Cu/Cr_2O_3 catalyst, which has approximately the same adsorption coefficients b_A and b_{H_2} as Cu/Al_2O_3, is characterised by a significantly greater (by a factor of 40–50) rate constant k_L for the rate-limiting stage (Table 3).

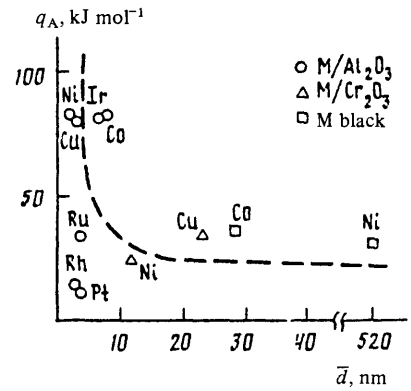


Figure 3. Dependence of the heat of adsorption of acetone on the degree of dispersion of the metal.

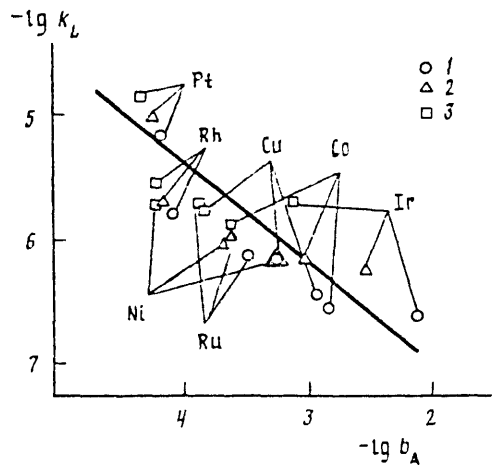


Figure 4. Dependence of the rate constant for the rate-limiting stage of the hydrogenation of acetone on the adsorption coefficient of acetone at different temperatures (K): *1*, 337; *2*, 348; *3*, 364.

In the case of metals deposited on the same carrier (γ-Al_2O_3) and having approximately the same degrees of dispersion ($\bar{d} \simeq 3$–7 nm), the specific catalytic activity r diminishes in the sequence

$$Pt > Ir > Rh > Ni > Ru > Cu > Co \gg Fe,\ Pd\ . \quad (XIV)$$

This series can be naturally interpreted on the basis of the mechanism proposed for the hydrogenation of acetone (Scheme 2). The bonds formed by the ketone and H_2 with the surface are ruptured in the rate-determining stage 3. One should therefore expect a decrease in the rate constant for the rate-limiting stage with increasing strength of the reactant–metal adsorption bond. Fig. 4 shows that k_L does indeed diminish with increase in b_A. b_A diminishes steadily, in its turn, with increase in the electronegativity of the metal χ_M (Fig. 5). This can be explained by the dominant role of the dative interaction in the formation of the adsorption π-complex (I): with increase in χ_M, the energy of this interaction falls, since the ability of the metal to give up electrons to the ketone molecule being adsorbed decreases.

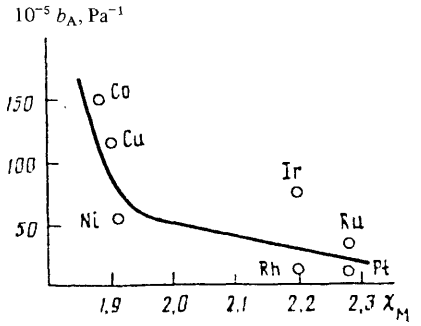


Figure 5. Relation between the adsorption coefficients of acetone (337 K) for metals deposited on Al_2O_3 and the Pauling electronegativities of the metals.

The fact that $\lg k_L$ is correlated satisfactorily solely with the strength of the acetone bond can be explained in the following manner. We formulate the Brønsted–Temkin equation for k_L:

$$k_L = gK_L^{\alpha}, \qquad (12)$$

where g and α are constants and k_L is the equilibrium constant for stage 3 (Scheme 2). In its turn, $K_L = b_{AH}K/b_A\sqrt{b}_{H_2}$ [b_{AH} is the adsorption coefficient of the semihydrogenated form $(CH_3)_2COH$ and K is the equilibrium constant, independent of the catalyst, of the gas-phase reaction $(CH_3)_2CO + 0.5H_2 = (CH_3)_2COH$]. Since the M–H bond is ruptured in stage 3 (Scheme 2) and the analogous M–C σ-bond is formed in the intermediate compound $(CH_3)_2C(M)–OH$, one can assume that the ratio $b_{AH}/\sqrt{b}_{H_2}$ changes little on passing from one metal to another. Therefore $K_L \simeq (\text{const.})b_A^{-1}$, so that

$$k_L = g\,(\text{const})\,b_A^{-\alpha} = (\text{const}')\,b_A^{-\alpha}. \qquad (13)$$

The transfer coefficient α can be found from the slope of the linear plot of $\lg k_L = f(\lg b_A)$ (Fig. 4). It proved to be 0.7, which is close to the typical value $\alpha = 0.5$.

In comparing the rates of the overall reaction (I) on different metals, one should use the kinetic equation (2), which can be put in the form $r = k\theta_A\theta_H$ (θ_A is the degree of surface coverage by acetone). Since saturation of the active centres Z_H by hydrogen ($\theta_H \simeq 1$) was attained in most cases for the conditions selected (Table 3), it follows that $r = k_L\theta_A$.

Consider the dependence of r on the heat of adsorption of acetone q_A. By differentiating $\ln r$ with respect to q_A and setting the derivative $d \ln r/dq_A$ equal to zero, we find [taking into account Eqn. (13)] the condition for the optimum $(\theta_A)_{opt} = 1 - \alpha$. This means that the highest rate of hydrogenation is attained for a degree of saturation at the centres Z_A by acetone equal to $1 - \alpha$. The optimum adsorption coefficient of acetone corresponds to this:

$$(b_A)_{opt} = [(\theta_A)_{opt}/(1 - (\theta_A)_{opt})]\,P_A^{-1} = [(1 - \alpha)/\alpha]\,P_A^{-1}.$$

The calculated quantity $(b_A)_{opt} = 4.3 \times 10^{-5}$ Pa^{-1} is close to the experimental value b_A for Pt (6×10^{-5} Pa^{-1} at 364 K), which explains why Pt occupies the first place in the series (XIV). For acetone–metal bond energies exceeding the optimum value, the activity should fall and, when $q_A < (q_A)_{opt}$ the activity should increase with increasing q_A, which is in fact observed in practice (Fig. 6).

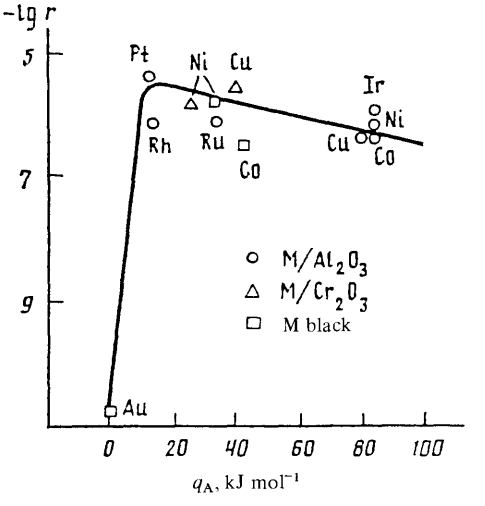


Figure 6. Dependence of the catalytic activities of metals in the hydrogenation of acetone at 364 K on the heat of adsorption of the ketone.

When cyclopentanone is hydrogenated on metallic films[97] the following metal activity series holds: Pt > Pd > Rh > W > Ni. It is in general similar to the sequences (XII) and (XIV) (with the exception of the position of Pd), which justifies the hypothesis that the rules established for the hydrogenation of acetone are fairly typical for the reactions of compounds of this class.

2. Selectivity

Together with hydrogenation reactions of type (I), the complete reduction of ketones with formation of the corresponding hydrocarbons [reaction (II)] can take place on metal catalysts. This process is analogous to the synthesis of methane from CO and H_2.

In the hydrogenation of acetone in the temperature range from 300 to 370 K on deposited metal, the formation of propane was observed[15] in the initial period of the reaction only on platinum (the selectivity with respect to C_3H_8 was 100%) and on iridium. In the latter case, propane and isopropyl alcohol were detected in the reaction products.

In catalysis on metallic films,[44] the activity of the metals in reaction (II) diminishes in the sequence

$$Pt > W > Ni > Fe \gg Pd, Au, \qquad (XV)$$

which resembles the activity series (XIV) in relation to the overall acetone hydrogenation process.

In order to interpret the selectivity with respect to C_3H_8, it is sufficient to supplement Scheme 3 by a complex stage involving further interaction of the adsorbed alcohol with the adsorbed H atoms:

$$6)\ Z_H(CH_3)_2CHOH + Z_HH \rightarrow (I) \xrightarrow[fast]{Z_HH} C_3H_8 + H_2O + 3Z_H,$$

where (I) is an intermediate compound.

Thus the selectivity with respect to the hydrocarbon is

$$S_{C_3H_8} = k_6\theta_H/(k_6\theta_H + k_5).$$

At fairly high pressures P_{H_2}, where $\theta_H \simeq 1$, we obtain

$$S_{C_3H_8} = [1 + (k_5/k_6)]^{-1}.$$

The constants k_5 and k_6 depend equally on the bond energy between the alcohol molecule and the surface, so that the ratio k_5/k_6 does not depend on this energy. At the same time, the constant k_5 is also independent of the M–H bond energy, whereas k_6 increases as this bond is weakened. Consequently the selectivity with respect to propane is given by

$$S_{C_3H_8} = [1 + \exp(\alpha q_{H_2}/2RT)\ (\text{const})]^{-1}. \qquad (20)$$

According to Eqn. (20), one should expect the formation of hydrocarbons in the hydrogenation of ketones on metals which bind hydrogen least strongly. Among the deposited catalysts tested in the acetone hydrogenation reaction, such metals are Pt, Ir, and Cu. The formation of propane on Pt and Ir only shows that an obligatory condition is also the involvement in stage 6 of atomic hydrogen (hydrogen is adsorbed on Cu in the form of molecules[43]).

The activity r of transition metals in relation to the overall acetone hydrogenation process diminishes with increase in the heat of adsorption of the ketone q_A (Fig. 6). Comparison of the values of q_A with known[23] values of q_{H_2} shows that q_A and q_{H_2} vary in general in parallel. The activity of the metal r therefore falls with increasing q_{H_2}. Since $S_{C_3H_8}$ also diminishes with increasing q_{H_2} according to Eqn. (20), one should expect a similarity between the overall metal activity series and the activity series in relation to reaction (II), which is in fact observed [cf the series (XIV) and (XV)].

The extensive hydrogenation of ketones is promoted by the presence of atomic hydrogen weakly bound to the metal surface. On passing from a deposited metal to a metal film, the strength of the M–H bond should diminish as a consequence of the increase in the size of the metal crystals. This can also be used to account for the finding that, in the case of metallic films, the formation of propane could be detected on a greater number of metals than on deposited catalysts having a high degree of dispersion.

It follows from Eqn. (20) that, with increase in temperature, the selectivity with respect to the hydrocarbon should increase, which is also in agreement with experimental data.[44]

VI. The rules for the selection of carbon monoxide hydrogenation catalysts

1. Catalytic activity

Data for the specific catalytic activities of a large number of transition metals in relation to the overall conversion of CO have been obtained in a number of studies.[86–88] The activities of metals deposited on Al_2O_3, measured at atmospheric pressure and 548 K,[86] decrease in the sequence

$$Ru > Fe > Ni > Co > Rh > Pd > Pt > Ir. \qquad (XVI)$$

The activity series for metals deposited on SiO_2 is somewhat different:[88]

$$Co > Fe > Ru > Ni > Rh > Ir,\ Pt > Pd > Cu. \qquad (XVII)$$

The data which we have obtained[98] for the specific catalytic activities of metal catalysts in relation to the hydrogenation of CO and also for their selectivities with respect to CH_4 are presented in Table 4. It is seen that at 548 K the activities of the metals deposited on γ-Al_2O_3 and having approximately the same degrees of dispersion ($\sim$2–7 nm) decrease in the sequence

$$Ru > Rh > Co > Ni > Pt > r > Pd \gg Fe, Cu. \qquad (XVIII)$$

In general the series (XVI)–(XVIII) are similar: among group VIII metals, the metals of the iron and ruthenium subgroups are the most active, while platinum, palladium, and iridium are least active. Activity series, analogous to the series (XVIII), established at atmospheric and elevated pressures have been described.[82,99]

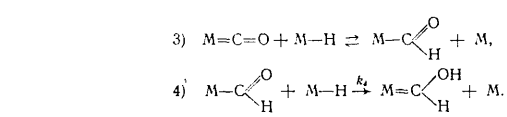
The catalytic activities of deposited cobalt catalysts in the Fischer–Tropsch synthesis at 540 K diminish in the following sequence of carriers:

$$SiO_2 > TiO_2 > ZrO_2 > BeO > Cr_2O_3 > Al_2O_3 > MgO \gg WO_3. \qquad (XIX)$$

At the same temperature, the activities of deposited nickel catalysts diminish in the sequence of carriers

$$ZrO_2 > TiO_2 > BeO > MgO > Al_2O_3 > SiO_2 > Cr_2O_3 \gg WO_3. \qquad (XX)$$

The variation of the activities of the metals in the sequence (XVIII) can be explained on the basis of the CO hydrogenation mechanism (Scheme 8). For this purpose, we specify in a more concrete form the chemistry of stages 3 and 4. If one begins with the assumption that the key intermediate compound ZX_O represents the adsorbed "enolic" form of formaldehyde,[82] the stages indicated can be formulated as follows:



At low temperatures, at which the activity series (XVIII) has been attained, the degree of surface coverage by CO molecules (θ_{CO}) is close to unity. Eqn. (5) then assumes the form

$$r = k_4 K_3 b_{H_2} P_{H_2} (b_{CO} P_{CO})^{-1}. \quad (14)$$

We shall consider the dependence of the constant of this equation on the heats of the stages, assuming that the entropy terms are approximately constant in a series of isotypical catalysts. It is also evident that

$$b_{CO}^{-1} \propto \exp(-q_{CO}/RT), \quad (15)$$

$$b_{H_2} \propto \exp(q_{H_2}/RT). \quad (16)$$

Since the M–H bond is ruptured and the M=C bond is partly ruptured, in stage 3, it follows that

$$K_3 \propto \exp(-q_{CO}/2RT - q_{H_2}/2RT). \quad (17)$$

We have the following expression for the equilibrium constant for stage 4:

$$K_4 \propto \exp(q_{CO}/2RT - q_{H_2}/2RT),$$

On the basis of the Brønsted–Temkin relation, we formulate the following expression for the rate constant for this stage:

$$k_4 \propto \exp(\alpha q_{CO}/2RT - \alpha q_{H_2}/2RT) \quad (18)$$

where α is the transfer coefficient, usually equal to 0.5.

On substituting Eqns. (15)–(18) in Eqn. (14) and taking into account the fact that the comparison is carried out at a constant P_i, we obtain (for $\alpha = 0.5$)

$$\ln r \propto -1.25(q_{CO}/RT) + 0.25(q_{H_2}/RT).$$

Since the absolute value of the numerical coefficient of q_{CO} is much greater than that of q_{H_2} and in addition $q_{CO} > q_{H_2}$,[23,42] one can write

$$\ln r \cong -1.25(q_{CO}/RT) + \text{const}, \quad (19)$$

i.e. the catalytic activity should decrease with increase in the heat of adsorption CO, which is confirmed qualitatively by the data in Fig. 7.

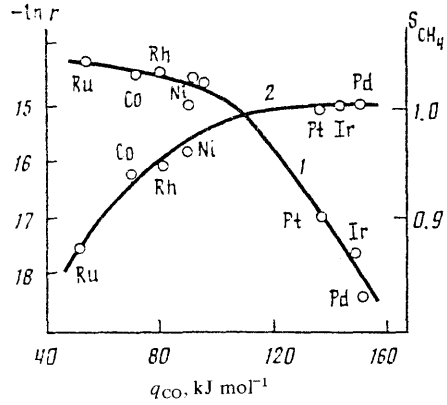


Figure 7. Dependence of the catalytic activities of metals (curve *1*) in the hydrogenation of CO and of their selectivities with respect to methane (curve *2*) on the heat of adsorption of CO.

In its turn, q_{CO} depends on the average metal particle size d: the smaller d, the greater q_{CO}. Evidently the influence of carriers [see the series (XIX) and (XX)] on the activity of a given metal is manifested primarily by a change in the degree of dispersion of the deposited metal M, on which depends the heat of adsorption of CO. With increase in $\bar{d}$, r initially rises, since this entails a decrease in q_{CO}, reaching a maximum in the presence of Co/SiO_2 ($\bar{d}$ = 38 nm) and Ni/ZrO_2 ($\bar{d}$ = 97 nm) (Table 5), but on further increase in $\bar{d}$, the M–CO bond is apparently weakened so much that r decreases in the presence of Co/TiO_2 ($\bar{d}$ = 46 nm) and Co/WO_3 ($\bar{d}$ = 60 nm). The same also applies to nickel catalysts: on Ni/TiO_2 ($\bar{d}$ = 103 nm) and Ni/WO_3 ($\bar{d}$ = 181 nm), r decreases. A similar dependence of the activity of the metal on the degree of dispersion was observed by Boudart and McDonald[68] and Kuznetsov et al.[100] Furthermore, the yield of oxygen-containing compounds (mainly ethanol) increased with increase in the degree of dispersion of cobalt deposited on the same carrier.[100]

The coefficient α in the Schultz–Flory equation also diminishes with increasing degree of dispersion of the metal. If account is taken of Eqn. (7) and the fact that q_{CO} increases as $\bar{d}$ diminishes, the dependences of r and α on $\bar{d}$ described above become analogous to the dependences of r and S_{C_n} on q_{CO} obtained whilst varying the chemical nature of the metal (Fig. 7).

2. Selectivity

It is seen from the data in Table 4 that the selectivity in the hydrogenation of CO to methane diminishes (and that with respect to higher hydrocarbons increases) in the following sequence of metal catalysts:

$$Pd,\ Ir > Pt > Ni > Rh > Co > Ru. \quad (XXI)$$

The selectivity with respect to higher hydrocarbons S_{C_n} of the CO catalyst diminishes in the sequence of carriers

$$ZrO_2 > MgO > BeO > Al_2O_3,\ Cr_2O_3 > SiO_2 > TiO_2 > WO_3 \quad (XXII)$$

and that of the nickel catalyst diminishes in the sequence

$$ZrO_2 > Al_2O_3 > Cr_2O_3 > MgO > BeO,\ SiO_2 > TiO_2 > WO_3. \quad (XXIII)$$

Comparison of the series (XVIII) with (XXI) shows that there is an antiparallel relation between the activity and the selectivity with respect to methane S_{CH_4}: the higher r, the smaller S_{CH_4} (Fig. 8). It has been shown in a study[92] where this empirical relation was noted for the selectivity with respect to CH_4 can be put in the form $S_{CH_4} = (1 + \eta)^{-1}$, where $\eta = r_6/r_5$ is the ratio of the rates of stages 6 and 5 in the CO hydrogenation mechanism (Scheme 8). Bearing in mind that, on passing from one metal to another, the changes in η are associated mainly with the changes in the rate constants (k_6 and k_5) for the stages indicated and the formation of ZX_0' and ZX_1 does not involve the appearance of new bonds with the catalyst (H which adds to the adsorbed species of CO is inserted in the M–C bond), we obtain[92,98]

$$S_{CH_4} = [1 + \text{const}' \cdot \exp(-\alpha q_{CO}/RT)]^{-1} \quad (21)$$

(it is assumed that the changes in q_{CO} predominate over the changes in q_{H_2}). It follows from Eqn. (21) that the selectivity with respect to CH_4 should increase (whilst that with respect to higher hydrocarbons should diminish) with increase in q_{CO}, which is in fact

actually observed (Fig. 7). Simultaneous solution of Eqns. (19) and (21) leads (after the elimination of q_{CO} from them) to the expression[92,98]

$$S_{CH_4} = (1 + Br^c)^{-1} \quad (22)$$

(B and c are constants). Eqn. (22) explains the observed antiparallel variation of the activity S_{CH_4} (Fig. 8). Furthermore, it follows from Eqn. (22) (in conformity with experimental data) that $S_{CH_4} \to 1$ when $r \to 0$ and $S_{CH_4} \to 0$ when $r \to \infty$.

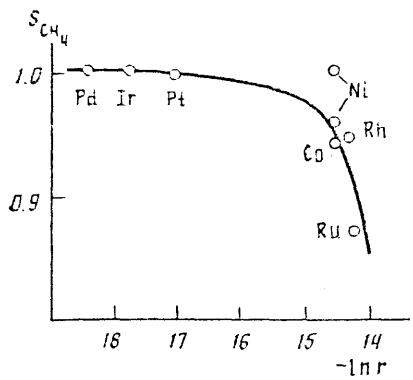


Figure 8. Relation between the activities and selectivities of metals in the CO hydrogenation reaction.

The relations examined refer to the case where the normal Schultz–Flory distribution holds and when the carrier of the metal can be regarded as inert.

For the same metal deposited on different carriers [see the series (XXII) and (XXIII)], the changes in q_{CO} are due to different degrees of dispersion of the metal, so that according to Eqn. (21) a dependence of S_{C_n} on $\bar{d}$ is also to be expected, which has in fact been observed for both cobalt and nickel catalysts (Table 5). However, the changes in S_{C_n} are not induced solely by changes in the degree of dispersion of the metal and hence by the different values of q_{CO}. In each group of catalysts, deposited on different carriers (Table 5), it is possible to differentiate M/L specimens (L is the carrier) having virtually the same degrees of dispersion and hence the same heats of adsorption q_{CO}. At the same time, the selectivities S_{C_n} of such catalysts differ by 24–34%, which means that the subsequent reactions of the intermediate ZX_0 take place with a direct involvement of the carrier particles (apparently at the metal–carrier interface[101]).

In conformity with the mechanism of the hydrogenation of CO (Scheme 8) it has been suggested that the hydrocarbon chain grows via the interaction of the adsorption complex of ZCHOH (ZX_0) with ZCO. Under these conditions, the complex ZCHOH can be partly bound to the carrier (Lewis acid) as a result of the interaction of the unshared electron pair of the oxygen atom with the carrier cation (M_1^{n+}):

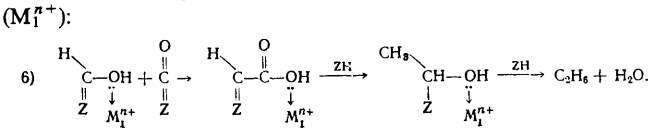


Table 5. Specific catalytic activities and selectivities of deposited metal catalysts in the hydrogenation of CO.

Carrier	$\bar{d}$ for metal, nm	$10^7 r^*$, mol m^{-2} s^{-1}	Selectivity w.r.t. higher hydrocarbon S_{C_n}, %
CO catalyst			
SiO_2	38	52	26
TiO_2	46	9.0	17
ZrO_2	33	8.4	50
BeO	18	5.5	38
Cr_2O_3	15	5.3	30
Al_2O_3	6	4.3	30
MgO	3	1.0	46
WO_3	60	<1	0
Ni catalyst			
ZrO_2	97	262	66
TiO_2	103	54	32
BeO	21	27	36
MgO	1	23	43
Al_2O_3	2	11.4	54
SiO_2	6	3.2	36
Cr_2O_3	12	1.9	44
WO_3	181	<1	0

Note. Mixture composition: P_{CO} = 20 kPa, P_{H_2} = 50 kPa.

* Obtained at 540 K.

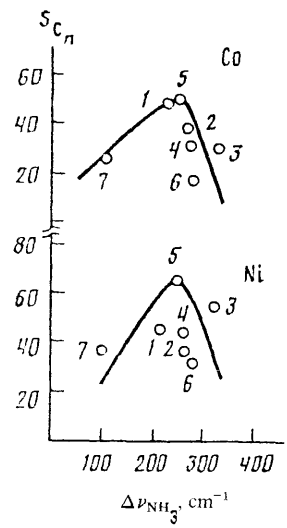


Figure 9. Dependence of the selectivities of deposited Ni and Co catalysts on the acidity of the carriers; carrier: *1*, MgO; *2*, BeO; *3*, Al_2O_3; *4*, Cr_2O_3; *5*, ZrO_2; *6*, TiO_2; *7*, SiO_2.

Then the rate of stage 6 and hence S_{C_n} should depend on the acidity of the carrier. Experimental data have shown that such a relation does indeed exist (Fig. 9): with increase in acidity [with increase in the vibration frequency of the ammonia adsorbed on $(M_1^{n+})_x O_y$ 102], the selectivity with respect to higher hydrocarbons also increases, reaching a maximum for M/ZrO_2. Further increase in the acidity of the carrier diminishes S_{C_n}, the catalyst deposited on carriers with the maximum acidity (M/WO_3) exhibiting 100% selectivity with respect to CH_4. The existence of the optimum acidity can be explained by the fact that, when the bond between the

complex ZCHOH and M_l^{n+} is both too strong and too weak, the probability of the hydrocondensation process is reduced.

In this case the following relation can be written for the selectivity of the Fischer–Tropsch synthesis:

$$S_{C_n} = S_{C_n}(q_{CO}) + S_{C_n}(q_L),$$

where $S_{C_n}(q_{CO})$ is the contribution to the selectivity determined solely by the heat of adsorption of CO and $S_{C_n}(q_L)$ is the contribution to selectivity which depends on the energy of the acid–base interaction.

VII. Hydrogenation of aldehydes

The hydrogenation of saturated aldehydes is of practical importance for the preparation of primary alcohols, mainly 1-propanol, 1-butanol, isobutyl alcohol, and certain higher alcohols:

$$R{-}CHO + H_2 = R{-}CH_2OH. \qquad \text{(XXIV)}$$

Reaction (XXIV) is the concluding stage of the preparation of alcohols by oxo synthesis from alkenes, CO, and H_2. The hydrogenation reaction is carried out as a rule on the catalyst (CO/kieselguhr) used for oxo synthesis. In addition, the Ni–Cu–Cr[103] and Cu–Zn–Al catalysts (synthesis of methanol from CO and H_2),[104] the Ni–Cr and Cu–Cr catalysts,[105] as well as mixed catalysts based on platinum metals[106] are used for the hydrogenation of aldehydes. The detailed mechanism of reaction (XXIV) has not been investigated.

VIII. Conclusion

Certain generalisations, necessary for the rational selection of catalysts and the prediction of the catalytic activity of substances in the hydrogenation of different carbonyl compounds and CO may be based on the data described in this review for the mechanisms and kinetics of such reactions. The activity and selectivity of metal catalysts depend significantly on the energy of the bond (q_R) between the molecule hydrogenated, R, and the catalyst. While the general character of the variation of the catalytic activity with the metal–R bond strength is similar, the optimum values of q_R depend significantly on the nature of the molecule hydrogenated: $(q_{CO})_{opt} \gg (q_{ketone})_{opt}$. As a result of this, an antiparallel variation of the activities of transition metals as a function of their positions in the Periodic Table is observed for the ketone and CO hydrogenation reactions.[107]

The quantity q_R may be varied by altering either the chemical nature of the metal or the degree of its dispersion. The size of the crystals can be regulated in its turn by introducing various additives[107] or by varying the conditions in the reduction of metal oxides.[61]

Consequently, for "structure-sensitive" hydrogenation reactions of carbonyl compounds and CO, where the differences between the adsorption and catalytic activities are not abolished under the influence of the reaction medium, the unequal degrees of dispersion of the metal have just as strong an influence on the catalytic properties as the chemical nature of the metal. Another factor determining the activity and selectivity of the deposited metals may be the variation of q_{CO} under the influence of the "strong metal–carrier interaction" (SMCI).[108,109] The SMCI effect is manifested as a rule for small values of $\bar{d}$ (< 2 nm[109]) and when the carrier cations M_l^{n+} are able to undergo a change in the oxidation state.

The selectivity of the hydrogenation of carbonyl compounds depends to a large extent on the form of the adsorption of the molecule hydrogenated, which is in its turn determined by the chemical composition of the catalyst. Thus, when the "planar" π-complex (I) is formed, acetone is hydrogenated only as far as isopropyl alcohol, while the transition to the "perpendicular" alkoxy-structure (II) promotes the complete reduction of ketones to hydrocarbons.[69]

The CO molecule is also adsorbed in different forms depending on the nature of the catalyst. On transition metals, where carbon monoxide can form bridged and linear structures [see reaction (X)], the carbon–oxygen bond is weakened as a consequence of the predominance of the dative bond.[110] The main CO hydrogenation products on transition metals are therefore hydrocarbons. Among transition metal (Ni, Cu, Zn, Cr) oxides, the preferential formation of oxygen-containing compounds is observed. This reaction pathway is determined by the formation of the CO–M_xO_y donor–acceptor bond. In this case, the C–O bond is seen to be strengthened and the M–C bond is weakened.[110]

The general features of the selective heterogeneous-catalytic hydrogenation reactions of carbonyl compounds and CO listed above will help in the future to achieve a general treatment of new experimental results concerning particular reactions and alternative bases for the specific rational choice of selective catalysts for these processes.

References

1. A M Sokol'skaya *Kataliticheskie Reaktsii v Zhidkoi Faze* (Catalytic Liquid-Phase Reactions), Izd. Nauka, Alma-Ata, 1972, p. 317
2. D V Sokol'skii, A M Sokol'skaya *Metaily–Katalizatory Gidrogenizatsii* (Metals as Hydrogenation Catalysts), Izd. Nauka, Alma-Ata, 1970, 434 pp
3. A M Pak, D V Sokol'skii *Selektivnoe Gidrirovanie Neprede 'nykh Oksosoedinenii* (Selective Hydrogenation of Unsaturated Oxo-compounds), Izd. Nauka, Alma-Ata, 1983, 229 pp
4. A I Lyashenko, Abstract of Candidate's Thesis in Chemical Sciences, IOKE of the Academy of Sciences of the Kazakh SSR, Alma-Ata, 1975
5. N V Pavlenko *Kataliz i Katalizatory* (Catalysis and Catalysts) (Edited by V M Vlasenko), Izd. Naukova Dumka, Kiev, 1983, p. 55
6. E V Prokhorenko, N V Pavlenko *Ukr. Khim. Zh. (Russ. Ed.)*, 1986, **52**(6) 54
7. D R Stull, E S Westrum, G T Sinke *The Chemical Thermodynamics of Organic Compounds* (Translated into Russian), Izd. Mir, Moscow, 1971, 807 pp
8. Yu M Zhorov *Termodinamika Khimicheskikh Protsessov* (Thermodynamics of Chemical Processes), Izd. Khimiya, Moscow, 1985, 458 pp
9. G Blyholder, W V Wyatt *J. Phys. Chem.*, 1966, **70** 1745
10. R P Young, N Sheppard *J. Catal.*, 1971, **20** 333
11. D V Sokol'skii, V F Vozdvizhenskii, A Sh Kuanyshev, A I Lyashenko *Dokl. Akad. Nauk SSSR*, 1975, **224** 887

12. V F Vozdvizhenskii, A Sh Kuanyshev *Vzaimodeistie Karbonilsoderzhashchikh Soedinenii s Katalizatorami Gidrirovaniya* (The Interaction of Carbonyl-Containing Compounds with Hydrogenation Catalysts), Izd. Nauka, Alma-Ata, 1981, Vol. 26, p. 83
13. N V Pavlenko, A I Tripol'skii, G I Golodets, G M Tel'biz *Kinet. Katal.*, 1985, **26** 115
14. A I Tripol'skii, N V Pavlenko, G I Golodets *Kinet. Katal.*, 1985, **26** 1131
15. N V Pavlenko, A I Tripol'skii, G I Golodets *Teor. Eksp. Khim.*, 1986, **22** 698
16. N V Pavlenko, A I Tripol'skii, G I Golodets *Teor. Eksp. Khim.*, 1985, **21** 329
17. A V Kiselev, V I Lygin *Infrakrasnye Spektry Poverkhnostnykh Soedinenii* (Infrared Spectra of Surface Compounds), Izd. Nauka, Moscow, 1971, 485 pp
18. R E Dickerson, H Grey, J Heyt *Chemical Principles* (Translated into Russian), Izd. Mir, Moscow, 1982, Vol. 1, 643 pp
19. G Blyholder, L D Neff *J. Phys. Chem.*, 1966, **70** 893
20. G I Golodets, N V Pavlenko, V M Gun'ko, G M Tel'biz *Teor. Eksper. Khim.*, 1988, **24** 545
21. I B Bersuker *Stroenie i Svoistva Koordinatsionnykh Soedinenii* (The Structure and Properties of Coordination Compounds), Izd. Khimiya, Leningrad, 1971, 311 pp
22. L V Krylov, V G Kiselev *Adsorbtsiya i Kataliz na Perekhodnykh Metallakh i Ikh Oksidakh* (Adsorption and Catalysis on Transition Metals and Their Oxides), Izd. Khimiya, Moscow, 1981, 285 pp
23. N M Popova, L V Babenkova, G A Savel'eva *Adsorobtsiya i Vzaimodeistvie Prosteishikh Gazov s Metallami VIII Gruppy* (Adsorption and Interaction of the Simplest Gases with Group VIII Metals), Izd. Nauka, Alma-Ata, 1979, 227 pp
24. A A Davydov *IK-Spektroskopiya v Khimii Poverkhnosti Okislov* (IR Spectroscopy in the Chemistry of the Surfaces of Oxides), Izd. Nauka, Novosibirsk, 1984, 241 pp
25. A V Sklyarov *Poverkhnostnye Soedineniya v Geterogennom Katalize* (Surface Compounds in Heterogeneous Catalysis) (Edited by O V Krylov), Izd. Nauka, Moscow, 1975, Vol. 16, p. 238 [*Problemy Kinetiki i Kataliza* (Problems of Kinetics and Catalysis)]
26. N N Kavtaradze *Mekhanizm Vzaimodeistviya Metallov s Gazami* (The Mechanism of the Interaction of Metals with Gases), Izd. Nauka, Moscow, 1964, p. 36
27. M A Vannice *Catal. Sci. Technol.*, 1983, **3** 139
28. M H Woligang, W M H Sachtler *Chem.-Ing-Tech.*, 1982, **54** 901
29. V A Zasukha, L M Roev *Teor. Eksp. Khim.*, 1970, **6** 608
30. R P Eischens, W A Pliskin *Adv. Catal.*, 1968, **10** 1
31. R P Eischens, W A Pliskin *Catalysis–Investigation of Surface of Catalysts* (Translated into Russian), Inostr. Lit., Moscow, 1960, p. 9
32. N N Kavtaradze, N P Sokolova *Dokl. Akad. Nauk SSSR*, 1965, **162** 847
33. N N Kavtaradze, N P Sokolova *Dokl. Akad. Nauk SSSR*, 1971, **168** 140
34. N P Sokolova *Zh. Fiz. Khim.*, 1972, **46** 170 [English translation in *Russ. J. Phys. Chem.*, 1972(1)]
35. R L Bol'shedvorskaya, L I Vereshchagin *Usp. Khim.*, 1973, **42** 511 [English translation in *Russ. Chem. Rev.*, 1973(3)]
36. Ya T Eidus *Sintezy Organicheskikh Soedinenii na Osnove Okisi Ugleroda* (The Syntheses of Organic Compounds Based on Carbon Monoxide), Izd. Nauka, Moscow, 1984, 360 pp
37. A L Lapidus, S D Pirozhkov, V D Kapkin, A Yu Krylova *Tekhnologiya Organicheskikh Veshchestv: Sintezy na Osnove Sintez-Gaza* (Technology of Organic Substances; Syntheses Based on the Synthesis Gas), Izd. VINITI, Moscow, 1987, Vol. 13, p. 3
38. R A Sheldon *Catalysis by Metal Complexes*, Vol. 3, *Chemicals from Synthesis Gas* (Translated into Russian), Izd. Khimiya, 1987, 247 pp
39. V Ya Danyushevskii, L I Lafer, V I Yakerson, A M Rubinshtein *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, 2151
40. V I Yakerson, L I Lafer, A M Rubinshtein *Poverkhnostnye Soedineniya v Geterogennom Katalize Surface Compounds in Heterogenous Catalysis) (Edited by O V Krylov), Izd. Nauka, Moscow*, 1975, Vol. 16, p. 49 [*Problemy Kinetiki i Kataliza* (Problems of Kinetics and Catalysis)]
41. N V Pavlenko, A I Tripol'skii, G I Golodets, G M Tel'biz *Teor. Eksp. Khim.*, 1985, **21** 333
42. J Anderson *The Structure of Metal Catalysts* (Translated into Russian), Izd. Mir, Moscow, 1978, 482 pp
43. N V Pavlenko, A I Tripol'skii, G I Golodets *Kinet. Katal.*, 1987, **28** 437
44. C T H Stoddart, G Kemball *J. Colloid. Sci.*, 1956, **11** 532
45. S Watanabe *Sci. Ind.*, 1957, **31** 195
46. T Freund, H M Hulbert *J. Phys. Chem.*, 1957, **61** 909
47. T P Gegenava *Izv. Akad. Nauk Gruz. SSR. Ser. Khim.*, 1976, **2** 259
48. Zh. V Strel'nikova, L V Rusalina, L E Martyshkina *Zh. Fiz. Khim.*, 1977, **51** 2611 [English translation in *Russ. J. Phys. Chem.*, 1977(10)]
49. P B Babkova, A K Avetisov, G D Lyubarskii, A I Gel'bshtein *Kinet. Katal*, 1969, **10** 1086
50. P B Babkova, A K Avetisov, G D Lyubarskii, A I Gel'bshtein *Kinet. Katal*, 1970, **11** 1451
51. P B Babkova, A K Avetisov, G D Lyubarskii, A I Gel'bshtein *Kinet. Katal*, 1972, **13** 345
52. P B Babkova, A K Avetisov, G D Lyubarskii, A I Gel'bshtein *Kinet. Katal*, 1972, **13** 915
53. T Kwan *Catalysis, Investigation of Heterogeneous Processes* (Translated into Russian), Inostr. Lit., Moscow, 1956, p. 314
54. V F Khor'kov, G D Lyubarski, A I Gel'bshtein *Zh. Fiz. Khim.*, 1971, **45** 2853 [English translation in *Russ. J. Phys. Chem.*, 1971(11)]
55. G H Twigg *Discuss. Faraday Soc.*, 1950, **8** 152
56. L O Apel'baum, M I Temkin *Zh. Fiz. Khim.*, 1961, **34** 2060 [English translation in *Russ. J. Phys. Chem.*, 1961(9)]
57. C M Satterfield *Heterogeneous Catalysis in Practice* (Translated into Russian), Izd. Mir, Moscow, 1984, 520 pp
58. A L Kiperman *Usp. Khim.*, 1978, **47** 3 [English translation in *Russ. Chem. Rev.*, 1978(1)]
59. J Simonikova, L Hillaire, J Pănek, K Kochloefl *Z. Phys. Chem. (Munich)*, 1973, **73** 287
60. A I Tripolski, N V Pavlenko, G M Telbiz, G I Golodets *React. Kinet. Catal. Lett.*, 1983, **22** 367
61. N V Pavlenko, A I Tripol'skii, G I Golodets, et al. *Kinet. Katal.*, 1985, **26** 108
62. G I Golodets, N V Pavlenko, A I Tripol'skii *Kinet. Katal.*, 1985, **26** 637

63. A I Tripol'skii, N V Pavlenko, G I Golodets *Kinet. Katal.*, 1985, **26** 1494
64. G I Golodets, N V Pavlenko, A I Tripol'skii *Kinet. Katal.*, 1986, **27** 346
65. N V Pavlenko, A I Tripol'skii, G I Golodets *IV Vsesoyuznaya Konferentsiya po Mekhanizmu Kataliticheskikh Reaktsii: Tezisy Dokladov* (The IVth All-Union Conference on the Mechanisms of Catalytic Reactions: Abstracts of Reports), Moscow, 1986, Vol. 1, p. 385, Preprint 84
66. M I Temkin *Zh. Fiz. Khim.*, 1938, **11** 169
67. G I Golodets *Heterogeneous Catalytic Reactions Involving Molecular Oxygen*, Elsevier, Amsterdam, 1983, 880 pp
68. M Boudart, M A McDonald *J. Phys. Chem.*, 1984, **88** 2185
69. A I Tripol'skii, Abstract of Candidate's Thesis in Chemical Sciences, Institute of Physical Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev, 1986
70. N V Pavlenko, A I Tripol'skii, G I Golodets *Teor. Eksp. Khim.*, 1987, **23** 250
71. G I Golodets *Geterogenno-Kataliticheskoe Okislenie Organicheskikh Veshchestv* (Heterogeneous-Catalytic Oxidation of Organic Substances), Izd. Naukova Dumka, Kiev, 1978, 374 pp
72. A Ozaki *Isotopic Studies of Heterogeneous Catalysis* (Translated into Russian), Atomizdat, Moscow, 1979, 229 pp
73. L S Glebov, A I Mikaya, V I Smetanin, et al. *J. Catal.*, 1985, **93** 75
74. A I Mikaya, A E Yatsenko, L S Glebov, et al. *IV Vsesoyuznaya Konferentsiya po Mekhanizmu Kataliticheskikh Reaktsii: Tezisy Dokladov* (The IVth All-Union Conference on the Mechanisms of Catalytic Reactions: Abstracts of Reports), Moscow, 1986, Vol. 1, p. 333. Preprint 73
75. N S Barinov, D V Mushenko, E G Lebedeva, A A Balandin *Dokl. Akad. Nauk SSSR*, 1967, **172** 1109
76. B R Serebryakov, N A Smirnova. V G Gabuzov *Azerb. Khim. Zh.*, 1977, (6) 135
77. L S Glebov, G A Kliger, A N Bashkirov *Neftekhimiya*, 1978, **18** 803
78. L S Glebov, G A Kliger, A N Bashkirov, et al. *Kinet. Katal.*, 1978, **19** 1339
79. G D Lyubarskii, Yu S Snagovskii, M M Strelets *Kinet. Katal.*, 1975, **16** 1191
80. M M Strelets, Abstract of Candidate's Thesis in Chemical Sciences, Karpov Physicochemical Institute, Moscow, 1973
81. Yu S Snagovskii, M M Strelets, V V Borisov, G D Lyubarskii *Protsessy s Uchastiem Molekulyarnogo Vodoroda* (Processes with Participation of Molecular Hydrogen), Izd. Nauka, Novosibirsk, 1973, p. 73
82. H Storch, N Golumbic, R Anderson *The Fischer–Tropsch and Related Syntheses* (Translated into Russian), Inostr. Lit., Moscow, 1954, 516 pp
83. M Dry *Catalysis in Industry* (Translated into Russian), Izd. Mir, Moscow, 1986, Vol. 2, p. 161
84. P Biloen, W M H Sachtler *Adv. Catal.*, 1981, **30** 165
85. A L Lapidus, Kh N Minachev *Zh. Vses. Khim. Ova. Im. D I Mendeleeva*, 1984, **29** 407
86. M A Vannice *J. Catal.*, 1975, **37** 449
87. M A Vannice *J. Catal.*, 1975, **37** 462
88. M A Vannice *J. Catal.*, 1977, **50** 228
89. G I Golodets, N V Pavlenko, A I Tripolskii *React. Kinet. Catal. Lett.*, 1986, **32** 481
90. G I Golodets, N V Pavlenko, A I Tripolskii *Kinet. Katal.*, 1987, **34** 373
91. G I Golodets, N V Pavlenko, A I Tripolskii *Kinet. Katal.*, 1987, **28** 883
92. G I Golodets *Teor. Eksp. Khim.*, 1985, **21** 549
93. Yu B Naumov, E S Startsev, Yu I Berezina, et al. *Kinet. Katal.*, 1984, **25** 1365
94. H Duncan, V Lygin *Quantum Chemistry of Adsorption on the Surface of Solids* (Translated into Russian), Izd. Mir, Moscow, 1980, 288 pp
95. M Boudart *Adv. Catal.*, 1969, **20** 153
96. N I Il'chenko *Usp. Khim.*, 1972, **41** 84 [English translation in *Russ. Chem. Rev.*, 1972(1)]
97. C van Mechelen, J C Jungers *Bull. Soc. Chim. Belg.*, 1950, **59** 597
98. G I Golodets, N V Pavlenko, A I Tripol'skii *Kinet. Katal.*, 1987, **28** 888
99. Ya B Gorokhovatskii (Editor), *Kataliticheskie Svoistva Veshchestv* (Catalytic Properties of Substances), Izd. Naukova Dumka, Kiev, 1977, Vol. 4, p. 115
100. V L Kuznetsov, A S Lisitsin, A V Golovin, Yu I Ermakov *Vsesoyuznoe Soveshchanie 'Khimicheskie Sintezy na Osnove Odnouglerodnykh Molekul': Tezisy Dokladov* (All-Union Conference on 'Chemical Syntheses Based on One-Carbon Molecules': Abstract of Reports), Izd. Nauka, Moscow, 1984, p. 21
101. O V Krylov *Fizicheskaya Khimiya. Sovremennye Problemy.* 1986 (Physical Chemistry. Modern Problems. 1986) (Edited by Ya M Kolotyrkin), Izd. Khimiya, Moscow, 1986, p. 41
102. N E Tret'yakov, V N Filimonov *Kinet. Katal.*, 1973, **14** 803
103. DDR P. 150 195, 1981
104. K Aika, H Sekiya, A Ozaki *Chem. Lett.*, 1983, 301
105. Polish P. 77 554, 1975
106. M V Shimanskaya (Editor), *Kontaktnye Reaktsii Furanovykh Soedinenii* (Catalytic Reactions of Furan Compounds), Izd. Zinatne, Riga, 1985, 301 pp
107. G I Golodets *Kinet. Katal.*, 1987, **28** 35
108. G C Bond *Catalysis* 1983, **6** 27
109. A A Slinkin *Kinetika i Kataliz: Struktura i Kataliticheskie Svoistva Nanesennykh Metallov* (Kinetics and Catalysis: The Structure and Catalytic Properties of Deposited Metals), Izd. VINITI, Moscow, 1982, Vol. 10, p. 5 [*Itogi Nauki i Tekhniki* (Advances in Science and Engineering)]
110. L M Roev *Kataliz i Katalizatori* (Catalysis and Catalysts) (Edited by V A Roiter), Izd. Naukova Dumka Kiev, 1974, p. 98

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α-Nitronitriles

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ABSTRACT. **The methods of synthesis and chemical reactions of nitrocyano-compounds, in which the nitro- and cyano-groups are joined by a common carbon atom, are examined.**

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I. Introduction

This review is devoted to the consideration of the methods of synthesis and chemical properties of nitrocyano-compounds in which the nitro- and cyano-groups are linked to a common carbon atom. Compounds of this type have found application as biologically active substances,[1-3] as initiators of chain polymerisation reactions,[4] as inhibitors of the thermooxidative ageing of polymers,[5] as components of energy absorbing compositions,[6-8] and also as intermediates for their preparation.[9-12]

α-Nitrocyano-compounds are widely used in organic synthesis. The presence in their molecules of several reaction centres makes it possible to involve these compounds in numerous reactions leading to a wide assortment of polyfunctional aliphatic and heterocyclic products. Many reactions proceed in a non-trivial manner under these conditions, which is associated with the specific features of the mutual influence of the functional groups and the ability of the reaction intermediates to enter into secondary intramolecular processes.

α-Nitronitriles have been used to investigate the inductive and resonance effects of substituents[13-18] and the electronic and steric structures of carbanions.[19-24]

The chemical properties of nitriles and nitro-compounds have been described in detail in monographs and reviews,[25-28] while the methods of synthesis and chemical reactions of α-nitronitriles have been described in a fragmentary manner in only one book.[27]

II. Methods of synthesis

1. Methods of synthesis of α-nitrocyanoalkanes

The first member of the series—nitroacetonitrile—has been synthesised by the dehydration of metazonic acid.[29-35] Its homologues have been obtained by the oxidation[36,37] and photolysis[39] of α-nitrosocyanoalkanes, by the oxidation of α-hydroxyaminocyanoalkanes,[38] by the pyrolysis of 1,1-azobis-1,1-dicyanoalkanes,[40] and by the reaction of α-bromocyanoalkanes with $NaNO_2$.[41,42]

The methods of synthesis of α-nitrocyanoalkanes involving the nitration of nitriles or the cyanation of salts of nitroso-compounds are general in character. The nitration of nitriles by acid nitrating agents cannot be stopped, with rare exceptions,[43] at the stage involving the formation of mononitrocyanoalkanes. One nitro-group can be introduced by carrying out the reaction under alkaline conditions:[44,45]

$$RCH_2CN \xrightarrow[t\text{-}C_4H_9OK]{C_5H_{11}ONO_2} R{-}C^{\ominus}(CN)(NO_2)\,K^{\oplus},$$

$R = C_2H_5$, n-C_4H_9, C_6H_5,

$$NCCH_2(CH_2)_nCH_2CN \xrightarrow[t\text{-}C_4H_9OK]{C_5H_{11}ONO_2} K^{\oplus}{}^{\ominus}C(CN)(NO_2){-}(CH_2)_n{-}C^{\ominus}(CN)(NO_2)K^{\oplus},$$

$n = 2$–4, 6.

α-Nitrocyanoalkanes have been synthesised in 60–80% yields by the oxidative cyanation of salts of secondary nitroalkanes and nitrocycloalkanes.[46,47] A one-electron redox mechanism has been proposed:[47]

$$R^1R^2C^{\ominus}{-}NO_2 \xrightarrow[{}^{\ominus}CN]{K_3Fe(CN)_6} NC{-}C(R^1)(R^2){-}NO_2,$$

$R^1 = CH_3$, $R^2 = CH_3$, C_2H_5, n-C_5H_{11}; $R^1R^2 = -(CH_2)_n-$.

The preparation of functional derivatives of nitroacetonitrile containing aminocarbonyl,[48-51] alkoxycarbonyl,[51] and acyl[52] groups has been described.

2. Methods of synthesis of α-polynitrocyanoalkanes

The interaction of cyanoacetic acid and its derivatives (amide, esters, nitrile, as well as their mono- and di-nitro-derivatives) with the nitrating mixture leads to the formation of trinitroacetonitrile (I).[53,54] However, the nitration of methyl cyanoacetate affords methyl dinitrocyanoacetate (II):[55]

$$R{-}C(X^1)(X^2){-}C{\equiv}N \xrightarrow[H_2SO_4]{HNO_3} (O_2N)_3CCN,$$

(I)

X^1, $X^2 = H$, NO_2,
$R = COOH$, $CONH_2$, $C{\equiv}N$.

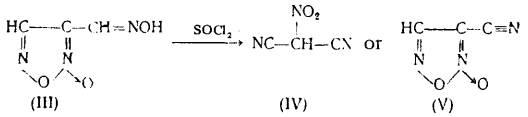
$$CH_3OCOCH_2C{\equiv}N \xrightarrow[H_2SO_4]{HNO_3} CH_3OCOC(NO_2)(NO_2){-}C{\equiv}N.$$

(II)

The nitration of α-hydroxyiminonitriles is a more general method of synthesis of αα-dinitrocyanoalkanes.[4,55-57] The cyanation of the silver salt of trinitromethane by iodocyanogen, leading to trinitroacetonitrile, can serve as an example of another approach to the synthesis of α-polynitrocyanoalkanes.[58]

3. Methods of synthesis of α-polycyanonitroalkanes

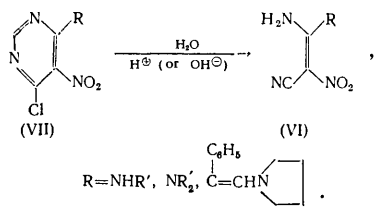
The dehydration of furoxanealdoxime (III), to which the structure of nitrocyanoacetaldoxime was erroneously attributed previously,[59] gives rise to dicyanonitromethane (IV) or to the cyanofuroxane (V).[51] The ammonium, potassium, and silver salts of compound (IV) have been obtained:[59,60]



(III) (IV) (V)

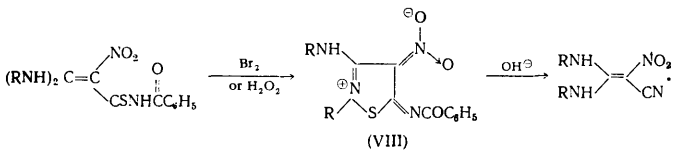
4. Methods of synthesis of α-nitronitriles whose functional groups are linked to an sp^2-hybridised carbon atom

The simplest representative of α-nitrocyanoalkenes, namely α-nitroacrylonitrile, is unstable,[61] but many of its β-substituted derivatives are stable. 1-Amino- and 1,1-diamino-2-nitro-2-cyanoalkenes (VI) are formed in the degradative hydrolysis of chloronitropyrimidines (VII) under acid[62–64] or alkaline[65] conditions:



(VII) (VI)

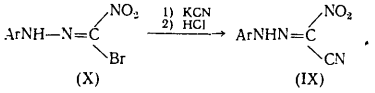
The alkaline hydrolysis of derivatives of isothiazoline (VIII), obtained by oxidising nitroketen aminals, also leads to 1,1-diamino-2-nitro-2-cyanoethylenes:[66]



(VIII)

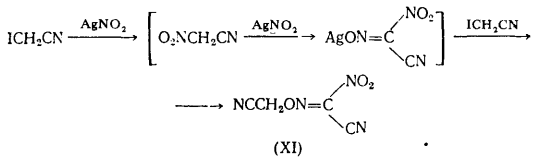
Methods have been developed for the preparation of 1-amino-2-nitro-2-cyanoethylenes by the interaction of 3-chloro-4-nitroisothiazole[67] and 5-methyl-4-nitroisooxazole[68] with amines.

The cyanation of the arylhydrazones of bromonitroformaldehyde (X) constitutes a general method of synthesis of the arylhydraxones of cyanonitroformaldehyde (IX):[2,69]



(X) (IX)

The interaction of iodoacetonitrile with $AgNO_2$ leads to a derivative of cyanonitroformaldoxime (XI):[70]



(XI)

III. Properties

1. The structure and acid–base properties of α-nitrocyanoalkanes

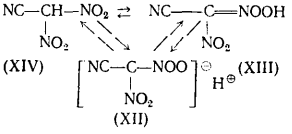
α-Nitronitriles containing hydrogen atoms in the α-position relative to the nitro- and cyano-groups are strong CH acids and are able to form salts with metals or organic bases. The thermodynamic stability of the α-nitrocyanoalkane anions is due to the strong-*I* effects of nitro- and cyano-groups (the Taft σ* constants are 3.9 and 3.6 respectively[71]) and also by the ability of the latter to participate in the delocalisation of the charge of the carbanion (mesomeric effect). The pK_a for certain α-nitrocyanoalkanes are listed in Table 1.

Table 1. The pK_a values for α-nitrocyanoalkanes in water.[72]

Compound	pK_a	T, °C
$NCCH_2NO_2$	4.86	27
$NCCH(C_6H_5)NO_2$	0.29	20
$NCCH(CO_2CH_3)NO_2$	−5.20	20
$NCCH(NO_2)_2$	−6.22	20

The dinitroacetonitrile anion has an almost planar structure, which follows from the results of X-ray diffraction analysis of its potassium, rubidium, and caesium salts.[22–24] Its C ≡ N bond length (1.20 Å) exceeds the C≡N bond length in cyanoalkanes (1.14–1.16 Å), while the C–C(N) bond is shorter (1.36 Å) than the usual C–C single bond (1.43 Å), which indicates the involvement of the nitrile group in conjugation. This conclusion has been confirmed by the results of IR spectroscopic[22] and ^{14}N NMR[19,20] studies on the dinitroacetonitrile anion.

It has been established by IR and UV spectroscopic methods that dinitroacetonitrile can exist in solutions in three tautomeric forms: as the ion pair (XII) (in water and polar organic solvents),[73] as the thermally labile *aci*-form (XIII) (in 100% H_2SO_4 or anhydrous dichloroethane),[74] and as the "true" dinitro-compound (XIV):



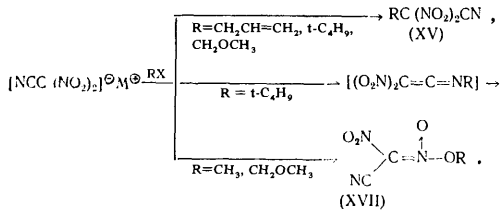
(XIV) (XII) (XIII)

The structures of the α-nitronitriles whose nitro- and cyano-groups are linked to an sp^2-hybridised carbon atom have not been investigated.

2. Reactions of α-nitronitriles with electrophiles

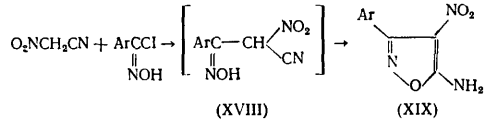
(a) Alkylation of α-nitrocyanoalkanes. The interaction of the silver salt of dinitrocyanomethane with alkylhalides can take place at the carbon atom linked to the nitro- and cyano-groups (*C*-alkylation), at the nitrogen atom of the nitrile group (*N*-alkylation), and at the oxygen atom of the nitro-group (*O*-alkylation) depending on the

nature of the alkylating agent. The reaction products are dinitrocyanoalkanes (XV), dinitrocarboxamides (XVI), and nitronic esters (XVII)[75,76,134] respectively:



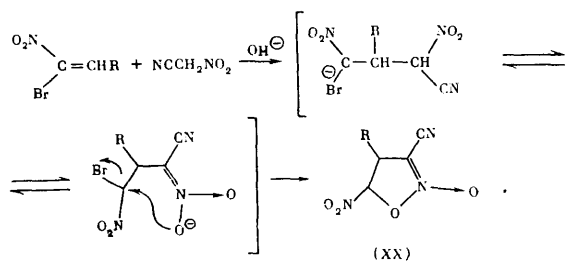
The interaction of the silver salt of phenylnitroacetonitrile with trityl chloride leads only to the *O*-alkylation product.[77] The formation of nitronic esters is observed in the alkylation of α-nitrocyanoalkanes by diazomethane.[78–80] Nitronates with a low stability can enter into further interactions under the reaction conditions.[81]

The interaction of nitroacetonitrile with Mannich bases[33,61] or with arylchloroximes[52] affords the *C*-substitution products. In the latter case the product of the cyclisation of the intermediate (XVIII)—5-amino-3-aryl-4-nitroisoxazole (XIX)—was isolated:



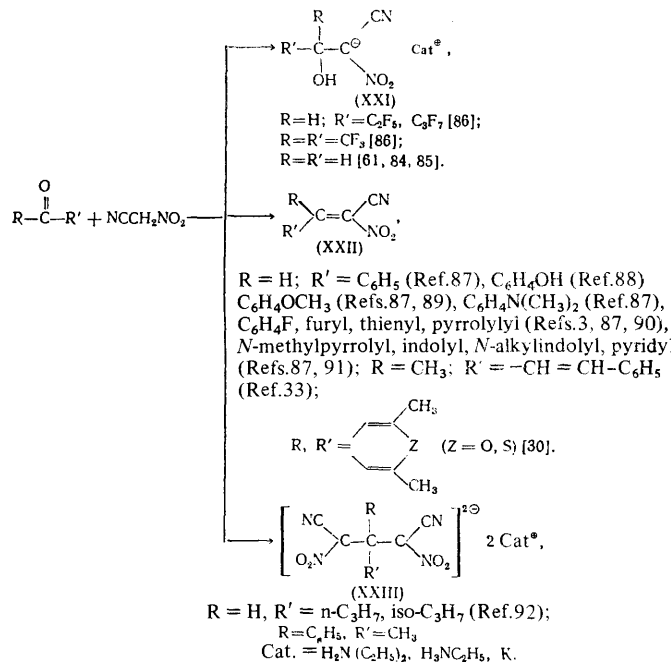
The ability of the nitrile group to enter into intramolecular condensation reactions under mild conditions is a characteristic property of α-nitronitriles, which distinguishes them from other types of cyano-compounds and makes it possible to construct on their basis various heterocyclic systems (see below).

(b) Reactions of α-nitrocyanoalkanes with alkenes containing activated double bonds. The α-nitrocyanoalkanes containing a mobile hydrogen atom in the α-position relative to the nitro- and cyano-groups are able to add to compounds containing the C = C double bond activated by strong electron-accepting substituents. The reactions of dinitroacetonitrile with methyl acrylate, acrylamide, acrolein, butenone, methylenebisacrylamide, and *NN'N''*-triacryloylperhydro-*s*-triazine lead to the formation of the corresponding Michael adducts.[76] The process does not require base catalysis owing to the high acidity of dinitroacetonitrile. The reaction of nitroacetonitrile with vinyl ketones can afford products of the addition to both the C = C double bond and to the carbonyl group.[82] The interaction of the sodium salt of nitroacetonitrile with 1-bromo-1-nitroalkenes results in the formation of 4-alkyl(aryl)-3-cyano-5-nitroisoxazolines (XX) in accordance with the following scheme:[83]

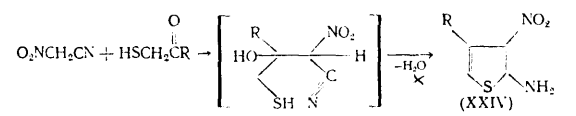


(c) Reactions of α-nitrocyanoalkanes with compounds containing C = O or C = N bonds. The interaction of nitroacetonitrile with aldehydes leads as a rule to three types of products: the salts of 1-nitro-1-cyano-2-hydroxyalkanes (XXI), 1-nitro-1-cyanoalkenes (XXII), and the salts of the dinitriles of substituted 2,4-dinitroglutaric acids (XXIII). The reaction can be stopped at the stage involving the formation of compound (XXI) by using formaldehyde,[61,84,85] perfluoroaldehydes, and perfluoroketones[86] as carbonyl components. The products of the reaction of nitroacetonitrile with aromatic and heteroaromatic aldehydes are unsaturated compounds (XXII).[6,61,87–91] When nitroacetonitrile interacts with aliphatic aldehydes, the salts (XXII) formed initially combine with a second nitroacetonitrile molecule and are converted into salts of dinitrodinitriles (XXIII).[61,92]

The reaction of nitroacetonitrile with ketones also leads to the formation of compounds (XXII) and (XXIII). The first possibility obtains in the case of benzylideneacetone,[33] 2,6-dimethyl-γ-pyrone, and 2,6-dimethyl-γ-thiapyrone[30] and the second arises in the reactions of nitroacetonitrile with acetophenone and cyclohexanone:[33]



The interaction of nitroacetonitrile with α-mercaptoketones is accompanied by intramolecular condensation and derivatives of 1-amino-2-nitrothiophen (XXIV) are formed:[9]

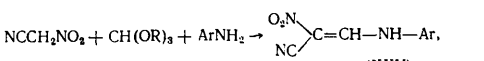


The product of the reaction of dinitroacetonitrile with formaldehyde is 2,2-dinitro-2-cyanoethanol.[76]

The reactions of α-nitrocyanoalkanes with carbonyl compounds require as a rule base[33,86,88,89,92] or acid[91] catalysis. Certain reactions take place readily also in the absence of catalysts.[31,76]

Nitroacetonitrile enters into three-component reactions with formaldehyde–amine and alkyl orthoformate–amine systems. In the former case, the process proceeds like the Mannich reaction and leads to the formation of 2-amino-1-nitro-1-cyanoalkanes[33] while in

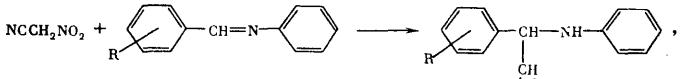
the latter derivatives of 2-amino-1-nitro-1-cyanoethylene (XXV) are prodduced:[93,94]



$$NCCH_2NO_2 + CH(OR)_3 + ArNH_2 \rightarrow \begin{matrix} O_2N \\ NC \end{matrix}\!\!>\!C{=}CH{-}NH{-}Ar,$$

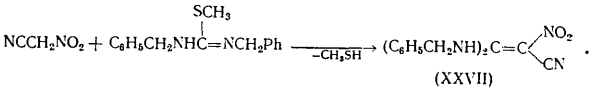
$Ar = C_6H_5$, p-ClC_6H_4, p-$CH_3C_6H_4$. (XXV)

The addition of α-nitrocyanoalkanes to C = N double bonds has been little investigated. The interaction of nitroacetonitrile with benzylideneaniline and its derivatives is completed by the formation of the adducts (XXVI).[33] The product of the reaction of nitroacetonitrile with *NN'*-dibenzyl-*S*-methylisothiourea is 1,1-di(benzylamino)-2-nitro-2-cyanoethylene (XXVII):[34]



$NCCH_2NO_2$ + (R-substituted) $CH{=}N$ — $\rightarrow$ (R-substituted) $CH{-}NH$ — $CH(CN)(NO_2)$,

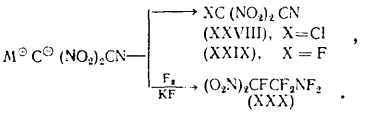
R = H, *o*-Cl, *p*-Cl. (XXVI)



$$NCCH_2NO_2 + C_6H_5CH_2NHC(SCH_3){=}NCH_2Ph \xrightarrow[-CH_3SH]{} (C_6H_5CH_2NH)_2C{=}C(NO_2)(CN).$$

(XXVII)

(d) Reactions of α-nitrocyanoalkanes leading to the formation of a carbon–heteroatom bond. The salts of α-nitro-[29,44,45] and α-dinitrocyanoalkanes[53] are readily brominated with formation of α-bromo-derivatives. The product of the interaction of the sodium salt of dinitroacetonitrile with Cl_2 is chlorodinitrocyanomethane(XXVIII).[53] Chlorine fluorosulphonate[95] and the $HCl-H_2O_2$ system[53] have also been used as chlorinating agents for the synthesis of compound (XXVIII). Fluorination of salts of dinitroacetonitrile by elemental fluorine in an aqueous medium[96] and in the CaF_2-Ni system[97] leads to the formation of fluorodinitroacetonitrile (XXIX). In the presence of KF, the nitrile (XXIX) formed initially combines with two molecules of F_2 at the C = N double bond, affording 2-difluoroamino-1,1-dinitrotrifluoroethane (XXX):[97]

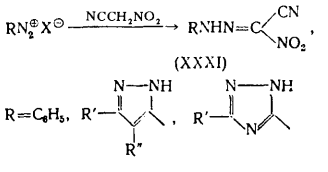


$M^{\oplus}C^{\ominus}(NO_2)_2CN$ — $\rightarrow XC(NO_2)_2CN$ (XXVIII), X=Cl (XXIX), X = F; $\xrightarrow[KF]{F_2} (O_2N)_2CFCF_2NF_2$ (XXX).

The reaction of the sodium salt of dinitroacetonitrile with perchloryl fluoride does not permit the synthesis of compound (XXIX),[98] but fluorination of the potassium salt of ethyl nitrocyanoacetate by this fluorinating agent affords ethyl fluoronitrocyanoacetate.[99]

Dinitroacetonitrile is smoothly nitrated by fuming HNO_3 and sulphuric acid–nitric acid mixtures to trinitroacetonitrile.[53] The reaction is described by a third-order kinetic equation, which includes the concentrations of dinitroacetonitrile, HNO_3, and the water or H_2SO_4 present in the system.[100]

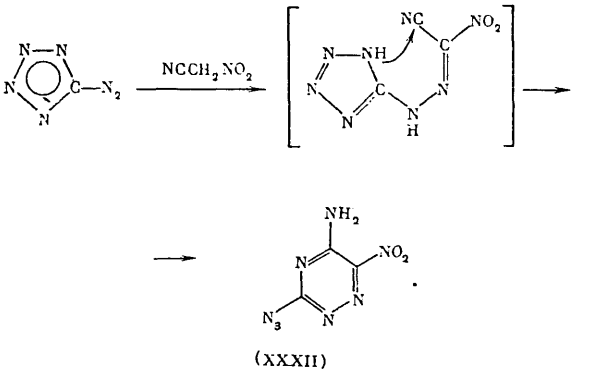
The interaction of nitroacetonitrile with aromatic[29] and heteroaromatic[32] diazonium salts leads to the formation of the corresponding hydrazones of nitrocyanoformaldehyde (XXXI):



$RN_2^{\oplus}X^{\ominus} \xrightarrow{NCCH_2NO_2} RNHN{=}C(CN)(NO_2)$, (XXXI)

R=C_6H_5, R'= , R'=

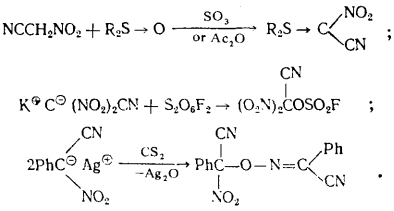
In the case of diazotetrazole, the process cannot be stopped at the hydrazone formation stage; the hydrazone is converted under the reaction conditions into 5-amino-3-azido-1,2,4-triazine (XXXII), which cannot be obtained in other ways:[101]



(XXXII)

In contrast to nitroacetonitrile, dinitroacetonitrile reacts with aromatic diazo-compounds to form only arenediazonium salts containing the anion $(O_2N)_2\bar{C}CN$.[102]

In a number of instances, the reactions of α-nitrocyanoalkanes with electrophiles lead to the formation of a bond between the carbon atom and the atoms of Group VI elements. The formation of the ylide C ← S bond is observed in the interaction of nitroacetonitrile and its salts with dialkyl sulphoxides[103,104] [Eqn. (1)]. The formation of the C–O bond accompanies the reactions of the potassium salt of dinitroacetonitrile with peroxysulphuryl difluoride[105] [Eqn. (2)] and of the silver salt of α-nitrophenylacetonitrile with CS_2[106,107] [Eqn. (3)]:



$$NCCH_2NO_2 + R_2S \rightarrow O \xrightarrow[or\ Ac_2O]{SO_3} R_2S \rightarrow C(NO_2)(CN); \quad (1)$$

$$K^{\oplus}C^{\ominus}(NO_2)_2CN + S_2O_6F_2 \rightarrow (O_2N)_2C(CN)OSO_2F; \quad (2)$$

$$2PhC^{\ominus}(CN)(NO_2)Ag^{\oplus} \xrightarrow[-Ag_2O]{CS_2} PhC(CN)(NO_2)-O-N{=}C(Ph)(CN). \quad (3)$$

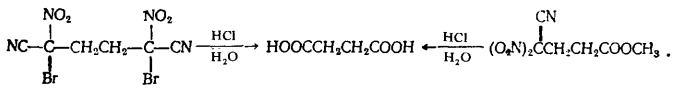
3. Reactions of α-nitronitriles with nucleophiles

(a) Reactions of α-nitrocyanoalkanes with nucleophiles accompanied by the elimination of functional groups. α-Nitrocyanoalkanes exhibit dual reactivity in relation to nucleophiles. The attack by a nucleophile on the carbon atom of the nitrile group leads to the formation of adducts. The attack on the carbon atom linked to the nitro- and cyano-group is accompanied by the elimination of one of them.

The mode of elimination depends on the nature of the nucleophile and the structure of the α-nitrocyanoalkane. Thus, treatment of trinitroacetonitrile[53] or fluorodinitroacetonitrile[98] with the OH^- anion, which has a high oxidation potential, results in the nitrile group being split off. However, the reactions of trinitroacetonitrile with reductants (H_2S, $Br^{\ominus}$) lead to the elimination of the nitro-group.[53,54]

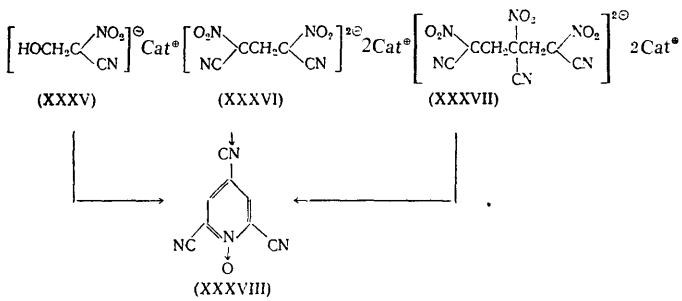
Treatment of alkyl derivatives of nitro- and dinitro-acetonitrile is accompanied in all cases by decyanation and the formation of the salts of the corresponding nitroalkanes.[45,56,76] Under fairly severe conditions (heating with aqueous alkali), the salts of α-nitrocyanoalkanes also undergo decyanation on treatment with nucleophiles.[44,57]

The elimination of functional groups is observed in the reactions of α-nitrocyanoalkanes with aqueous acids. The product of the reactions of compounds (XXXIII) and (XXXIV) with HCl is succinic acid;[45,76]



(XXXIII) (XXXIV)

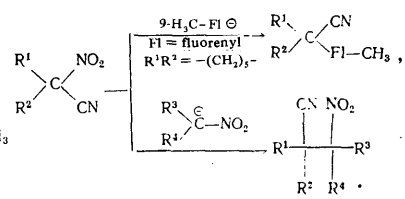
The acid hydrolysis of the salts (XXXV)–(XXXVII) proceeds with retention of the cyano-groups and the formation of 2,4,6-tricyanopyridine *N*-oxide (XXXVIII):[61,84,85]



(XXXV) (XXXVI) (XXXVII) (XXXVIII)

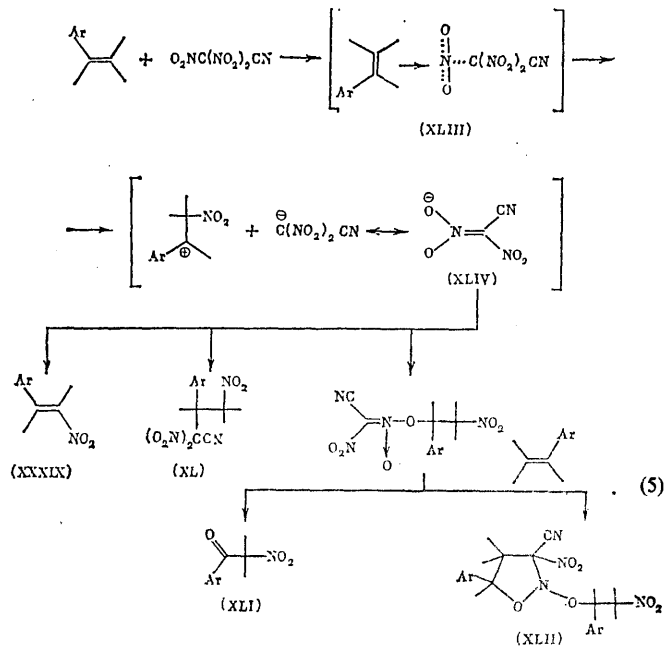
The cyano-groups are retained also in the reactions involving the "degradative alkylation" of dialkyl derivatives of nitroacetonitrile by the 9-methylfluorenyl anion[108] or salts of nitroalkanes,[109–111] leading to the formation of highly branched cyano-compounds [Eqn. (4)]:

R^1, R^2	R^3, R^4
$-(CH_2)_4-$	CH_3, CH_3
CH_3, CH_3	CH_3, CH_3
CH_3, CH_3	$-(CH_2)_5-$
CH_3, CH_3	CH_3, $CH_2CH_2COOCH_3$



(4)

The reaction of trinitroacetonitrile with arylalkenes, which behave in this case as nucleophiles, is accompanied by denitration. The reaction may result in the formation of a whole series of products: conjugated nitroalkenes (XXXIX), 1-cyano-1,1,3-trinitroalkanes (XL), α-nitroketones (XLI), and 2-(β-nitroalkoxy)-3-cyano-3-nitroisoxazolidines (XLII).[112–115] A reaction mechanism has been proposed,[113,115] including the formation of a charge-transfer complex (XLIII) and an ion pair (XLIV), which is stabilised either by splitting off H^+ from the cation or by the *C*- or *O*-alkylation of the dinitroacetonitrile anion [Eqn. (5)]:

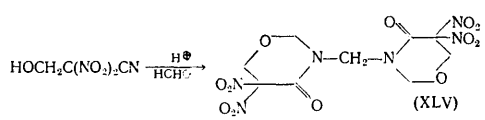


(XLIII) (XLIV) (XXXIX) (XL) (XLI) (XLII)

(5)

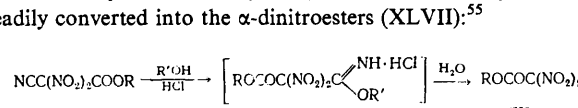
(b) Reactions of α-nitrocyanoalkanes with nucleophiles accompanied by addition to the C ≡ N bond. The nitrile group in α-nitrocyanoalkanes is activated by the neighbouring nitro-group and readily combines with nucleophiles: water, alcohols, amines, and chlorine fluorosulphate.

The hydrolysis of α-nitrocyanoalkanes can be stopped at the stage involving the formation of amides of carboxylic α-nitroacids on treatment with HCl in inert organic solvents[96,116] or when the reaction is carried out in 85–99% H_2SO_4.[99,117] The hydrolysis of 2,2-dinitro-2-cyanoethanol in the presence of formaldehyde is accompanied by condensation reactions and leads to the formation of the bicyclic methylenebisamide (XLV):[76]



(XLV)

The products of the reactions of α-nitrocyanoalkanes with alcohols in the presence of HCl are iminoester hydrochlorides (the Pinner reactions).[55,118] In the case of dinitrocyanoacetates, the imonoester hydrochlorides (XLVI) have a low stability and are readily converted into the α-dinitroesters (XLVII):[55]

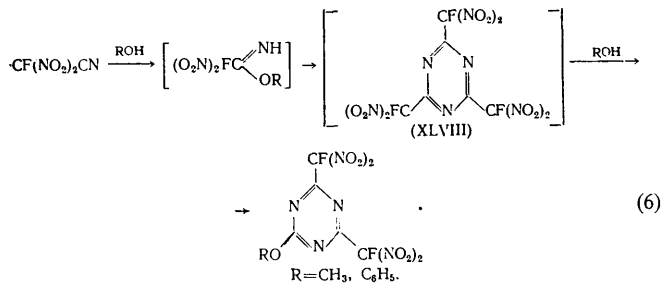


(XLVI) (XLVII)

R = CH_3, C_2H_5, n-C_4H_9, C_6H_{11}, CH_2CH_2Br, $CH_2CH_2ONO_2$.

Fluorodinitroacetonitrile combines with alcohols in the presence of basic catalysts [CH_3ONa, $N(C_2H_5)_3$][97] or without a catalyst,[98] affording the free iminoesters. The iminoester formation stage apparently includes the cyclotrimerisation of fluorodinitroacetonitrile to 1,3,5-triazine derivatives (XLVIII) in the presence of alcohols

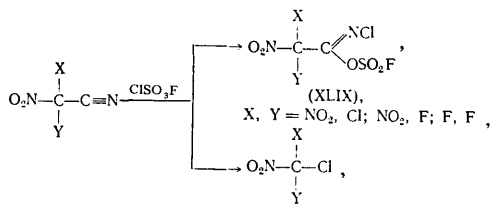
under a pressure of 8–10 kbar in accordance with reaction (6):[119]



(6)

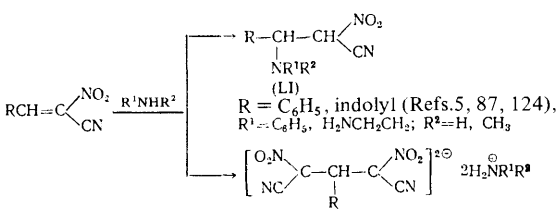
The interaction of α-nitrocyanoalkanes with amines usually leads to the formation of amidines.[97,120] In a number of cases, amidines are capable of undergoing further interactions (hydrolysis,[10] cyclisation[121]) under the reaction conditions. The addition of hydroxylamine to nitroacetonitrile results in the formation of the amidoxime of nitroacetic acid.[29]

Chlorine fluorosulphate adds to the C≡N bond of chlorodinitro-, fluorodinitro-, and difluoronitro-acetonitriles, affording chloroimino-fluorosulphonylesters (XLIX).[95,122] However, the reaction with ethyl dinitrocyanoacetate leads not to the adduct but to the product (L) of the substitution of the nitrile group by chlorine:[95]



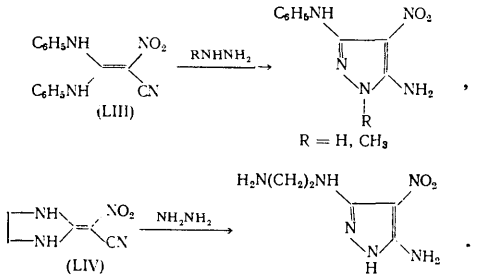
(L), X = NO_2, Y = $CO_2C_2H_5$.

(c) Reactions of α-nitronitriles whose functional groups are linked to an sp^2-hybridised carbon atom with nucleophiles. α-Nitrocyanoalkenes can combine with nucleophiles in the β-position. The interaction of 1-aryl- and 1-heteroaryl-2-nitro-2-cyanoethylenes with amines affords two types of products depending on the basicity of the amines: 1-amino-2-nitro-2-cyanoethylenes (LI) and the salts of the dinitriles of 3-substituted 2,4-dinitro-glutaric acids (LII). The less basic aromatic amines (pK_b = 9.0–9.5) form the adducts (LI),[5,87,124] while alkylamines (pK_b = 3.0–4.8) (with the exception of ethylenediamine) afford the salts (LII):[87–89,123,126,128]



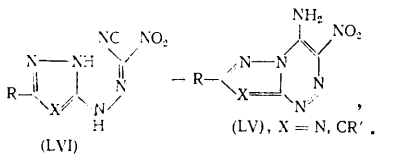
R = C_6H_5 (Refs.87, 123), thienyl (Refs.125, 126, 128), C_6H_4OH (Ref.88), $C_6H_4OCH_3$ (Ref.89), C_6H_4F (Ref.3), furyl (Ref.127);
R, R^1 = H, alkyl, cycloalkyl.

In a number of instances, the addition of nucleophiles to derivatives of 1-nitro-1-cyanoethylene may be accompanied by intramolecular condensation involving the nitrile group. Thus the reaction of nitrocyanoketen aminals (LIII) and (LIV) with hydrazine leads to polyfunctional compounds of the pyrazole series:[129]



R = H, CH_3

Cyclisation with formation of condensed derivatives of 1,2,4-triazine (LV) is observed in the case of pyrazolyl- and triazolyl-hydrazones of cyanonitroformaldehyde (LVI).[32] One of the nitrogen atoms of the heterocycle plays the role of the nucleophile attacking the carbon atom of the nitrile group under these conditions:

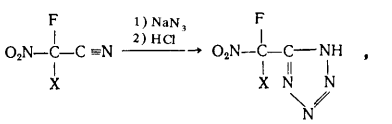


(LV), X = N, CR′.

4. Cycloaddition reactions of α-nitronitriles

α-Nitrocyanoalkanes are capable of entering into 1,3-dipolar cycloaddition reactions. The dipolarophile activity of the nitrile group in these compounds exceeds the activity of the majority of aliphatic nitriles owing to the presence in their composition of the electron-accepting nitro-groups.

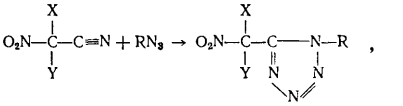
Fluorodinitro-, and difluoronitro-acetonitriles readily combine with NaN_3, forming the corresponding tetrazole derivatives (LVII):[130,131]



(LVII), X = F, NO_2.

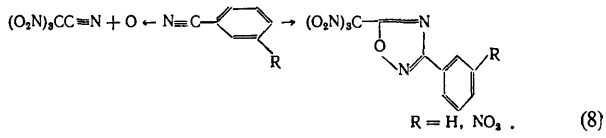
Sodium azide adds also to the salts of α-nitrocyanoalkanes, but the reaction requires much more severe conditions.[132]

The reactions of α-nitrocyanoalkanes with organic azides lead as a rule to the formation of 1,5-disubstituted tetrazole derivatives. The reaction conditions depend on the steric structure of the azide. Whereas methyl azide adds to fluoridinitro- and difluoronitro-acetonitrile even at room temperature,[130] the cycloaddition of the sterically more hindered n-hexyl and trimethylsilyl azides occurs only after heating for many hours at 60–70 °C[131] [Eqn. (7)]:



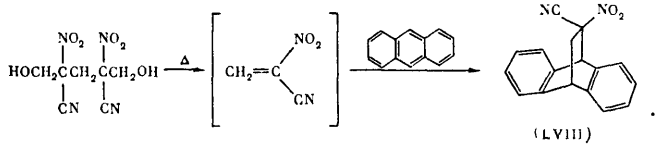
X = Y = F; R = CH_3;
X = NO_2, Y = F; R = CH_3, n-C_6H_{13}, Si $(CH_3)_3$;
X = Y = NO_2; R = Si $(CH_3)_3$. (7)

The reaction of trinitroacetonitrile with aromatic nitrile oxides, leading to the trinitromethyl derivatives of 1,2,4-oxadiazole in high yields[133] [Eqn. (8)], takes place under mild conditions:



(8)

α-Nitrocyanoalkenes can enter into the Diels–Alder reaction. 1-Nitro-1-cyanoethylene, generated *in situ* from the dinitrile of 2,4-di(hydroxymethyl)-2,4-dinitroglutaric acid, combines with anthracene to form the adduct (LVIII):[61]



(LVIII)

IV. Applications of α-nitronitriles

Many α-nitronitriles whose functional groups are linked to an sp^2-hybridised carbon atom exhibit biological activity. Thus 2-(nitrocyanomethylene)-1,3-dithiacyclobutane exhibits a fungicidal activity.[1] The arylhydrazones of cyanonitroformaldehyde possess insecticidal and fungicidal activities.[2]

The bis-2,2-dichlorodiethylammonium salt of 2,4-dinitro-3-phenylglutaronitrile exhibits an antitumour activity[32] and a number of nitronitrile salts are inhibitors of the thermooxidative ageing of polymers.[5]

The potassium, sodium, and barium salts of dinitroacetonitrile have been recommended as regulators of the rate of combustion of rocket fuels.[6,7]

α-Dinitrocyanoacetates have been proposed as additives to explosive and combustible mixtures, as initiators of chain polymerisation reactions, and as reagents for the determination of OH and NH_2 groups.[4]

Epoxy-αα-dinitrocyanoalkanes have been patented at monomers for the synthesis of high-energy polymeric binders.[8] Trinitro- and fluorodinitro-acetonitriles can be used as intermediates for the preparation of mixtures of trinitromethyl- and fluorodinitromethyltetrazoles—components of solid rocket fuels.[11,12]

References

1. N V Philips Gloeilampenfabrieken Dutch Appl., 710 529., 1972, **77** 152151
2. M O Lozinskii, L S Pupko, A I Dichenko, et al. *Fiziol. Akt. Veshchestva*, 1971(3), 131
3. T D Meshkov, Z I Demireva *Zh. Org. Khim.*, 1985, **21** 1884
4. C O Parker US P. 2925434
5. Z I Demireva, A S Polyanskaya, I Mladenov, V V Perekalin *Zh. Org. Khim.*, 1976, **12** 1192
6. C O Parker US P. 3415867
7. J L Chaille, R W Walker US P. 3450583, 1969, **71** 51834
8. M B Frankel, N N Ogimachi US P. 4092336 38
9. Nippon Kayaku Co. Japanese P. 81 100780, 1982, **96** 1954
10. C Shibuya, K Isgii, H Ito, et al. Japanese P. 7759181, 1977, **87** 135369
11. V Grakauskas, T H Albert Report 1979. UCRL-15119. From *Energy Res. Abstr.*, 1980, **5(6)**(8926); 1980, **93** 204553
12. V Grakauskas, T H Albert Report 1980. UCRL-15187. From *Energy Res. Abstr.*, 1980, **5(16)**(26207); 1981, **94** 84021
13. S T Hamdi, K A K Ebraheem, J R Jones *Indian J. Chem., Sect. A.*, 1979, **18** 66
14. A Talvik, A Pihl, O Parve, A Haller *Org. React. (Tartu)*, 1978, **15** 559
15. H Jonson, B Klewe, E Tjelta *Acta Chem. Scand., Ser. A.*, 1977, **31** 151
16. A Talvik, V Pal *Reakts. Sposobn. Org. Soedin.*, 1974, **11** 285
17. V A Petrosyan, V V Paramonov, V I Slovetskii, A A Fainzil'berg *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1978, 793
18. V V Paramonov, V A Petrosyan, V I Slovetskii *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1978, 786
19. M Ya Myagi, E T Lippmaa, I V Tselinskii *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1972, **9** 9
20. E T Lippmaa, M Ya Myagi, Ya O Past, et al. *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1971, 1006
21. I V Tselinskii, A S Kosmynina, V N Dronov, I N Shokhor *Reakts. Sposobn. Org. Soedin.*, 1970, 7 50
22. N V Grigor'eva, N V Margolis, I N Shokhor, et al. *Zh. Strukt. Khim.*, 1969, **10** 943
23. N V Grigor'eva, N V Margolis, I N Shokhor, et al. *Zh. Strukt. Khim.*, 1968, **9** 550
24. N V Grigor'eva, N V Margolis, I N Shokhor, et al. *Zh. Strukt. Khim.*, 1967, **8** 175
25. E N Zil'berman *Reaktsii Nitrilov* (Reactions of Nitriles), Izd. Khimiya, Moscow, 1972
26. H Feuer (Editor) *The Chemistry of the Nitro and Nitroso Groups* (Translated into Russian), Izd. Mir, Moscow, 1972
27. S V Novikov, G A Shvekhgeimer, V V Sevost'yanova, V A Shlyapochnikov *Khimiya Alifaticheskikh i Alitsiklicheskikh Nitrosoedinenii* (The Chemistry of Aliphatic and Alicyclic Nitro-Compounds), Izd. Khimiya, Moscow, 1974
28. V V Perekalin, A S Sopova *Nepredel'nye Nitrosoedineniya* (Unsaturated Nitro-Compounds), Izd. Khimiya, Moscow–Leningrad, 1966
29. W Steinkopf, L Bohrmann *Chem. Ber.*, 1908, **41** 1044
30. J Belsky, H Dodiuk, Y Shvo *J. Org. Chem.*, 1974, **39** 989
31. A S Polyanskaya, V V Perekalin, N I Aboskalova, et al. *Zh. Org. Khim.*, 1979, **15** 2057
32. V L Risinov, A Yu Petrov, O N Chupakhin, et al *Khim. Geterotsikl. Soedin.*, 1985, 682
33. W Reid, E Kohler *Liebigs. Ann. Chem.*, 1956, **598** 145
34. M I Kanishchev, N V Korneeva, S A Shevelev *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1986, 2342
35. V E Matthews, D G Kubler *J. Org. Chem.*, 1960, **25** 266
36. O Piloty *Ber.*, 1898, **31** 1878
37. O Piloty *Ber.*, 1901, **34** 1863
38. W Steinkopf, A Supan *Ber.*, 1911, **44** 2891
39. B G Growenlock, J Pfab, G Kresze *Liebigs. Ann. Chem.*, 1975, 1903
40. J F Tilney-Bassett, W A Waters *J. Chem. Soc.*, 1957, 3129
41. W M Weaver, PhD. Thesis, Purdue University, West Lafayette, 1958

42. S D Boyd, PhD. Thesis, Purdue University, West Lafayette, 1971
43. U Schöllkopf, P Tonne, H Schäfer, P Markusch *Lieb. Ann. Chem.*, 1969, **722** 45
44. H Feuer, C Savides *J. Am. Chem. Soc.*, 1959, **81** 5826
45. H Feuer, C Savides *J. Am. Chem. Soc.*, 1959, **81** 5830
46. Z Matacz, H Piotrowska, T Urbanski *Pol. J. Chem.*, 1979, **53** 187
47. N Kornblum, H K Singh, W J Kelly *J. Org. Chem.*, 1983, **48** 332
48. J Liebig *Ann. Chem. Pharm.*, 1856, **95** 282
49. L Schischkoff *Ann. Chem. Pharm.*, 1857, **97** 53
50. M Conrad, A Schulze *Ber.*, 1909, **42** 735
51. C Grundmann, R K Bansal, P S Osamaski *Lieb. Ann. Chem.*, 1973, 898
52. V D Piaz, S Pinzauti, P Lacrimini *Synthesis*, 1975, 664
53. C O Parker, W D Emmons, H A Rolewicz, K S McCallum *Tetrahedron*, 1962, **17** 79
54. L Schisckoff *Ann. Chim. Phys. [3]*, 1861, **49** 310
55. C O Parker *Tetrahedron*, 1962, **17** 109
56. L W Kissinger, H E Ungnade *J. Org. Chem.*, 1960, **25** 1471
57. V Grakauskas, A M Guest *J. Org. Chem.*, 1978, **43** 3485
58. A Hantzsch, A Rickenberger *Ber.*, 1899, **32** 628
59. W Ruske, E Ruske *Chem. Ber.*, 1958, **91** 2505
60. H Köhler, B Eihler, A Kolbe *Z. Chem.*, 1970, **10** 154
61. A Garming, D Redwan, P Gelbke, et al. *Ann. Chem.*, 1975, 17
62. J Clark, J Gelling, J W Southon, M S Morton *J. Chem. Soc.*, 1970, 494
63. J Clark, M Curphey, J W Southon *J. Chem. Soc., Perkin Trans.*, 1974, 1611
64. J A Montgomery, A G Laseter *J. Heterocycl. Chem.*, 1972, **9** 1077
65. J Clark, B Parvizi, R Colman *J. Chem. Soc., Perkin Trans. I.*, 1976, 1004
66. S Rajappa, B G Advani, R Sreenivasan *Tetrahedron*, 1977, **33** 1057
67. M Winn *J. Org. Chem.*, 1975, **40** 955
68. A Alberola, L F Antolin, A M Gonzalez, et al. *J. Heterocycl. Chem.*, 1986, **23** 1035
69. L S Pupko, A I Dychenko, P S Pel'kis *Zh. Org. Khim.*, 1972, **8** 39
70. T P Pillai, J H Boyer *Org. Prep. Proced. Int.*, 1982, **14** 365
71. V Palm *Usp. Khim.*, 1961, **30** 1069 [English translation in *Russ. Chem. Rev.*, 1961(9)]
72. A Talvik *Reakts, Sposobn. Org. Soedin.*, 1972, **9** 233
73. V I Slovetskii, A I Ivanov, A A Fainzil'berg, et al. *Zh. Org. Khim.*, 1966, **2** 937
74. G I Oleneva, A I Ivanov, V V Shlyapochnikov, S S Novikov *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1972, 638
75. G S Hammon, W D Emmons, C O Parker, et al. *Tetrahedron*, 1963, **19**(1) 177
76. C O Parker, W D Emmons, A S Pagano, et al. *Tetrahedron*, 1962, **17** 89
77. J H Boyer, T Manimaran *Heterocycles*, 1986, **24** 2813
78. R Gree, R Carrie *Tetrahedron Lett.*, 1971, 4117
79. R Gree, R Carrie *Bull. Soc. Chim. Fr.*, 1975, 1314
80. R Gree, F Tonard, R Carrie *Tetrahedron.*, 1976, **32** 675
81. V V Mel'nikov, I V Tselinskii, A A Mel'nikov, et al. *Zh. Org. Khim.*, 1984, **20** 658
82. L M Pechenko, A S Polyanskaya, V V Perekalin, et al. *XXXI Gertsenovskie Chteniya* (The XXXIst Gertsen Lectures), Izd. Khimiya, Leningrad, 1978, p. 63
83. E L Metelkina, A S Sopova, V V Perekalin, V I Ionin *Zh. Org. Khim.*, 1974, **10** 209
84. K D Gundermann, H U Alles *Angew. Chem.*, 1966, **78** 906
85. K D Gundermann, H U Alles *Chem. Ber.*, 1969, **102** 3014
86. V F Martynov, V M Grebenkina *Zh. Obshch. Khim.*, 1968, **38** 2338
87. A S Polyanskaya, N I Aboskalova, Z I Demireva, et al. *XXVI Gertsenovskie Chteniya* (The XXVIth Gertsen Lectures), Izd. Khimiya, Leningrad, 1973, No. 2, p. 34; *Ref. Zh. Khim.*, 1973, 21Zh227
88. Ts. Mechkov, Z Demireva *Godishn. Vys. Khim.-Tekhnol. Inst. Burgas*, 1984 (1985), **19**(2) 73; *Ref. Zh. Khim.*, 1986, 5Zh176
89. T Metchkov, Z Demireva *Z. Chem.*, 1985, **25** 169
90. L N Sokolova, A S Polyanskaya, N I Aboskalova, et al. *XXX Gertsenovskie Chteniya* (The XXXth Gertsen Lectures), Izd. Khimiya, Leningrad, 1977, p. 59; *Ref. Zh. Khim.*, 1978, 7Zh142
91. N I Aboskalova, A S Polyanskaya, V V Perekalin, et al. *Zh. Org. Khim.*, 1972, **8** 1332
92. V Yu Shadrin, A S Polyanskaya, N I Aboskalova *Metody Sinteza, Stroenie i Khimicheskie Prevrashcheniya Nitrosoedinenii. Mezhvuzovskii Sbornik Nauchnykh Trudov* (The Methods of Synthesis, Structure, and Chemical Reactions of Nitro-Compounds. Intercollegiate Collection of Reports), Leningrad, 1980, p. 85
93. O S Wolfbeis *Chem. Ber.*, 1977, **110** 2480
94. O S Wolfbeis *Chem. Ber.*, 1981, **114** 3471
95. A V Fokin, Yu N Studnev, A I Rapkin, et al. *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1976, 489
96. R A Wiesboeck, J K Ruff *J. Org. Chem.*, 1968, **33** 1257
97. A V Fokin, V S Palakhov, A T Uzun, et al. *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1974, 456
98. A V Khutoretskii, L V Okhlobystina, A A Fainzil'berg *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1970, 387
99. H G Adolph, R E Oesterling, M E Sitzmann *J. Org. Chem.*, 1968, **33** 4296
100. E S Mints, E L Golod, L I Bagal *Zh. Org. Khim.*, 1970, **6** 1137
101. V L Rusinov, T V Dragunova, V A Zyryanov, et al. *Khim. Geterotsikl. Soedin.*, 1984, 557
102. M S Pevzner, A K Pan'kov, I N Shokhor, et al. *Zh. Org. Khim.*, 1972, **8** 118
103. O P Shitov, V N Kondrat'ev, A P Seleznev, V A Tartakovskii *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1976, 479
104. O P Shitov, V N Kondrat'ev, A P Seleznev, V A Tartakovskii *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1977, 240
105. J K Ruff, R F Merritt *Inorg. Chem.*, 1968, **7** 1219
106. N E Alexandrov *J. Org. Chem.*, 1965, **30** 1335
107. N E Alexandrov, P S Lianis *Tetrahedron Lett.*, 1975, 421
108. F G Bordwell, A N Clemens *J. Org. Chem.*, 1982, **47** 2510
109. N Kornblum, S D Boyd *J. Am. Chem. Soc.*, 1970, **92** 5784
110. N Kornblum, S D Boyd, F W Stuchal *J. Am. Chem,. Soc.*, 1970, **92** 5783
111. N Ono, H Miyake, R Tamura, A Kaji *Tetrahedron Lett.*, 1981, **22** 1705
112. E V Ratsino, L M Andreeva, K V Altukhov, T D Zheved' *XXVI Gertsenovskie Chteniya* (The XXVIth Gertsen Lectures), Izd. Khimiya, Leningrad, 1973, No. 2, p. 68; *Ref. Zh. Khim.*, 1973, 24Zh441

113. E V Ratsino, L M Andreeva, K V Altukhov, V V Perekalin *Zh. Org. Khim.*, 1974, **10** 728
114. T D Zheved', K V Altukhov, L M Andreeva, E V Ratsino *XXVIII Gertsenovskie Chteniya* (The XXVIIIth Gertsen Lectures), Izd. Khimiya, Leningrad, 1976, p. 141; *Ref. Zh. Khim.*, 1977, 5Zh306
115. T D Zheved', K V Altukhov *Tezisy VI Soveshchaniya po Khimii Nitrosoedinenii* (Abstracts of Reports at the VIth All-Union Conference on the Chemistry of Nitro-Compounds), Moscow, 1977, p. 98
116. C O Parker *Tetrahedron*, 1962, **17** 105
117. E S Mints, R S Tesler, E L Golod, L I Bagal *Zh. Org. Khim.*, 1970, **6** 698
118. W Ried, A Sinharay *Chem. Ber.*, 1963, **96** 3306
119. W M Koppes, H G Adolph *J. Org. Chem.*, 1981, **46** 406
120. E R Bissel *J. Org. Chem.*, 1963, **28** 1717
121. A I Kiprianov, T I Verbovskaya *Zh. Obshch. Khim.*, 1962, **32** 3703
122. A V Fokin, Yu N Studnev, A I Rapkin, et al. *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1981, 2370
123. Z I Demireva, I G Binev, I N Juchnovski *Tetrahedron Lett.*, 1976, 1523
124. Z I Demireva *Godishn. Vys. Khim.-Tekhnol. Inst. Burgas*, 1977 (1978), **12**(2) 37; *Ref. Zh. Khim.*, 1979, 12Zh163
125. Z I Demireva, Ts D Mechkov *Godishn. Vys. Khim.-Tekhnol. Inst. Burgas*, 1980 (1981), **15**(2) 19; *Ref. Zh. Khim.*, 1982, 17Zh192
126. T Metchkov, Z Demireva, E Tontcheva *Z. Chem.*, 1985, **25** 62
127. T D Metchkov, Z I Demireva *J. Chem. Eng. Data.*, 1984, **29** 483
128. T Metchkov, Z Demireva, E Tontcheva *Z. Chem.*, 1985, **25** 62
129. S Rajappa, B G Advani *Indian J. Chem.*, 1978, **15** 890
130. A V Fokin, Yu N Studnev, A I Rapkin, et al. *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1981, 1592
131. V Garakauskas, A Albert *J. Heterocycl. Chem.*, 1981, **18** 1477
132. F Eiberg *J. Org. Chem.*, 1964, **29** 2021
133. T G Ladyzhnikova, K V Altukhov, N A Solov'ev *Zh. Org. Khim.*, 1986, **22** 2618
134. E K Kyung, G A Horst *Synthesis*, 1987, 1029

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Advances in the chemistry of isochroman

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ABSTRACT. Data on the synthesis and chemical and biological properties of isochroman and its derivatives dating from 1923 (the start of research into this field) until 1985 inclusive are examined and described systematically.

The bibliography includes 235 references.

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I. Introduction

The synthesis of the oxygen-containing heterocyclic isochroman {3,4-dihydro-1*H*-benzo[*c*]pyran} system has been known for a long time but intensive research undertaken to investigate the chemistry of this heterocycle and to seek biologically active compounds (BAC) in the isochroman series date back to the 1970s. The increasing number of publications and patent data during the last 10–15 years indicate the undoubted value of the isochroman ring as the structural basis of a large number of BAC.

The isochroman ring enters into the composition of many substances of natural origin: compounds obtained by the cultivation of micro-organisms,[1] the antibiotic isochroman quinone,[2,3] various metabolites,[4–15] compounds isolated from Oidiodendron rhodogenum,[16] and other substances of plant origin.[17–23] Some of the compounds indicated[1] are of practical value (for example, in the treatment of ulcers and oedemas).

Isochroman derivatives are structural analogues of biogenic amines and derivatives of tetrahydroisoquinoline. In particular, 1-alkylaminoisochromans can be regarded as cyclic analogues of arylalkanolamines incorporating the phenylethylamine fragment in a rigidly fixed structure, which is of definite interest, since it can promote a more specific interaction with a bioreceptor.[24] The analogy between the isochroman and tetrahydroisoquinoline derivatives is determined not only by their structures but also by their interconversions. A series of studies devoted to the conversion of tetrahydroisoquinoline derivatives into isochroman derivatives[25–32] and conversely [33–34] have been published.

Isochroman derivatives, in particular isochromanones, serve in their turn as synthons in the synthesis of nitrogen-containing bicyclic and polycyclic compounds: galanthamine,[35] phthalazones,[36] yohimbine and its derivatives,[37,38] the seleno-analogue of yohimbine,[39] heterocyclic steroids,[40,41] and other compounds.[42–44] Furthermore, isochroman derivatives can be used also for the synthesis of iridoids,[45] analogues of prostaglandin,[46] indole derivatives,[47] tricyclic systems,[48] and dibenzotropolone.[49] Compounds resembling the last one, especially its derivatives involving the carbonyl group, have a pronounced biological activity, which is accounted for by their structural relation with a natural alkaloid–colchicine.

Despite the very considerable interest in isochroman derivatives, they have been scarcely surveyed in the literature (with the exception of a brief review[50]).

The present review surveys the methods of synthesis and the chemical and biological properties of isochroman and its derivative, mainly of synthetic origin, with different positions of the substituents in the benzene and dihydropyran rings. It does not include isochromanone derivatives, which, in view of the extensive nature of the data available, can be the subject of a separate review.

II. Methods of synthesis of isochroman and its derivatives

There are many features in common between the methods of synthesis of isochroman and its derivatives, but, depending on the position of the substituents and the need to employ different starting materials, there are also specific features in the synthetic approach. It is therefore useful to subdivide isochroman derivatives into the following groups: (a) with substituents in the dihydropyran ring; (b) with substituents in the aromatic ring; (c) with substituents in both the dihydropyran and benzene rings.

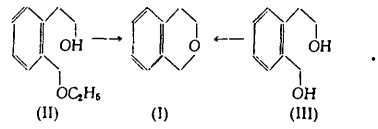
1. Methods of synthesis of isochroman

Isochroman (I) was first synthesised in 1923[51] by heating 2-(2-ethoxymethylphenyl)ethanol (II) with a fourfold excess of fuming hydrobromic acid for 32 h at 100 °C. The homoxylylene dibromide formed simultaneously can be converted into compound (I) by heating with water or a dilute solution of potassium carbamate. The initial alcohol (II) can be obtained by a multistage synthesis. This method is merely of historical interest.

One of the ways of obtaining isochroman involves the cyclisation of 2-(2-hyroxymethylphenyl)ethanol (III), which was obtained from homophthalic anhydride.[52,53] Cyclisation at 45 °C in the presence of potassium bisulphate[52] or on treatment with a mixture of hydrobromic and acetic acids[53] leads to isochroman in 50% yield. In the second case, homoxylylene dibromide is formed together with isochroman.

The most effective method, which ensures an almost quantitative yield of compound (I), involves the direct distillation of the diol (III) at 70 °C and a pressure of 3 mmHg in the presence of catalytic amounts of concentrated sulphuric acid.[54] Isochroman has been synthesised in

80% yield by the reaction of 2-phenylethanol with formaldehyde in the presence of concentrated sulphuric acid:[55]



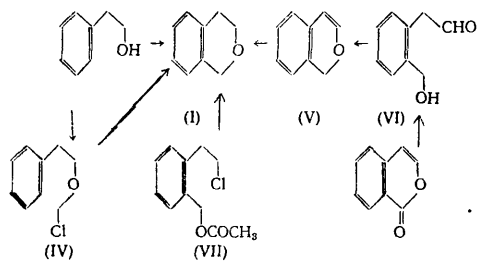
Methods of synthesis of compound (I) based on the chlorometallation of 2-phenylethanol with subsequent cyclisation were developed subsequently. Such a method was first described in 1935.[56,57] Treatment of 2-phenylethanol with paraformaldehyde and hydrogen chloride results in the formation of the chloromethyl derivative, which is then converted into isochroman in 50% yield on treatment with inorganic acids, preferably at 100 °C. Compound (I) with m.p. +3 °C was thus obtained. In 1954, the method was improved and the yield of isochroman reached 90%.[58] The intermediate chlorometallation product was cyclised in this case when the temperature of the reaction mixture rose spontaneously to 45–50 °C without the addition of concentrated hydrochloric acid. Consequently the decrease in the cyclisation temperature leads to an appreciable increase in the yield of compound (I).

Up to 1956, it was assumed that the chlorometallation of 2-phenylethanol results in the formation of 2-(2-chloromethylphenyl)ethanol which subsequently cyclises to isochroman. However, detailed study of the chemistry of this reaction showed[59] that the first stage of the reaction involves the formation of chloromethyl 2-phenylethyl ether (IV), which then cyclises to isochroman. By carrying out the reaction in the temperature range –5–0 °C, it is possible to isolate the intermediate (IV) in 76% yield. The cyclisation product (isochroman) was obtained in 67% yield by heating the ether (IV) with hydrochloric acid at 20–40 °C. The yield of compound (I) increases appreciably (by 30%) when the intermediate (IV) is refluxed in carbon disulphide in the presence of aluminium trichloride.[59] The ether (IV) has been cyclised[60,61] in the presence of alkali or without it, a high yield of compound (I) being ensured in both cases (the yield is 10% higher in the former case than in the latter).

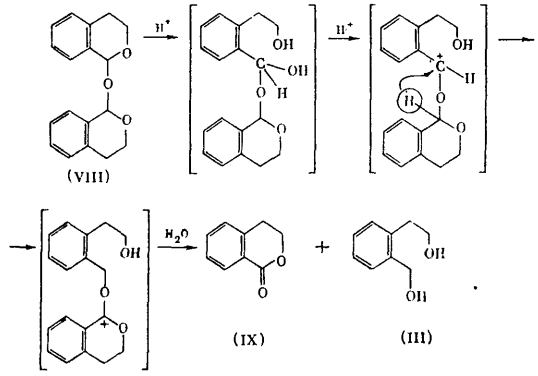
From the standpoint of increasing the yield (to 95%), the synthesis of isochroman from 2-phenylethanol and formaldehyde in the presence of a mixture of hydrochloric acid and phosphorus trichloride also merits attention.[62]

The preparation of isochroman by hydrogenating isochromen (V) in acetic acid in the presence of 10% palladium on charcoal has been described.[63] Isochromen was synthesised from isocoumarin via the hydroxyaldehyde (VI).

Isochroman can be obtained in 70% yield from the acetyl derivative (VII) by treatment with alcoholic alkali:[64]



Isochroman has been isolated after cleaving di-1-isochromanyl ether (VIII) in the presence of sulphuric acid.[65] The ether then disproportionates to the diol (III) and 1-isochromanone (IX):

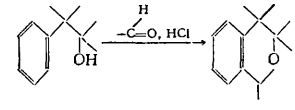


2-(2-Hydroxymethylphenyl)ethanol formed under the reaction conditions readily cyclises to isochroman.

Thus the most effective procedures for the synthesis of isochroman are the methods[58,62] involving the cyclisation of chloromethyl 2-phenylethyl ether in the temperature range 45–50 °C.

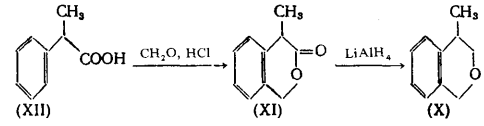
2. Derivatives of isochromans with substituents in the dihydropyran ring

There are several methods of synthesis of isochroman derivatives containing one or several substituents in the 1-, 3-, and 4-positions. One of them is the chloroalkylation of 2-phenylalkanol, analogous to the chloromethylation described in the previous Section:



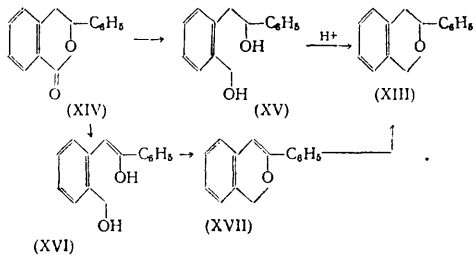
However, chloroalkylation and even more so chloroarylalkylation take place with low yields. 1-Methylisochroman and 1-phenylisochroman have been obtained in this way in 50% yield in the former case and in a yield as low as 7% in the latter case.[60,66]

3-Methylisochroman,[59,67–70] 3-ethyl- and 3-benzyl-isochromans,[68] 4-methylisochroman,[57,67,68] 4-nitroisochroman,[57] and 4,4-dimethylisochroman[71] have been synthesised by the chloromethylation of chain-substituted 2-phenylethanols. 4-Methylisochroman (X) has also been obtained by reducing 4-methyl-3-isochromanone (XI).[66] The latter is formed when hydratropic acid (XII) is chloromethylated:

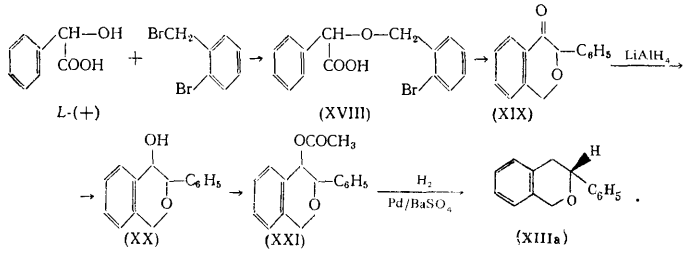


3-Phenylisochromanone (XIII) has been synthesised from 3-phenylisocoumarin (XIV).[52] The reduction of the latter with lithium aluminium hydride (LAH) afforded 2-(2-hydroxymethylphenyl)-1-phenylethanol (XV), which cyclises to compound (XIII) in an acid medium. The reduction of 3-phenylisocoumarin by LAH has been studied in greater detail by a series of investigators. Thus,

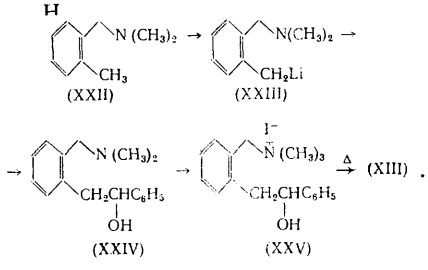
together with the main product, another readily oxidisable compound—the enediol (XVI)—has been obtained.[72] By reducing compound (XIV) at 0 °C, it was possible to isolate compound (XVI) as the main product in 86% yield. The enediol (XVI) cyclises on distillation with formation of 3-phenylisochromen (XVII), which is reduced to compound (XIII) in ethyl acetate by hydrogen in the presence of palladium on charcoal:



A stereoselective synthesis of (*R*)-(+)-3-phenylisochroman (XIIIa) has been achieved with the aid of consecutive reactions: the condensation of L-(+)-mandelic acid with *o*-bromobenzyl bromide; the cyclisation of the carboxyether (XVIII) formed in the presence of butyl-lithium to 3-phenyl-4-isochromanone (XIX); the reduction of the latter with LAH to the corresponding alcohol (XX); the conversion of the alcohol into the acetyl derivative (XXI); the hydrogenation of compound (XXI) to compound (XIIIa):[74]



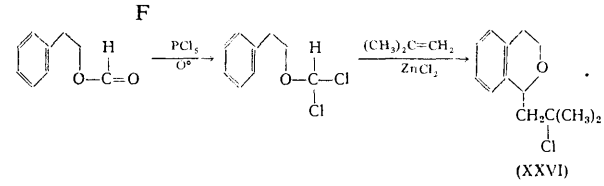
The synthesis of 3-phenylisochroman from dimethyl(*o*-methylbenzyl)amine (XXII) is unusual:[72]



By treating compound (XXII) with n-butyl-lithium, it is possible to obtain the lithio-derivative (XXIII), whose condensation with benzaldehyde affords the aminoalcohol (XXIV). 3-Phenylisochroman is then obtained via a stage involving the formation of the methiodide (XXV) and its subsequent decomposition by heating. 1,3-Diphenyl- and 3,3-diphenyl-isochroman have been obtained similarly.[72] 1,3-Diphenylisochroman has been synthesised by reducing 2,3-diphenylindene ozonide with sodium tetrahydroborate in trifluoroacetic acid.[75] 1,3-Diphenylisochroman has also been isolated as a side product in the reaction of benzaldehyde with benzylmagnesium chloride.[76]

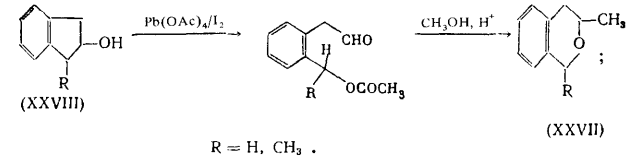
1-Methoxy-4,4-dimethyl-1,3-diphenylisochroman has been obtained by UV irradiation 2-(2-methyl-1-phenylpropenyl)benzophenone in methanol.[77]

It is of interest to note the synthesis of 1-β-chloroisobutylisochroman (XXVI) in accordance with the scheme[78]



The same compound can be obtained from 1-chloroisochroman and isobutene in the presence of a Friedel–Crafts catalyst.[79]

Substituted isochromans (XXVII) have been synthesised from indan derivatives (XXVIII) in accordance with the scheme[80]



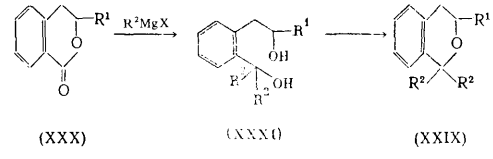
The cyclisation of allyl *o*-bromobenzyl ether on treatment with triethylamine in the presence of palladium acetate and tri-*o*-tolylphosphine leads to a mixture of isomeric derivatives of 2-benzopyran. One of them is 4-methyleneisochroman (XXI).[81]

The photochemical oxidation of 1,1-dimethylindene in methanol results in the formation, together with other products, of 3-hydroxy-1-methoxy-4,4-dimethylisochroman.[82]

The cyclisation of an *o*-polyene-substituted β-phenylethanol in the presence of a Lewis acid, leading to an isochroman derivative with a tetracyclic substituent in the 1-position, has been described.[83] It is notable that the compound cyclised was obtained by multistage synthesis.

Yet another unusual method of synthesis of isochroman derivatives involves the cyclisation of *o*-mercuriobenzyl alcohols with conjugated or non-conjugated dienes in the presence of a palladium catalyst.[84]

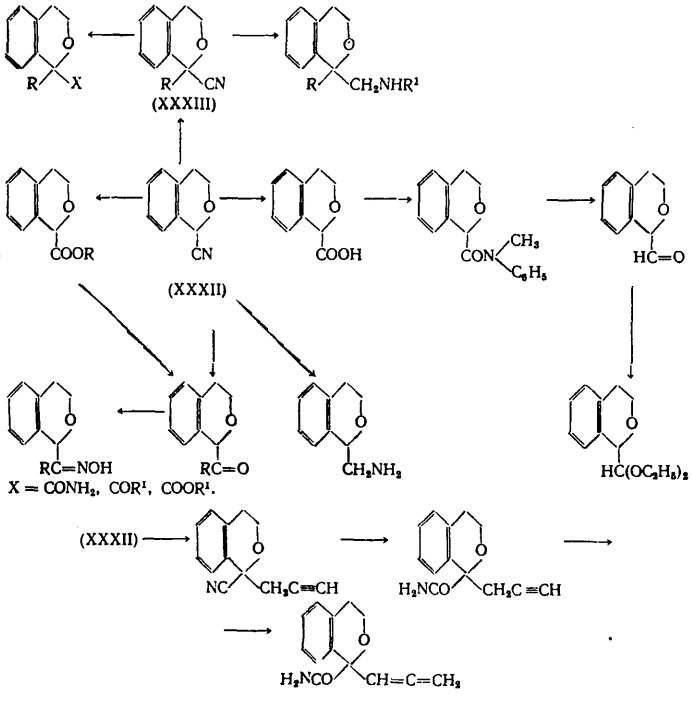
1,1-Disubstituted and 1,1,3-trisubstituted isochroman derivatives (XXIX) have been obtained from substituted 1-isochromanones (dihydroisocoumarins) (XXX).[59,66] Treatment of the lactones (XXX) with a fourfold excess of a Grignard reagent afforded the diols (XXXI). The latter cyclise to the final compounds (XXIX) at 100 °C in the presence of an equimolar amount of phosphoric acid:



The methods of synthesis of 1-monosubstituted and 1,1-disubstituted isochroman derivatives based on the reactivity of the methylene group in the 1-position in isochroman are of great practical value (Scheme 1). Thus 1-halogenoisochromans have been obtained by halogenating isochroman. On reaction with copper cyanide[58] or mercury cyanide,[85] they form 1-cyanoisochroman (XXXII). The latter has been converted into various 1-substituted isochromans: ketones,[85,86] aldehydes,[87] oximes,[24,86] an amine,[24,88,89] a carboxylic acid,[85,88] esters,[86,89] etc. (Scheme 1).

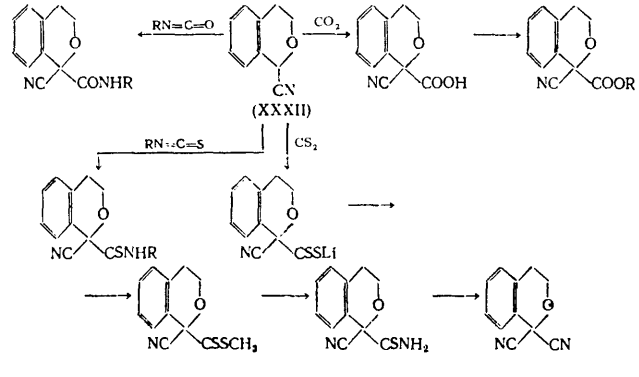
In the presence of strong bases (sodium amide or hydride, organosodium compounds), 1-cyanosiochroman (XXXII) was converted, on treatment with various halides, into a wide variety of 1,1-disubstituted isochromans (XXXIII) by virtue of the high reactivity of the hydrogen in the α-position relative to the nitrile group.[85,90–95] The isochromans (XXXIII) were then subjected to numerous transformations indicated in Scheme 1.

Scheme 1



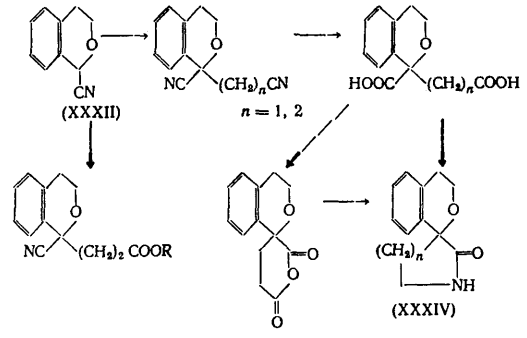
The dithioester, carboxy-, nitrile, and thiocarbamide groups have been introduced in the 1-position of 1-cyanoisochroman in the presence of phenyl-lithium (Scheme 2).[96,97] As in the previous case, certain reactions involving the final compounds obtained were carried out.[96,97]

Scheme 2



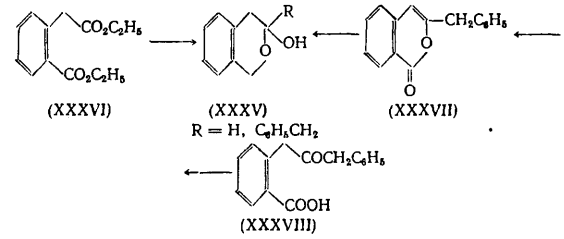
The cyanoethylation of 1-cyanoisochroman has also been achieved.[98,99] It has been shown that condensation takes place best in the presence of tetraethylammonium hydroxide.[99] The series of reactions of the bifunctional isochromans obtained leads to the spirocyclic product (XXXIV, n = 2)[98,99] (Scheme 3). Compounds (XXXIV, n = 1) have been obtained similarly.[91]

Scheme 3

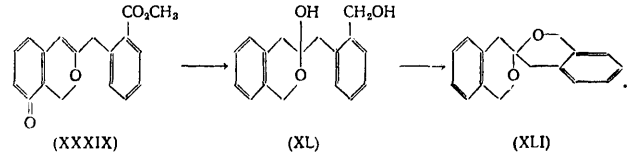


Thus syntheses based on 1-cyanoisochroman lead to extensive possibilities for the preparation of a wide range of varied 1,1-disubstituted isochroman derivatives.

Apart from the compounds with functional-group substituents described above, hydroxyisochromans are also of interest. 3-Hydroxyisochroman (XXXV, R = H) has been synthesised by reducing diethyl homophthalate (XXXVI) with three equivalents of di-isobutylaluminium hydride.[100] 3-Benzyl-3-hydroxyisochroman (XXXV, R = $C_6H_5CH_2$) has been obtained by reducing 3-benzylisocoumarin (XXXVII) with LAH.[73] The isocoumarin (XXXVII) was synthesised by the intramolecular condensation of benzyl 2-carboxybenzyl ketone (XXXVIII) in the presence of acetyl chloride:



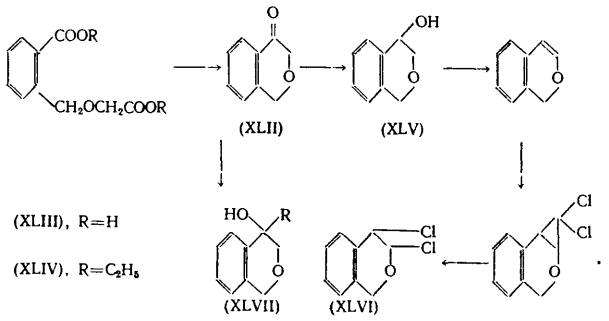
3-Hydroxy-3-(2-hydroxymethylbenzyl)isochroman (XL) has been obtained by reducing 3-(2-methoxycarbonylbenzyl)isocoumarin (XXXIX) with LAH.[101] On treatment with perchloric or sulphuric acid, compound (XL) is converted into the spiroketal (XLI):



The reduction of derivatives of 3,4-dihydroisocoumarin with sodium tetrahydroborate in the presence of boran trifluoride (hydroboration) leads to the elimination of the carbonyl group from the 1-position.[102]

The starting material for the synthesis of 4-hydroxy-derivatives is 4-isochromanone (XLII), obtained in 40% yield both by the Perkin reaction from (2-carboxyphenyl)methoxyacetic acid (XLIII) and via the Dieckman reaction from ethyl (2-ethoxycarbonylphenyl)-methoxyacetate (XLIV). 4-Hydroxyisochroman (XLV) has been obtained by the reduction of the ketone (XLII) with LAH[103,104] and was further converted into dichlorohomoisochroman (XLVI). The

same ketone has been converted into a 4-hydroxy-4-R-substituted isochroman (XLVII) by reaction with a Grignard reagent:[105]



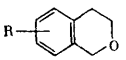
The reaction of DL-glyceraldehyde with benzene in the presence of liquid hydrogen fluoride is of interest. The interaction results in the formation of 1-(1,2-dihydroxyethyl)-3-hydroxymethyl-4-phenylisochroman.[106]

1,1,3,3,4,4-Hexachloroisochroman has been synthesised by treating 3,3,4,4-tetrachloroisocoumarin with phosphorus pentachloride.[107] The isocoumarin derivative was obtained by the reaction of homophthalic acid with the same chlorinating agent.

Thus the most convenient method of synthesis of isochroman derivatives with various substituents in the dihydropyran ring is the chloroalkylation of 2-phenylethanol and its derivatives substituted in the ethyl group. This method makes it possible to introduce substituents into the 1-, 3-, and 4-positions in any combination, usually with satisfactory yields of the substituted isochromans, with the exception of the 1-substituted derivatives. Synthesis based on 1-cyanoisochroman merits attention for the latter.

3. Derivatives of isochroman with substituents in the aromatic ring

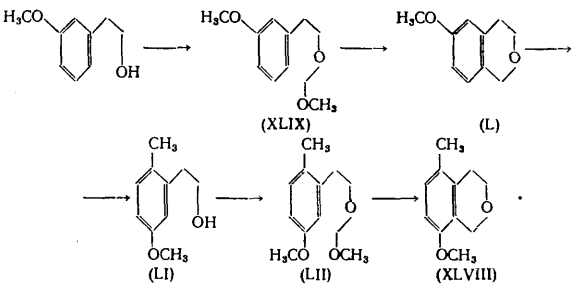
Compounds with substituents in the aromatic ring can be obtained by the chloromethylation reaction using arylethanols:[59,67,108,109]



R = 7-CH_3, 5,8-$(CH_3)_2$, 5,6-benzo, 6,7-$(OCH_3)_2$

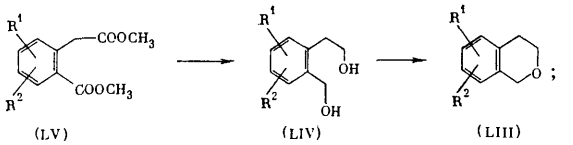
When hydrogen chloride is passed for a long time and also in the presence of an excess of formaldehyde, the chloromethyl group also enters in the *para*-position in the benzene ring relative to the chloromethoxyethyl substituent. 7-Chloromethyl- and 7-chloromethyl-5-methyl-isochromans were obtained respectively in this manner in the synthesis of isochroman and its 5-methyl derivative.[56,110] Various derivatives—the nitrile, the amide, and esters—have been synthesised by further reactions of 7-chloromethylisochroman.[110]

A method has been developed for the synthesis of 5,8-disubstituted derivatives of isochroman (XLVIII).[111] 2-(3-Methoxyphenyl)ethyl methoxymethyl ether (XLIX) has been synthesised by a Williamson reaction. The ether cyclises to 6-methoxyisochroman (L) in the presence of toluene-*p*-sulphonic acid and the isochroman is converted further into 8-methoxy-5-methylisochroman (XLVIII). The methyl group is introduced into the 5-position as a result of consecutive reactions: the degradative reduction of 6-methoxyisochroman in the presence of aluminium hydride, the condensation of 2-(5-methoxy-2-methylphenyl)ethanol (LI) with chloromethyl methyl ether, and the cyclisation of 2-(5-methoxyphenyl-2-methyl)ethyl methoxymethyl ether (LII):



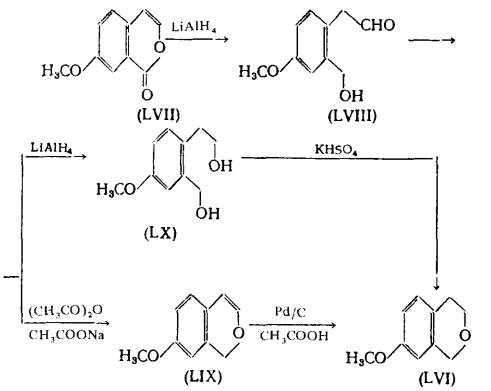
Thus an unusual feature of this method consists in the fact that the methyl group can be introduced into the 5-position in combination with various substituents in the 8-position in the isochroman ring.

A series of methoxy-derivatives of isochroman (LIII) have been synthesised by cyclising the arylethanols (LIV) on treatment with phosphorus pentoxide or potassium bisulphate.[112–116] The arylglycols (LIV) have been synthesised by reducing the diesters (LV):



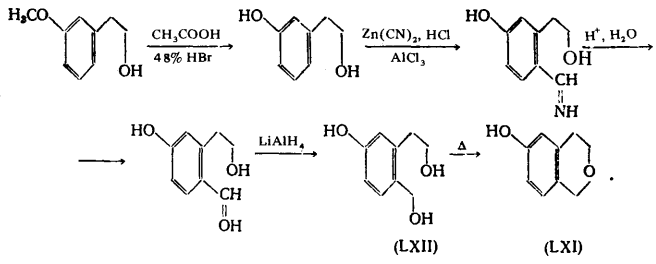
R^1=H, 5-OCH_3; 6-OCH_3;
R^2=H, 6-OCH_3, 7-CH_3, 7-OCH_3, 7-$OCH_2C_6H_5$; R^1R^2=6,7-OCH_2O.

7-Methoxyisochroman (LVI) has also been obtained as in the scheme[117]



(2-Hydroxymethyl-4-methoxyphenyl)acetaldehyde (LVIII) has been obtained by reducing 7-methoxyisocoumarin (LVII) with LAH. The acetaldehyde was converted into 7-methoxyisochroman (LVI) via two pathways: dehydration to 6-methoxyisochromene (LIX) and the catalytic hydrogenation of the latter or its reduction to the diol (LX) and then dehydration with ring closure. Both versions of the synthesis are of interest from the standpoint of the isolation of the intermediates (LVIII) and (LIX). On the other hand, in order to obtain the target product, it might be possible to reduce 7-methoxyisocoumarin immediately to the diol (LX) with its subsequent dehydration.

The hydroxy-derivative—6-hydroxyisochroman (LXI)—has been synthesised via the diol (LVII) using the Gatterman formulation:[118]

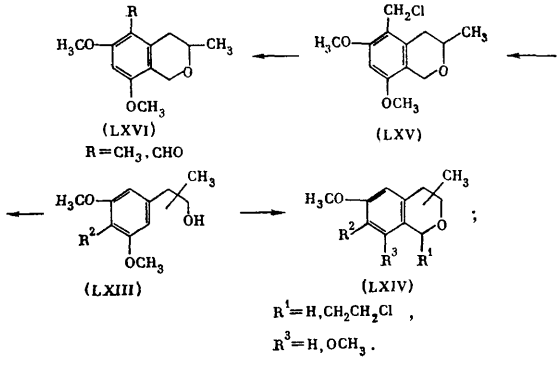


The above methods of synthesis of methoxy- and hydroxy-derivatives reduce mainly to the preparation of the substituted diols (LIV), (LX), and (LXII) with their subsequent cyclisation, described above for the synthesis of the unsubstituted derivative.

4. Derivatives of isochroman with substituents in the aromatic and dihydropyran rings

In order to obtain isochroman derivatives with substituents in both rings, the same cyclisation reactions are used as for the synthesis of the previous structures and sometimes the problem reduces to the preparation of the corresponding initial arylalkanols.

6,7,8-Trimethoxy-3-methyl- and 6,8-dimethoxy-3-methyl-isochromans (LXIV) have been obtained by the chloromethylation of 2-(3,4,5-trimethoxyphenyl)-1-methyl- and 2-(3,5-dimethoxyphenyl)-1-methyl-ethanols (LXIII).[119,120] Compound (LXIV) was synthesised in a low yield because of partial polymerisation of the phenol-formaldehyde type. A higher yield is obtained in the chloro-methylation of the arylalkanol (LXIII, $R^2 = H$) by monochloromethyl methyl ether in the presence of zinc chloride. The chloromethyl derivative (LXV) is formed for a specific ratio of the ether and zinc chloride and is subsequently converted into compound (LXVI):

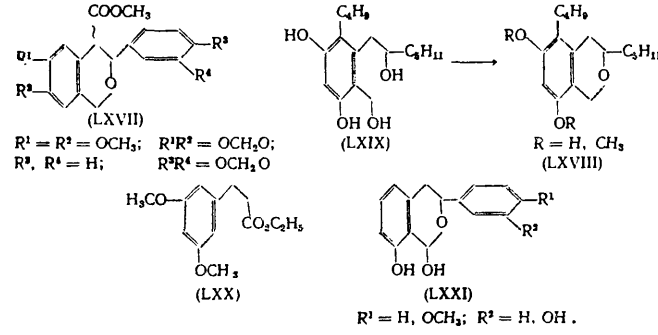


2-(3,4-Dimethoxyphenyl)-2-methylethanol has been condensed with chloroacetal in the presence of boron trifluoride to form 1-(2-chloroethyl)-6,7-dimethoxy-4-methylisochroman (LXIV, R^1 = CH_2CH_2Cl, R^2 = OCH_3, R^3 = H) and its stereochemistry has been investigated.[121]

The diastereoisomeric isochromans (LXVII) have been obtained from the methyl esters of *erythro-* and *threo*-2,3-diaryl-3-hydroxy-propionic acids and formaldehyde in methanol in the presence of sulphuric acids.[122]

The method of synthesis of (±)-5-butyl-6,8-dihydroxy-3-pentylisochromans (LXVIII) is based on the cyclisation of compound (LXIX). The latter has been obtained by multistage synthesis from ethyl β-(3,5-dimethoxyphenyl)propionate (LXX).[123]

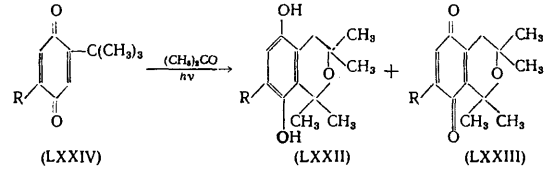
8-Hydroxy-4,4,7-trimethyl-1,3-diphenylisochroman has been obtained by the stepwise aromatisation of 4a-chloro-4,4,7-trimethyl-1,3-diphenyl-4a,5,6,7,8,8a-hexahydroisochroman-8-one. The latter was synthesised by condensing limonenone with benzaldehyde.[124,125] 8-Hydroxy-4,5,6,7-tetramethylisochroman has been obtained by reducing sclerin—8-hydroxy-4,5,6,7-tetramethylchroman-1,3-dione:[10]



Among hydroxy-derivatives, 3-aryl-1,8-dihydroxyisochromans (LXXI), obtained by reducing 8-hydroxyisocoumarins by complex hydrides, are also known.[126]

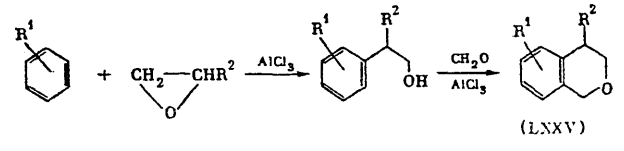
4-Hydroxyisochromans have been obtained from 4-isochromanone derivatives both by reduction[127] and by the Reformatskii reaction.[128]

The formation of the isochroman derivatives (LXII) and (LXIII) in the photolysis of the quinone (LXIV) in acetone[129] (other compounds are obtained as well) is of interest from the chemical standpoint:



The methods of synthesis of isochroman derivatives based on the cyclisation of *o*-alkenylbenzyl alcohols[130,131] and the catalytic reduction of indene ozonides[132] are distinguished by unusual features.

One of the common methods of synthesis of isochroman derivatives (LXXV) with substituents in the aromatic and dihydropyran rings involves the condensation of an arylalkanol with formaldehyde in the presence of aluminium chloride.[133,134] Arylalkanols can be synthesised in different ways. Thus they have been obtained[133,134] by the reaction of arenes with epoxyalkanes in the presence of aluminium chloride. Compounds (LXXV) have also been obtained by hydroxymethylation and cyclisation in the presence of a mixture of hydrochloric acid and phosphorus trichloride:[62]



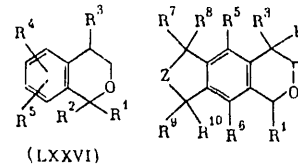
A number of investigators[135–141] have synthesised 1,1,6,7-tetrasubstituted isochromans (LXXVI) by condensing an arylethanol with carbonyl compounds (ketones, aldehydes or their acetals,

ketoacids). A solution of 3% trichloroacetic acid, toluene-*p*-sulphonic acid, and hydrogen chloride has been used as the initial catalyst.

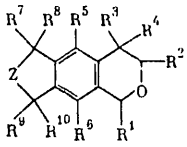
A similar condensation has been used to synthesise 1-substituted and 1,4-disubstituted isochroman derivatives (LXXVI) with different positions of substituents in the aromatic ring (including also condensed fragments in the 6,7-positions) in the presence of polyphosphoric acid or toluene-*p*-sulphonic acid.[142–145] It is notable that the above condensation yielded tricyclic isochromans (LXXVII) which can be used in the perfume industry.[146–149] The similar compounds (LXXVIII), obtained by the reaction of isochroman derivatives with dichloroalkanes in the presence of aluminium chloride,[150] have the same properties. 1-Alkoxyalkylisochromans (LXXIX) and (LXXX), with a wide variety of substituents in different positions in both the aromatic and dihydropyran ring, are also known.[151–153] The above compounds are intermediates in the synthesis of hypotensive and psychotropic preparations.

A series of isochroman derivatives (LXXXI)–(LXXXIII) have been obtained by condensing the corresponding arylalkanols with ketones or ketoacids.[154–157]

The hydrogenolysis of wood results in the formation of 1-ethyl-6-hydroxy-4-(4-hydroxy-3-methoxybenzyl)-7-methoxyisochroman.[158,159] Catalytic reduction of the *Chrysodin* metabolite yielded 3-hexyl-6,8-dihydroxy-7-methylisochroman:[160]

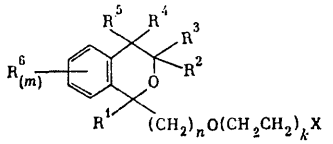


(LXXVI)



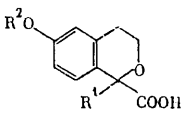
(LXXVII), $R^1=R^2=R^3=R^5=R^6=H$; R^4, R^7-R^{10} = Alk; $Z=CHR^{11}$, $R^{11}=H, CH_3$;

(LXXVIII), R^1-R^{10} = Alk; $Z=CH_2, CHCH_3, (CH_2)_2, CH_2CHCH_3$.



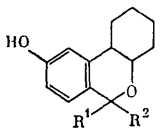
(LXXIX), X = OH;

(LXXX), X = Cl.



(LXXXI), R^1, R^2 = Alk;

(LXXXII), R^1 = Alk; R^2 = H.



(LXXXIII)

R^1, R^2 = Alk, Ar, alkoxycarbonyl; $R^1 + R^2$ = carbocycle.

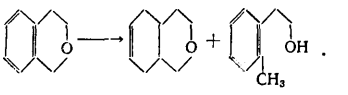
Thus isochroman derivatives with substituents in both the aromatic and dihydropyran rings can be obtained by the cyclocondensation of arylalkanols with various carbonyl compounds in the presence of both protic acids and Lewis acids. The variation of the substituents in the 1-position depends on the type of the carbonyl-containing component. It is notable that preference should be given to methods based on the application of polyphosphoric or toluene-*p*-sulphonic acid. When aluminium chloride is used as the catalyst, it is essential to take certain precautions, since the decomposition of the complexes formed is accompanied by the vigorous evolution of hydrogen chloride.

III. Chemical properties of isochroman and its derivatives

1. Hydrogenation

The catalytic hydrogenation of isochroman and its derivatives can involve hydrogenolysis accompanied by the opening of the cyclic ether as well as the reduction of the benzene ring. It is notable that the hydrogenolysis of isochroman derivatives is of practical value, especially in the perfume industry.[161–164]

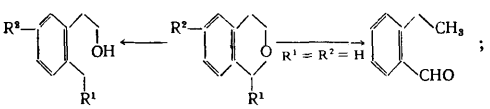
In the catalytic hydrogenation of isochroman in the presence of the Raney nickel catalyst at 200 °C and a pressure of 150 atm, the hydrogenolysis product 2-(2-tolyl)-ethanol was isolated in addition to the normal reduction product—tetrahydroisochroman:[58]



Other fractions have been isolated after distillation through a column as a result of a similar reaction but at normal pressure: (1) *cis*- and *trans*-1,2-dimethylcyclohexanes, 1,2-dimethylbenzene, and 2-ethyl-1-methylbenzene; (2) *trans*-hexahydroisochroman; (3) *cis*-hexahydroisochroman; (4) an unidentified high-boiling fraction.[165]

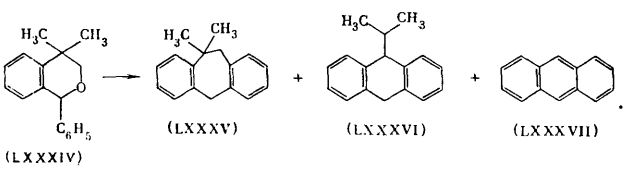
It is of interest that the tetrahydro- and hexahydro-derivatives of isochroman are obtained by special methods, involving the Dieckmann, Robinson, etc. cyclocondensation reactions, and not by the hydrogenation of the corresponding isochromans.[166–168]

Treatment of isochroman with hydrogen in the presence of Raney nickel at room temperature for 10 min affords a rearrangement product—2-ethylbenzaldehyde.[58] The catalytic reduction of 1-alkyl- or 1-aryl-isochromans in the presence of the Raney nickel catalyst at 200 °C and a pressure of 200 atm leads to ring opening with formation of 2-arylethanols.[58] The reduction of the benzene ring is not then observed. The substituent in the 1-position evidently increases the resistance of the aromatic ring to hydrogenation. Reduction with the opening of the dihydropyran ring occurs when 6-methoxyisochroman interacts with aluminium hydride:[111]



R^1 = H, Alk, Ar; R^2 = H, OCH_3.

The reduction of 4,4-dimethyl-1-phenylisochroman (LXXXIV) by hydriodic acid in the presence of red phosphorus is of interest from the chemical point of view.[169] The reaction results in a rearrangement with the opening of the heterocycle, which leads to the formation of three tricyclic compounds—10,10-dimethyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (LXXXV), 9-isopropyl-9,10-dihydroanthracene (LXXXVI), and anthracene (LXXXVII):



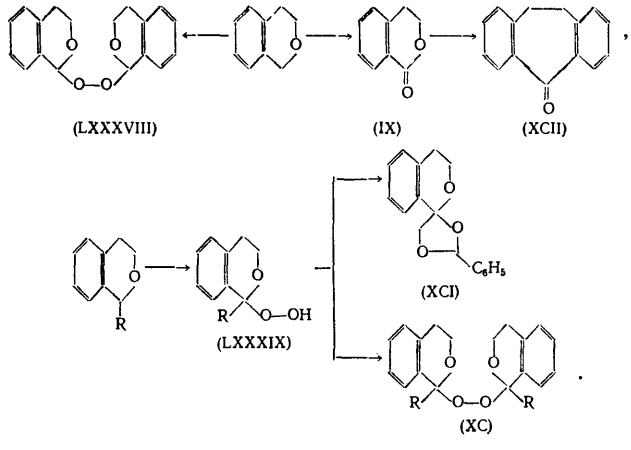
(LXXXIV) (LXXXV) (LXXXVI) (LXXXVII)

2. Oxidation

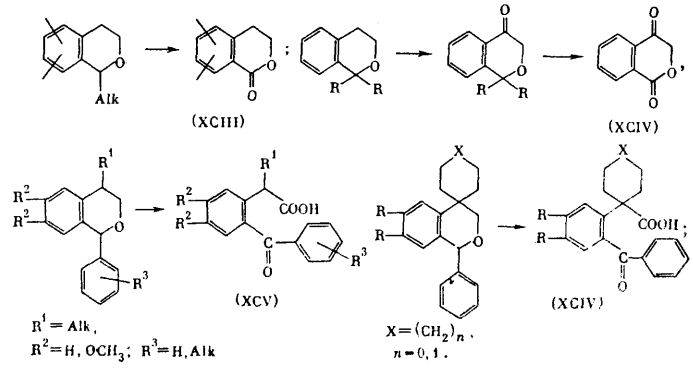
When isochroman is allowed to stand in air for several days at room temperature, the crystalline 1-isochromanyl peroxide (LXXXVIII) is formed, decomposing at 78 °C (2 mmHg).[52] It is possible to isolate the diastereoisomers of the peroxide (the *meso*-isomer and the racemate) from isochroman by allowing it to stand in the light for a month.[170] When isochroman and its 1-substituted derivative are oxidised by atmospheric oxygen at room temperature and under UV irradiation, the corresponding hydroperoxides (LXXXIX) are formed.[61,170] On treatment with dilute inorganic acids, the latter are readily converted into the symmetrical peroxides (XC). On interaction with benzaldehyde in the presence of potassium hydroxide, the hydroperoxide (LXXXIX, R = CH_3) affords 2-phenylspiro[1,3-dioxolan-4,1′-isochroman] (XCI).

The oxidation of isochroman by nitric acid leads to 1-isochromanone (3,4-dihydroisocoumarin).[66,171] It is of interest to note the formation of the tricyclic system 10,11-dihydro-5*H*-dibenzo[*a*,*d*]-cyclopentan-5-one (XCII) from the latter when it is involved in a Friedel–Crafts reaction in the presence of aluminium chloride in benzene:[171]

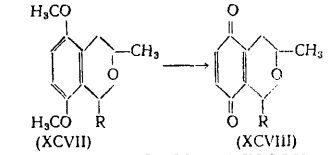
D1



Isochroman and its derivatives with the substituents in both the aromatic and dihydropyran rings have been oxidised by chromium trioxide, selenium dioxide, hydrogen peroxide, pyridinium chlorochromate, and sodium hypochlorite.[58,59,67,112–114,172–177] It has been shown that the oxidation takes place in the 1-position with formation of the dihydroisocoumarins (XCIII). On the other hand, if the 1-position is occupied by two alkyl substituents, then the oxidation takes place in the 4-position and more prolonged oxidation leads to the ketolactone (XCIV).[172] It is of interest to note the influence of allyl groups in the 1-position in isochroman on the oxidation process. In this case the reaction is accompanied by the opening of the dihydropyran ring and leads to (2-benzoylphenyl)acetic acid (XCV, $R^2 = R^3 = H$)[172] and its derivatives (XCV, $R^2 = OCH_3$, R^3 = Alk)[178] or (XCVI):[179]



The anodic oxidation of isochroman in the presence of *N*-hydroxyphthalimide is also directed to the 1-position.[180] The electrochemical oxidation of 6,7-dimethoxy-1-(3,4-dimethoxybenzyl)isochroman leads to a tetracyclic system containing in its structure the oxidised isochroman ring and to 1-(2-hydroxy-4,5-dimethoxybenzyl)-6,7-dimethoxyisochroman (oxidation of the aryl component of the side chain).[181] The oxidation of isochroman under UV irradiation in the presence of iron(III) chloride in the acetone–water mixture is notable. This entails the formation of 9% of 3,4-dihydroisocoumarin and 23% of β-(*o*-carboxyphenyl)ethanol.[182] The oxidative demethylation of 5,8-dimethoxyisochromans (XCVII) by silver oxide leads to the formation of the quinonoid structure (XCVIII):[138]



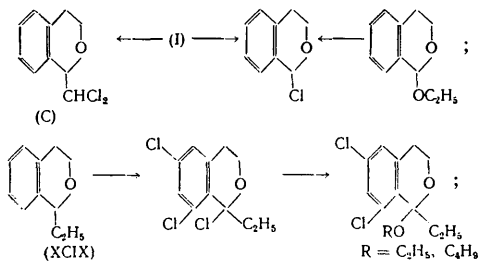
Thus the oxidation of isochroman and its derivatives is directed mainly to the 1-position. In addition, in certain cases the oxidation is accompanied, like the reduction, by the opening of the dihydropyran ring.

3. Halogenation

Both molecular halogens and bromosuccinimide are used for the halogenation of isochroman and its derivatives. It has been established that the halogenation proceeds preferentially in the 1-position, since this is most reactive. 1-Chloroisochroman was first obtained by chlorinating isochroman at −5 °C.[58] The same product has been synthesised in 60–80% yield by the reaction of 1-ethoxyisochroman with acetyl chloride.[60,61,183] The chlorination of 1-ethylisochroman (XCIX) at 0 °C is directed to the 1-, 6-, and 8-positions in the isochroman ring.[66,84] On treatment with an alkoxide, only the chlorine atom in the 1-position is substituted by the alkoxy-group.

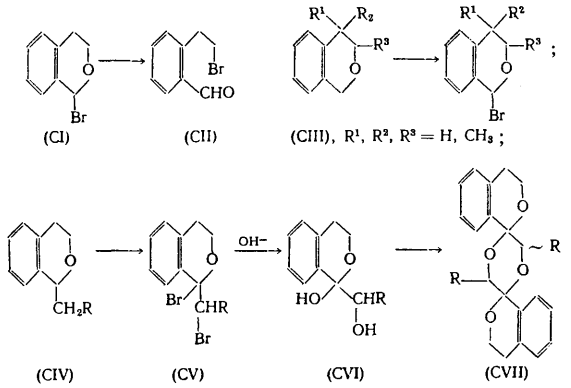
Isochroman is capable of being converted into 1-dichloromethylisochroman (C) on treatment with chloroform in an alkaline

medium in the presence of benzyltriethylammonium chloride by combining with dichlorocarbene:[87]

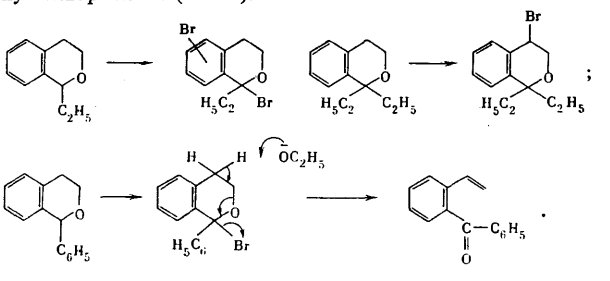


1-Bromoisochroman (CI) has been obtained by brominating isochroman in benzene or carbon tetrachloride under UV irradiation.[58,60,61,71,89] As a cyclic analogue of α-halogenoethers, this bromo-derivative rearranges to its structural isomer *o*-(β-bromoethyl)benzaldehyde (CII)[60,185] as a result of its high reactivity.[184] Isochromans substituted in the 3- or 4-position [compounds (CIII)] are also brominated in the 1-position under the same conditions.[70,71,90]

The bromination of 1-alkyl- and 1-benzyl-isochromans (CIV) does not stop at the stage involving the formation of the monobromo-derivative but leads to products of the substitution of the side chain, for example, the dibromo-derivatives (CV). The latter have been converted into the diols (CVI), which cyclise to the *cis,trans*-isomeric spirocyclic derivatives (CVII) in an acid medium:[61]

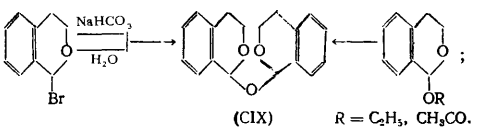


The bromination of isochroman and its 1-substituted-derivatives by *N*-bromosuccinimide has been investigated. It has been shown that, whereas isochroman is converted into 1-bromoisochroman,[58,84] its 1-ethyl derivative is brominated both in the 1-position and in the aromatic ring.[84] Furthermore, if the 1-position in isochroman is occupied by two alkyl groups, then bromination takes place in the 4-position.[84] The bromination of 1-phenylisochroman by *N*-bromosuccinimide in the presence of sodium ethoxide leads to 2-vinylbenzophenone (CVIII):[68]

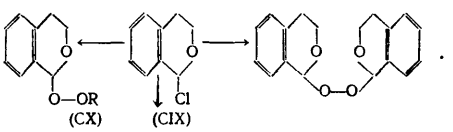


4. Certain substitution reactions of isochroman derivatives

Although 1-chloro- and 1-bromo-isochromans rearrange under certain conditions to structural isomers,[60] nevertheless, they are of special interest from the standpoint of their conversion into a wide variety of isochroman derivatives. Thus, when 1-bromoisochroman is treated with a solution of sodium bicarbonate or simply with water, di-1-isochromanyl ether (CIX) is obtained.[60] The latter is also formed from 1-ethoxy- or 1-acetoxy-isochroman in quantitative yield when they are allowed to stand in air:[40]

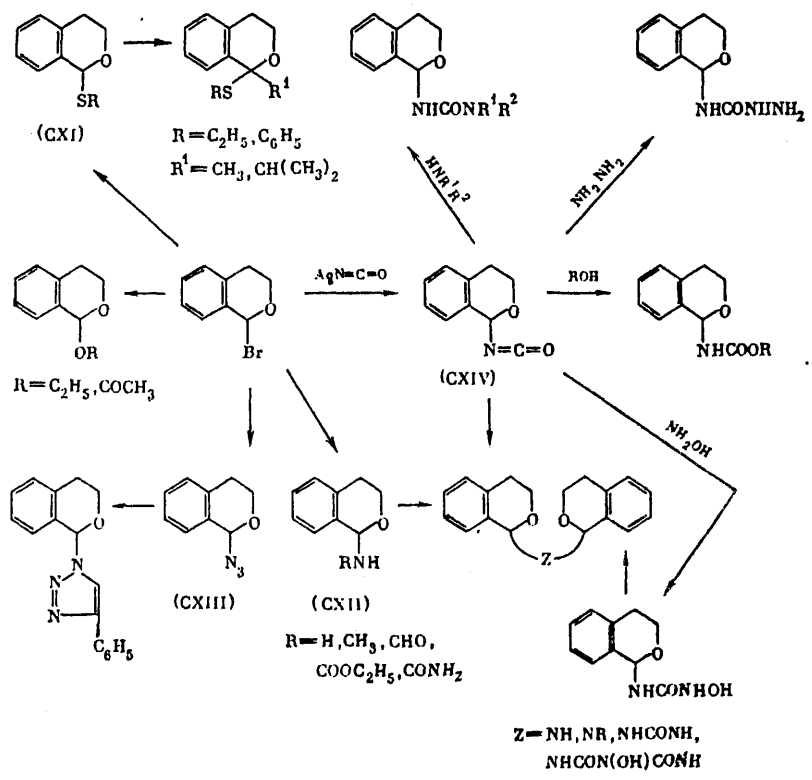


On treatment with water, 1-chloroisochroman behaves similarly to 1-bromoisochroman, forming di-1-isochromanyl ether.[58] 1-Chloroisochroman has been condensed with hydroperoxides with formation of the corresponding peroxides (CX) (yield 80–85%).[183] 1-Isochromanyl peroxide is obtained by treating 1-chloroisochroman with 30% hydrogen peroxide.[186] 1-Isochromanyl hydroperoxide is formed on treatment with 5.3% hydrogen peroxide:



The reactions of 1-halogenoisochromans with cyanide are described in Section II. We shall only note the formation of 1-cyano-4,4-R_2-substituted isochromans from the corresponding 1-bromo-4,4-R_2 derivatives and mercury(II) cyanide.[90] Compounds having different substituents in the 1-position have been synthesised in satisfactory yields by the reaction of a Grignard reagent and 1-halogenoisochroman as well as its 4,4-disubstituted derivatives.[58,60,61,66,165] Such 1-substituted isochroman derivatives are obtained in low yields on chloroalkylation of phenylalkanols. 1-Ethoxy- and 1-acetoxy-isochromans have been obtained by the reaction of 1-bromoisochroman with sodium ethoxide and potassium acetate.[58] 1-Acetoxyisochroman has been converted into 1-cyanoisochroman on treatment with trimethylsilyl cyanide in the presence of a Lewis acid.[187] 1-Ethoxyisochroman can be obtained also by treating 1-bromoisochroman with ethanol.[60] 1-Alkylthioisochromans (CXI) have also been obtained by an analogous procedure. They were then converted into 1,1-disubstituted isochromans.[188]

Scheme 4

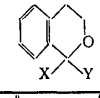


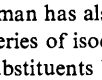
A series of nitrogen-containing compounds has been obtained from 1-bromoisochroman. Thus treatment of the latter with amines, aminoalcohols, amides, sodium azide, and silver isocyanate yielded the corresponding derivatives (CXII)–(XCIV).[189,190] These compounds were subjected to a series of transformations, which are illustrated in Scheme 4.

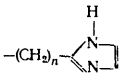
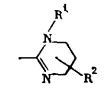
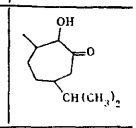
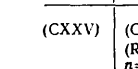
Isochroman derivatives containing substituents such as the alkoxy-, acyl-, acyloxy-, etc. groups in the 1-position are also capable of undergoing nucleophilic substitution reactions. The interaction of 1-ethoxyisochroman with sodium bisulphite, acetic anhydride,[60] aromatic and aliphatic alcohols,[191] nitrogen-containing compounds–amides, thioamides, sulphonamides, urea, thiourea,[192] and amines (aromatic, aliphatic, heterocyclic),[30,192] as well as benzoxazoline-2-thione has been achieved.[193] The final reaction products (CXVa–d), (CXVI), and (CXVIIa–c) are presented in Scheme 5.[33,191–193] It is notable that the reaction of 1-ethoxyisochroman with alcohols and amines takes place in different ways depending on their structure (type).

1-Ethoxyisochroman has also been used as the starting material for the synthesis of a series of isochroman derivatives (CXVIII) with functional group substituents by reaction with compounds having active methylene groups: diethyl malonate, α-tetralone, acetylacetone, malononitrile, and acetoacetic ester.[191,194] It is notable that the isochroman derivatives [CXVIII, XY = $(COOC_2H_5)_2$ or CHXY = 2-oxocyclohexyl] are converted into naphthalene or anthracene derivatives in the presence of alkali metal alkoxides.[194]

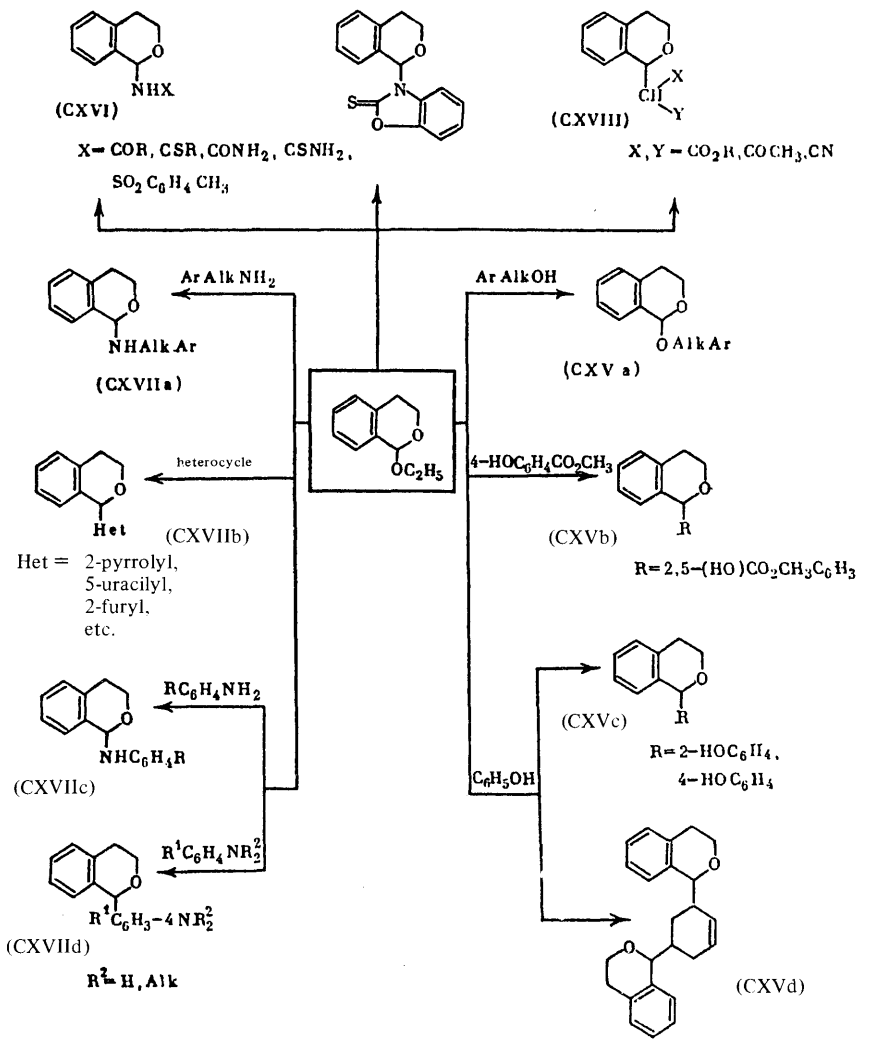
Table 1. Compounds (CXIX)–(CXXXI).



Compound	X	Y
(CXIX)	CH_2NHR (R=H, Alk)	H
(CXX)	$(CH_2)_nNHR$ (R=Ar, Alk, n=1,2)	H
(CXXI)	R^1CHNHR^2 (R^1=Alk, R^2=ArAlk)	H
(CXXII)	$CH_2NH(CH_2)_nNR_2$ (R=H, Alk, $C_6H_5CH_2$), 1-isochromanyl-methyl; NR_2=Het; n=2÷8)	H
(CXXIII)	 (Z=CH, N; R=H, Alk, allyl, Ar, ArAlk)	H
(CXXIV)	$(CH_2)_3NHR$ (R=H, CH_3)	C_6H_5
(CXXV)	$(CH_2)_nNR_2$ (R=C_6H_5; NR_2=Het; n=1,2)	CN

Compound	X	Y
(CXXVI)	$CH_2NHCOCH{=}CMe_2$	$(CH_2)_2N(C_2H_5)_2$
(CXXVII)	$COCH_3$	$(CH_2)_2N(C_2H_5)_2$
(CXXVIII)	R	
	H	
(CXXXI)	H	
X+Y		
(CXXIX)		(R=H, CH_3)
(CXXX)		

Scheme 5



IV. Biological activity of isochroman derivatives

Isochroman derivatives containing amino-groups in the dihydropyran ring have been most thoroughly investigated from the pharmacological point of view, since these compounds are in fact "rigidly fixed" analogues of arylalkylamines. They are all characterised by a broad spectrum of biological activity: antidepressant, diuretic, psychotropic, antiinflammatory, vasodilating, etc..

The study of the influence of 1-methylaminoisochromans (CXIX) [compounds (CXIX)–(CXXXI) are presented in Table 1] on the cardiovascular system[24] showed that compound (CXIX, R = H) exhibits a hypertensive activity. The corresponding *N*-methyl analogue (CXIX, R = CH_3) possesses considerable adrenoblocking properties, while 1-*N*-ethylamino- and 1-*N*-isopropylaminomethylisochromans (CXIX, R = C_2H_5 or iso-C_3H_7) possess a weak hypotensive activity. According to the results of some workers who have investigated the effect of phenylethylamines on adrenoreceptors, the replacement of the hydrogen at the nitrogen atom in 2-phenylethylamines by higher alkyl groups leads to a transition from adrenomimetic to adrenolytic properties. Although the analogous isochroman derivatives exhibit a weak activity, they give rise to the same pattern. On the other hand, the replacement of the hydrogen atom at the nitrogen atom of 1-aminomethylisochroman by arylalkyl groups as well as the introduction of an additional methylene group between the nitrogen atom and the isochroman ring lead to compounds (CXX), which possess some sympatholytic and adrenolytic activity and exert an effect on the central nervous system (CNS).[195] This activity persists also in 1-aminoalkylisochromans (CXXI) containing an alkyl substituent at the carbon atom linked to the isochroman ring.[196] Many compounds (CXXII) in which two 1-aminomethylisochroman fragments or a 1-aminomethylisochroman fragment and another basic residue are separated by different numbers of methylene groups have been synthesised.[197,198] It has been established that they all exhibit cholinolytic activity, while compounds (CXXII, n = 8) exert a pronounced blocking action on sympathetic nerve fibres and adrenoreceptors.[198] 1-Piperidino- and 1-piperazinoisochromans (CXXIII) have antihistamine properties.[199,200]

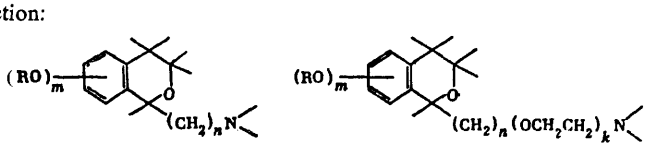
It is of interest to note that the simultaneous introduction of the phenyl and aminopropyl groups in the 1-position, as in compounds (CXXIV), leads to substances with a pronounced adrenomimetic effect, which can be used in psychotherapy, particularly in the treatment of endogenic depression.[200–202] The pharmacological properties also of other 1,1-disubstituted isochromans derivatives have been investigated. Thus 1-cyano-1-morpholinomethylisochroman [CXXV, $NR_2 = N(CH_2)_4O$, $n = 1$] exhibits a spasmolytic activity, while 1-cyano-1-(2-diethylaminoethyl)- and 1-cyano1-(2-piperidinoethyl)-isochromans [CXXV, $NR_2 = N(C_2H_5)_2$ or $N(CH_2)_5$, $n = 2$] exhibit an anti-cough effect whilst lacking spasmolytic activity.[94] In a dose of 2 mg kg^{-1}, the latter compound showed the same effect as the familiar drug Silomat in a dose of 5 mg kg^{-1}.[89] The diamino-derivative, namely 1-(β-diethylaminoethyl)-1-[*N*-(β-methylcrotonyl)amino-methyl]isochroman (CXXVI), is a muscle relaxant.[89]

1-Acetyl-1-(2-diethylaminoethyl)isochroman (CXXVII) exhibits a spasmolytic activity of the papaverine type and on an isolated intestine manifests an activity equal to that of papaverine in strength.[89]

The isochroman derivatives (CXXVIII), having nitrogen-containing cyclic fragments (imidazolylalkyl, tetrahydropyrimidyl) in the 1-position, are pesticides in large doses, while in small doses they exhibit a depressing effect on the CNS.[185] These compounds eliminate the convulsions induced by an electric shock more effectively than does hexobarbital and are corazole antagonists. They also show a local anti-inflammatory effect in the carrageenin oedema. Biological activity has also been discovered in a series of spiro-derivatives of isochroman. Spirooxazineisochromans (CXXIX) exhibit a psychotropic activity,[203] while 1-methyl-2,5-dioxopyrrolidine-3-spiro-1′-isochroman (CXXX) manifests a pronounced anti-inflammatory effect.[91]

In order to investigate the antitumour properties of 1-isochromanyl hydroperoxide, the latter was synthesised but did not exhibit a pronounced activity.[204] A compound of the isochroman series, namely 3-(1-isochromanyl)-6-isopropyltropolone (CXXXI),[205] showing an appreciable antitumour activity is known.[206] The introduction of substituents of different kinds (aryl, heteroaryl) in the 1-position in isochroman lowers appreciably the above activity.[207]

Further expansion of the research into biologically active isochroman derivatives has consisted in the simultaneous introduction of the amino-fragment in the 1-position and of hydroxy- or different alkoxy-groups in the aromatic ring of isochroman. Thus numerous 1-(aminoalkyl) derivatives of isochroman (CXXXII) have been patented.[141,208–217] Alkyl, arylalkyl, and heteroaryl groups are used as substituents at the nitrogen atom. In particular, many compounds containing substituted piperazine fragments have been described. The biological activity spectrum is extremely broad: anti-depressant, anticonvulsive, hypotensive, anti-inflammatory, analgesic, vasodilating, myorelaxing, anticoagulation, and other activities. Compounds (CXXXIII) are also of interest;[218,219] the presence of the poly(ethylene oxide) chain in them did not affect the selectivity of their action:



(CXXXII) (CXXXIII)

$m, n, k = 1–3$.

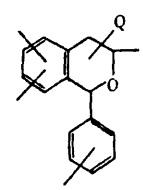
The biological properties of the isochroman derivatives (CXXXIV) and (CXXXV) containing a basic fragment in the 3- and 4-positions have also been investigated. Among them, 1-arylisochromans (CXXXIV) with the aminoalkylene chain in the 3-position, for example, can be used in the treatment of disturbances of the activity of the CNS: in particular, they exhibit anticonvulsant, anti-depressant, and appetite-depressant activities.[220,221] The most active compound—3-(*N*-methylaminomethyl)- and 3-(*NN*-dimethyl-aminomethyl)-1-phenylisochromans—exhibit a more pronounced activity than the familiar appetite depressant (d)-amphetamine. Furthermore, they are free from the disadvantages of the latter—the excitation of the CNS.[222] The introduction of a fluorine atom both in the aromatic ring of isochroman and in the phenyl group in the 1-position does not alter the activity. It is notable that the study of the pharmacodynamics of 3-aminomethyl-7-fluoro-1-phenylisochroman established that, in contrast to the anorexigenic preparations, this compound does not increase the pulmonary blood pressure.[223]

Isochroman derivatives (CXXXVI) containing simultaneously aryl and aminoalkyl substituents in the 3-position are known; in contrast to compounds (CXXXIV) and (CXXXV), they are effective drugs for the treatment of cardiovascular diseases (they exhibit hypotensive and diuretic activities).[224,225] Isochroman derivatives having the structure (CXXXVII) also possess hypotensive properties.[226] 1-Methyl- and 1-phenyl-isochromans with dialkylamino- or piperazinyl groups in the 4-position manifest antihistamine properties.[227] Piperidine-4-spiro-4′-isochromans (CXXXVIII) exhibit the same type of activity.[228] It is of interest that compounds (CXXXIX), which also contain the piperidine ring but the latter is linked to the isochroman ring by a C–C bond, manifest anti-allergic properties.[229,230]

N-Substituted piperidine-4-spiro-3′-isochromans (CXL) possess hypotensive and anti-depressant activities.[231]

Among semisynthetic cephalosporins, a substance with an isochromanyl residue exhibiting a bactericidal activity has been discovered.[232]

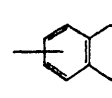
Among more complex structures (tri- and tetra-cyclic), dibenzopyran and morphine-like substances, possessing antipyretic, analgesic, and anti-inflammatory properties, are known.[233,234] Acids of the isochroman series also exhibit anti-inflammatory and antibacterial activities.[140,235]



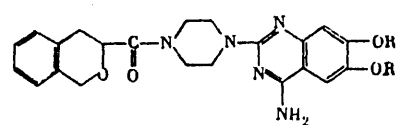
(CXXXIV), (CXXXV)

(CXXXIV): $Q = 3-$ or $4-(CH_2)_nNAlk_2$,

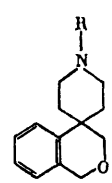
(CXXXV): $Q = 3-CHCH_2NR_2$ (CH_3)



(CXXXVI)

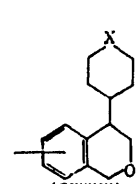


(CXXXVII), R = Alk



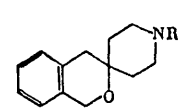
(CXXXVIII)

R = CH_3, $(CH_2)_nC_6H_5$; $n = 1,2$



(CXXXIX)

X = $CR^1R^2NR^1_2$; R^1, R^2 = H, Alk, ArAlk



(CXL)

R = H, $CH_2C_6H_5$, $COOC_2H_5$

Summarising, one should note that it is as yet too early to reach conclusions about the relation between the structure and activity of isochroman compounds, but the existence of a large number of substances with different biological activities suggests that deliberate search for preparations among individual groups of isochroman derivatives is desirable. The availability of the starting materials and the existence of methods of synthesis make it possible to use on a wide scale a series of isochroman derivatives as synthons for the preparation of biologically active substances.

References

1. French P. 2476085 (1981)
2. H G Floss *Antibiotics, 4 (Biosynthesis)*, 1981, p. 215
3. B Krone, A Zeeck, H G Floss *J. Org. Chem.*, 1982, **47** 4721
4. E Priers, R W Britton, N De Waal *Can. J. Chem.*, 1969, **47** 831
5. H H Warren, G Dougherty, E S Wallis *J. Am. Chem. Soc.*, 1949, **71** 3422
6. P S Steyn, C W Holzapfel *Tetrahedron*, 1967, **23** 4449
7. T Tokoroyama, S Maeda, T Nishikama, O Kubota *Tetrahedron*, 1969, **25** 1047
8. J Roberts, P Woollven *J. Chem. Soc. C.*, 1970, 278
9. M Yamazaki, Y Maebayashi, K Miyaki *Tetrahedron Lett.*, 1971, 2301
10. T Kubota, T Tokoroyama, T Kamitawa, V Satomura *Tetrahedron Lett.*, 1966, 5205
11. R F Curtis, C H Hassall, M Nazar *J. Chem. Soc. C*, 1968, 85
12. T Tokoroyama, T Kamikawa, T Kubota *Tetrahedron*, 1968, **24** 2345
13. R H Cox, O Hernandez, J W Dorner, et al. *J. Agric. Food Chem.*, 1979, **27** 999
14. Sh M Afzal, R Pike, N H Rama, et al. *J. Chem. Soc., Perkin Trans. 1*, 1978, 81
15. P Vleggaar, P S Steyn, D W Nagel *J. Chem. Soc., Perkin Trans. 1*, 1974, 45
16. US P. 4346039 (1982)
17. M Nukina, Sh Marumo *Tetrahedron Lett.*, 1977(30), 2603
18. P Boutibonnes, Y Auffray, C Malherbe, et al. *Mycopathologia*, 1984, **87**(1–2) 43
19. C G Crawley *J. Chem. Soc., Perkin Trans. 1*, 1981, 221
20. Y Nakada, Sh Ohno, M Yashimoto, Y Yura *Agric. Biol. Chem.*, 1978, **42** 1365
21. H Roensch *Symp. Pap. IUPAC Int. Symp. Chem. Nat. Prod. XI*, 1978, Vol. 2, p. 38
22. US P. 4256866; Chem. Abs., 1981, **94** 209514
23. N M Karayannis, S S Lee *Macromol. Chem.*, 1983, **184** 2275
24. A T Neyyarappally, J S Bindra, N Anand, R C Srimal *Indian J. Chem.*, 1971, **9** 89
25. W Wiegrebe, J Friecke, P L Budzikiewicz *Tetrahedron*, 1972, **28** 2849
26. W Wiegrebe, H Reinhart, J Friecke *Pharm. Acta Helv.*, 1973, **48**(6–7) 420
27. H M Stephan, G Langer, W Wiegrebe *Pharm. Acta Helv.*, 1976, **51**(6) 164
28. W Wiegrebe, S Prior *Chimia*, 1978, **32**(7) 256
29. W Wiegrebe, S Prior, K K Mayer *Arch. Pharm.*, 1982, **315** 262
30. S Prior, W Wiegrebe, G Sariyar *Arch. Pharm.*, 1982, **315** 273
31. R Ambros, S Prior, W Wiegrebe *Sci. Pharm.*, 1982, **51**(2) 179
32. S Prior, W Wiegrebe *Arch. Pharm., 1981,* **314** 577
33. M Yamato, T Ishikawa, T Kobayashi *Chem. Pharm. Bull.*, 1981, **29** 720
34. A S Rothenberg, G S Yayatilake, S F Hussain *Heterocycles*, 1976, **5** 41
35. V H Belgaonkar, R N Usgaonkar *Heterocycl. Chem.*, 1975, **15** 257
36. Japanese Appl. 8059171; *Chem. Abs.*, 1981, **94** 15758
37. W Meise, H Pfisterer *Arch. Pharm.*, 1977, **310** 501
38. W Meise, H Pfisterer *Arch. Pharm.*, 1977, **310** 495
39. L Laitem, L Christiaens, A Welter *Heterocycles*, 1976, **4** 1107
40. S R Ramadas, A P Chaudhuri, G K Prakash *Steroids*, 1976, **28**(2) 197
41. S R Ramadas, A P Chaudhuri *J. Chem. Soc., Chem. Comm.*, 1974, 521
42. Y Elliott, Y Nesley *J. Org. Chem.*, 1982, **47** 5398
43. N S Narasimhan, R S Mali, B K Kulkarni *Tetrahedron Lett.*, 1981, **22** 2797
44. S Yeganathan, D Kuila, M Srinivasan *Synthesis*, 1980, 469
45. S A Sisk, C R Hutchinson *J. Org. Chem.*, 1979, **44** 3500
46. F Kienzle, R E Minder *Helv. Chim. Acta*, 1980, **63** 1425
47. M Somei, T Shoda *Heterocycles*, 1982, **17** Spec. Issue, p. 417
48. T Kometani, E Yoshil *J. Chem. Soc., Perkin Trans. 1*, 1981, 1191
49. A V Bicherov, G N Dorofenko, E V Kuznetsov *Zh. Org. Khim.*, 1979, **15** 585
50. M Yamato *J. Synth. Org. Chem. (Japan)*, 1983, **41** 958
51. J Braun, F Zobel *Ber.*, 1923, **56B** 2142
52. S Siegel, S K Coburn *J. Am. Chem. Soc.*, 1951, **73** 5494
53. E L Anderson, F G Holliman *J. Chem. Soc.*, 1950, 1037
54. J L Warnell, R L Schriner *J. Am. Chem. Soc.*, 1957, **79** 3165
55. BRD P. 915811; *Chem. Abs.*, 1958, **52** 15593
56. German P. 614461; *Chem. Abs.*, 1935, **29** 5861
57. German P. 617646; *Chem. Abs.*, 1936, **30** 492
58. P Maitte *Ann. Chim. (Paris)*, 1954, **9** 431
59. J Colonge, P Boisde *Bull. Soc. Chim. Fr.*, 1956, **10** 1337
60. A Rieche, E Schmitz *Chem. Ber.*, 1956, **89** 1254
61. E Schmitz, A Rieche *Chem. Ber.*, 1956, **89** 2807
62. Japanese Appl. 8199467; *Chem. Abs.*, 1981, **95** 203757
63. J N Chatterjee *Chem. Ber.*, 1958, **91** 2636
64. J G Abramo, E C Chapin *J. Org. Chem.*, 1961, **26** 2671
65. A Rieche, E Schmitz *Chem. Ber.*, 1957, **90** 531
66. P Maitte *Colloq. int. CNRS*, 1955(64), 197; *Chem. Abs.*, 1961, **55** 10426
67. J Colonge, P Boisde *C. R. Acad. Sci.*, 1954, **239** 1047
68. J Thibault *Ann. Chim. (Paris)*, 1971, **6**(3–4) 263
69. C A R Baxter, G C Forward, D A Whitting *J. Chem. Soc. C.*, 1968, 1169
70. R P Singh, J N Srivastava *Indian J. Chem.*, 1982, **21B** 104
71. C Van der Stelt, P S Hofman, T N Nauta *Recl. Trav. Chim., Pays-Bas*, 1965, **84** 633
72. R L Vaulx, F N Jones, C R Hauser, *J. Org. Chem.*, 1964, **29** 1387
73. J Schnekenburger, R Kaufman *Arch. Pharm.*, 1970, **303** 760
74. E Von Angerer, W Wiegrebe *Arch. Pharm.*, 1979, **312** 385
75. T Fujisaka, M Nojima, S Kusabayashi *J. Org. Chem.*, 1985, **50** 275
76. S Siegel, S K Coburn, D R Levering *J. Am. Chem. Soc.*, 1951, **73** 3163
77. R K Huffman, E F Ullman *J. Am. Chem. Soc.*, 1967, **89** 5629
78. DDR P. 141159; *Chem. Abs.*, 1981, **94** 174884
79. DDR P. 141160; *Chem. Abs.*, 1981, **94** 192146

80. D G Talekar, A S Rao *Synthesis*, 1983, 595
81. L Shi, C K Narula, K T Mak, et al. *J. Org. Chem.*, 1983, **48** 3894
82. S L Mattes, S Farid *J. Am. Chem. Soc.*, 1982, **104** 1454
83. M E Garst, Y-F Cheung, W S Johnson *J. Am. Chem. Soc.*, 1979, **101** 4404
84. R C Larock, L W Harrison, M H Hsu *J. Org. Chem.*, 1984, **49** 3662
85. H Böhme, P Priesner, B Unterhalt *Arch. Pharm.*, 1966, **299**, 931
86. A G Samodurova, S O Vartanyan, E A Markaryan *Arm. Khim. Zh.*, 1979, **32** 397
87. H Böhme, P Sutoyo *Liebigs Ann. Chem.*, 1982, 1643
88. A L Mndzhoyan, V E Badalyan, A N Sadatierov, A G Samodurova *Arm. Khim. Zh.*, 1973, **26** 486
89. H Böhme, K lindenberg, R Priesner, B Unterhalt *Arch. Pharm.*, 1968, **301** 326
90. H Böhme, R Schweizer *Arch. Pharm.*, 1970, **303** 170
91. H Böhme, U Sitorus *Arch. Pharm.*, 1974, **307** 27
92. BRD P. 1 215 727; *Chem. Abs.*, 1966, **65** 15337
93. H Böhme, K Lindenberg *Arch. Pharm.*, 1968, **301 584**
94. H Böhme, F Ziegler *Arch. Pharm.*, 1974, **307** 287
95. H Böhme, U Sitorus *Arch. Pharm.*, 1974, **307** 24
96. H Böhme, F Ziegler *Synthesis*, 1973, 297
97. H Böhme, F Sitorus, F Ziegler *Arch. Pharm.*, 1974, **307** 218
98. H Böhme, K Lindenberg *Arch. Pharm.*, 1968, **301 544**
99. A L Mndzhoyan, V E Badalyan, A G Samodurova, et al., *Arm. Khim. Zh.*, 1973, **26** 591
100. G Kraiss, M Povarny, K Nador *Acta Chim. Acad. Sci. Hung.*, 1976, **88**(1) 93
101. J Knabe, K Schaller *Arch. Pharm.*, 1968, **301 457**
102. US P. 3 880 885; *Chem. Abs.*, 1975, **83** 58658
103. C Normant-Chefnay *Bull. Soc. Chim. Fr.*, 1971, 1362
104. C Normant-Chefnay, J Thibault, P Maitte *C.R. Acad. Sci.*, 1968, **267C** 547
105. J Thibault *Ann. Chim. (Paris)*, 1971, **6** 381
106. F Micheel, Z-H Schleifstein *Chem. Ber.*, 1972, **105** 650
107. V B Milevskaya, R V Belinskaya, L M Yagupol'skii *Zh. Org. Khim.*, 1973, **9** 2145
108. W Schneider, E Kaemmerer *Arch. Pharm.*, 1966, **299** 817
109. G Hazebroucq *Ann. Chim (Paris)*, 1966, **1** 221
110. US P. 2 701 254; *Chem. Abs.*, 1956, **50** 1088
111. A L Meyer, R B Turner *Tetrahedron*, 1971, **27** 2609
112. J N Srivastava, D N Chaudhury *J. Org. Chem.*, 1962, **27** 4337
113. D Mikhopadhyay, D N Chaudhury *J. Indian Chem. Soc.*, 1963, **40** 433
114. J N Srivastava, D N Chaudhury *J. Indian Chem. Soc.*, 1963, **40** 865
115. D Prasad, D N Chaudhury *J. Indian Chem. Soc.*, 1962, **39** 672
116. N K Bose, D N Chaudhury *J. Indian Chem. Soc.*, 1964, **41** 103
117. J N Chatterjee, B K Banerjee, H C Jha *Chem. Ber.*, 1965, **98** 3279
118. L Schieler, R D Sprenger *J. Am. Chem. Soc.*, 1951, **73** 4045
119. J N Chatterjee, C Bhakta, N D Sinhe *J. Indian Chem. Soc.*, 1975, **52** 158
120. J N Chatterjee, C Bhakta, S K Mukherjee *J. Indian Chem. Soc.*, 1981, **58** 888
121. J M McCall, R E Tenbrink, B V Kamdar, C Chidester *J. Heterocycl. Chem.*, 1979, **16** 363
122. M Palamareva, M Khaimova, B Kurtev *Chem. Ber.*, 1976, **109 274**
123. S M Afzal, W B Whalley *Pak. J. Sci. Rec.*, 1981, (Publ. 1984), **33**(1–4) 52
124. C A R Baxter, G C Forward, D A Whiting *J. Chem. Soc. C.*, 1968, 1162
125. C A R Baxter, G C Forward, D A Whiting *Tetrahedron Lett.*, 1967, 3997
126. M Yamato, T Ishikawa, T Nagamatsu, et al. *Chem. Pharm. Bull.*, 1980, **28** 723
127. P J Card *J. Org. Chem.*, 1982, **47** 2169
128. I R Trehan, R L Kaul, R K Sharma, J Singh *Indian J. Chem.*, 1982, **21B**(3) 197
129. S Farid *J. Chem. Soc. D.*, 1970, 303
130. R G Giles, I R Green, J A X Pestana *J. Chem. Soc., Perkin Trans. 1*, 1984, 2389
131. R C Larock, C L Liu, H H Lau, S Vareptath *Tetrahedron Lett.*, 1984, **25** 4459
132. G Bringman, J R Jansen *Liebigs. Ann. Chem.*, 1985, 2116
133. US P. 3 532 719.
134. Europ P. 61 267; *Chem. Abs.*, 1983, 71725
135. D Satoh, T Hashimoto, K Aoyama *Yakugaku Zasshi*, 1974, **94**, 774; *Chem. Abs.*, 1974, **81** 105333
136. D Satoh, T Hashimoto, K Aoyama *Yakugaku Zasshi*, 1975, **95** 1183
137. T A Dobson, L G Humber *J. Heterocycl. Chem.*, 1975, **12** 591
138. J I Retamal, V M Ruiz, R A Tapia, et al. *Synth. Commun.*, 1982, **12** 279
139. B P 1 049 538; *Chem. Abs.*, 1979, **91** 20326
140. US P. 4 021 451; *Chem. Abs.*, 1975, **87** 102303
141. A Miyake, K Itoh, N Tadu, Y Oka *Takeda Kenkyushoho*, 1982, **41**(1–2) 24; *Chem. Abs.*, 1982, **97** 215837
142. US P. 3 910 964.
143. US P. 3 978 090.
144. BRD P. 3 306 200; *Chem. Abs.*, 1985, **102** 6204
145. A Miyake, N Tada, Y Oka *Takeda Kenkyushoho*, 1982, **41**(1–2), 14; *Chem. Abs.*, 1982, **97** 215838
146. US P. 4 250 200; *Chem. Abs.*, 1981, **95** 60183
147. US P. 4 301 076.
148. US P. 4 308 412; *Chem. Abs.*, 1982, **96** 142708
149. US P. 4 315 951; *Chem. Abs.*, 1982, **97** 4915
150. French P. 1 369 595; *Chem. Abs.*, 1965, **62** 530
151. US P. 4 166 062.
152. US P. 4 191 665.
153. Japanese P. 77 105 174; *Chem. Abs.*, 1978, **88** 37614
154. Japanese Appl. 60-20390; *Byull. Izobret.*, 1985(23) 172
155. T Kometani, K Kigasawa, M Kiiragi, et al. *Heterocycles*, 1975, **3** 521
156. Japanese Appl. 60-11710; *Byull. Izobret.*, 1985(19), 165
157. Japanese Appl. 60-20391; *Byull. Izobret.*, 1985(23), 172
158. S Yasuda, A Sakakibara *Mokazai Yakkoishi*, 1976, **22** 606
159. S Yasuda, A Sakakibara *Mokazai Yakkaishi*, 1975, **21** 639
160. A Closse, D Hauser *Helv. Chim. Acta*, 1973, **56** 2694
161. US P. 6 546 208; *Chem. Abs.*, 1986, **104**, 174385
162. US P. 4 549 983; *Chem. Abs.*, 1986, **104** 192939
163. US P. 4 512 918; *Chem. Abs.*, 1985, **103** 42415
164. US P. 4 524 021; *Chem. Abs.*, 1985, **103** 128817
165. S F Birch, R A Dean, E V Whitehead *J. Org. Chem.*, 1954, **19** 1449
166. K Yoshida, P A Grieco *J. Org. Chem.*, 1984, **49** 5257
167. S A Godleski, E B Willhauer *J. Org. Chem.*, 1984, **49**, 2246
168. B Fraser-Reid, M A Rahman, D R Kelly, R M Srivastava *J. Org. Chem.*, 1984, **49** 1835

169. C Van der Stelt, P S Hofman, C Van der Vlies, F Bickelhaupt *Recl. Trav. Chim. Pays-Bas,* 1967, **86** 1316
170. A Rieche, E Schmitz *Chem. Ber.*, 1957, **90** 1082
171. Hungarian P. 28473; *Chem. Abs.*, 1984, **101** 38225
172. J Thibault, P Maitte *Bull. Soc. Chim. Fr, 1969, 915*
173. G Balavoina, C Eskenazi, F Meunier *J. Mol. Catal.*, 1985, **30**(1–2) 125
174. F Bonadies, R Di Fabio, C Bonini *J. Org. Chem.*, 1984, **49** 1647
175. S M Afzal, M Ashraf *Pak. J. Sci.*, 1981 (Publ. 1984), **33**(1–4) 80
176. N S Narasimhan, C P Bapat, *J. Chem. Soc., Perkin Trans. 1*, 1982, 2099
177. M Yamato, K Sato, A Taniguchi, et al. *Chem. Pharm. Bull.*, 1978, **26** 1990
178. F Gatta, G Settimj *Gazz. Chim. Ital.*, 1984, **114**, 103
179. F Gatta, G Settimj *J. Heterocycl. Chem.*, 1983, **20** 1267
180. M Masui, S Hara, T Ueshima, et al. *Chem. Pharm. Bull.*, 1983, **31** 4209
181. U Palmquist, A Nilson, T Petterson et al. *J. Org. Chem.*, 1979, **44** 196
182. M Barbier *Helv. Chim. Acta*, 1984, **67** 866
183. A Rieche, E Schmitz *Chem. Ber.*, 1957, **90** 1225
184. Yu V Pokonova *Galoidefiry* (Halogenoethers), Izd. Khimiya, Leningrad, 1966
185. US P. 3438995; *Chem. Abs.*, 1969, **71** 13126
186. A Rieche, E Schmitz *Chem. Ber.*, 1957, **90** 1094
187. M T Reetz, J Chatziiosifidis, H Kuenzer, H Mueller-Starke *Tetrahedron,* 1983, **39** 961
188. H Böhme, N Sutoyo *Arch. Pharm.*, 1983, **316** 505
189. H Böhme, F Ziegler *Liebigs Ann. Chem.*, 1974, 734
190. H Böhme, F Ziegler *Liebigs Ann. Chem.*, 1974, 1474
191. M Yamato, T Ishikawa, T Kobayashi *Chem. Pharm. Bull.*, 1980, **28** 2967
192. M Yamato, T Ishikawa, S Yamada *Chem. Pharm. Bull.*, 1982, **30** 843
193. M Yamato, Y Takeuchi, K Hashigaki, et al. *Chem. Pharm. Bull.*, 1983, **31** 1733
194. T Ishikawa, M Yamato *Chem. Pharm. Bull.*, 1982, **30** 1594
195. A G Samodurova, A S Tsatinyan, Zh S Zastukhova, E A Markaryan *Arm. Khim. Zh.*, 1984, **37** 493
196. A G Samodurova, S O Vartanyan, M R Barkhudaryan, et al., *Arm. Khim. Zh.*, 1979, **32** 481
197. V E Badalyan, A G Samodurova, D A Gerasimyan, et al., *Arm. Khim. Zh.*, 1977, **30** 762
198. A G Samodurova, A S Tsatinyan, D A Gerasimyan, et al., 1982, **35** 391
199. Japanese Appl. 57-159713; *Chem. Abs.*, 1983, **98**, 65460
200. B. P. 1102762.
201. Dutch Appl. 6603603; *Chem. Abs.*, 1967, **66** 37770
202. Dutch Appl., 6603606; *Chem. Abs.*, 1967, **66** 65392
203. H Böhme, K Lindenberg *Arch. Pharm.*, 1970, **303** 229
204. A Rieche, M Schulz *Z. Naturforsch.*, 1963, **18b**, 583; *Chem. Abs.*, 1964, **60** 2205
205. Japanese Appl. 59-134754; *Chem. Abs.*, 1984, **101** 210754
206. Japanese Appl. 59-134720; *Chem. Abs.*, 1985, **102** 17648
207. M Yamato, K Hashigaki, S Ishikawa, et al. *J. Med. Chem.*, 1985, **28** 1026
208. B. P. 1552004.
209. Japanese P. 76-125287; *Chem. Abs.*, 1977, **87** 23045
210. BRD P. 2624693; *Chem. Abs.*, 1977, **87** 152020
211. Japanese P. 77-83846; *Chem. Abs.*, 1978, **88** 37613
212. **Japanese P. 59-19549; *Byull. Izobret.*, 1985(1), 203**
213. US P. 4066648.
214. J M McCall, R B McCall, R E TenBrink, et al. *J. Med. Chem.*, 1982, **25** 75
215. US P. 4247553; *Chem. Abs.*, 1981, **95** 42940
216. BRD P. 2846043; *Chem. Abs.*, 1979, **91** 74447
217. A Kumar, J M Khana, P C Jain, N Anand *Indian J. Chem.*, 1978, **16B** 793
218. US P. 4206123.
219. US P. 4179510; *Chem. Abs.*, 1980, **92** 146636
220. US P. 3840561.
221. US P. 3840562.
222. US P. 3851062.
223. K U Seiler, O Wasserman, H Wensky *Clin. Exp. Pharmacol. Physiol.*, 1976, **3**(4) 323
224. B.P. 1374337.
225. French P. 2178718; *Chem. Abs.*, 1974, **80** 95735
226. BRD P. 3015676; *Chem. Abs.*, 1981, **94** 139832
227. S Ram, A K Saxena, P C Jain, G K Patnacik *Indian J. Chem.*, 1984, **23B** 1261
228. M Yamato, K Hashigaki, M Ikeda, et al. *J. Med. Chem.*, 1981, **24** 194
229. Japanese P. 60-97975; *Chem. Abs.*, 1985, **103** 123369
230. M Yamato, K Hashigaki, K Hiromatsu, K Tasaka *Chem. Pharm. Bull.*, 1983, **31** 521
231. US P. 3686186; *Chem. Abs.*, 1972, **77** 164534
232. G Alexandrscu, M Ungureanu, Z Cojocaru, V Zvoristeanu *Rev. Med. Chir.*, 1984, **88** 715
233. Japanese P. 76-138681; *Chem. Abs.*, 1977, **87** 39282
234. Japanese Appl. 52-105936; Ref. *Zh. Khim.*, 1980, 70136
235. Japanese P. 76-138680; *Chem. Abs.*, 1977, **87** 23046

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Thermal decomposition and photodecomposition of biscyclopentadienyl complexes of titanium, vanadium, and their analogues

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ABSTRACT. Data on the reactions involving the thermal decomposition and photodecomposition of the biscyclopentadienyl compounds Cp_2MR_n (M = Ti, Zr, Hf, V, or Nb) are surveyed. The pathways leading to the formation of RH as well as the rearrangement of the biscyclopentadienyl structure in the thermal and photochemical reactions are discussed. Processes involving hydrogen exchange and the exchange of the cyclopentadienyl rings are examined.

The bibliography includes 92 references.

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I. Introduction

Studies on the thermal decomposition of organometallic compounds (OMC) were published almost simultaneously with studies on their synthesis, but initially this was associated with the investigation of the theoretical aspects of the stability of the metal–carbon bond. Subsequently such investigations became of practical interest in relation to questions of analysis and, mainly, the preparation of metallic and inorganic coatings by the thermal decomposition of the corresponding OMC. Monographs[1,2] have been devoted to general problems of the study of the mechanism of the thermal decomposition of OMC and their practical use for the preparation of coatings.

Compounds of two types are most numerous among OMC of the titanium and vanadium subgroups: covalent, i.e. σ-alkyl or σ-aryl compounds, and sandwich-covalent compounds, i.e. π-cyclopentadienyl-σ-alkyl(aryl) complexes. The principal features of the thermal decomposition of the covalent derivatives have been examined in another review.[3]

The first studies on the thermal and photolytic decomposition of the sandwich-covalent compounds Cp_2TiR_2 (R = CH_3 or C_6H_5) were published at the end of the 1960's. These investigations established that the decomposition of Cp_2TiR_2 in solutions entails the homolytic cleavage of two Ti–R σ-bonds accompanied by the intermediate formation of paramagnetic trivalent titanium compounds, which has been demonstrated by EPR. When the reaction is carried out in CCl_4, the radicals formed react with metallic mercury. The interesting fact that the decomposition of Cp_2TiR_2 initiated the radical polymerisation of methacrylate, styrene, and vinyl chloride has been noted in addition. These studies have been surveyed.[4]

Various aspects of the thermal decomposition of the complexes Cp_2MR_n have been investigated in recent years. As the chemistry of the so called 'titanocene' developed, processes involving the cyclopentadienyl ligands, leading to a rearrangement of the initial biscyclopentadienyl structure of the compound, were examined. Such a rearrangement, inducing an increase in the coordinative unsaturation of the complex, leads to new applications of these compounds in processes involving the activation of the C–H bonds of hydrocarbons and the fixation of mercury or nitrogen, and also in organic synthesis.

Simultaneously with the investigation of the thermal decomposition of titanium subgroup compounds, studies were performed on the thermal decomposition of sandwich-covalent compounds of trivalent vanadium: Cp_2VR (R = CH_3 or C_6H_5). These studies demonstrated a sharp difference between the mechanisms of the decomposition of the reactions of the titanium and vanadium derivatives.

The first attempts at the synthesis of tetravalent vanadium compounds Cp_2VR_2 were unsuccessful, which helped to strengthen the concept that these derivatives are highly labile. However, in 1966 the compounds Cp_2VR_2 (R = CH_3, C_2H_5, or $C_6H_5CH_2$) were obtained and somewhat later their decomposition was also studied. The results made it possible to compare the decomposition reactions of titanium and vanadium compounds having the general formula Cp_2MR_2.

This review surveys the results of the thermal and photolytic decomposition of the sandwich-covalent compounds of titanium, vanadium, and their analogues having the general formula Cp_2MR_n as a function of the nature of the σ-substituents and the transition metals.

II. Thermal decomposition of titanium subgroup compounds

1. Thermal stability and decomposition products

The thermal stability of the majority of the compounds Cp_2MR_2 (M = Ti, Zr, or Hf) has been characterised by differential thermal analysis (DTA).[5–10] It has been established on the basis of DTA data that the compounds Cp_2TiR_2 (R = CH_3 or Ar) decompose exothermically in the temperature range from 80° to 160 °C. Among the compounds indicated, the methyl derivative, which decomposes appreciably even at room temperature, has the lowest thermal stability. The differences between the thermal stabilities of the aryl derivatives are insignificant. However, the increased stability of compounds containing methyl groups in the meta-position in the benzene ring compared with $Cp_2Ti(C_6H_5)_2$ is notable. This is probably caused by the steric effects of such ligands, which proved significant in the formation of the dehydrobenzene complex under the decomposition conditions.[6,7]

A kinetic study of the thermal decomposition of Cp_2TiR_2 [R = C_6H_5, $C_6H_5CH_2$, *m*-$CH_3C_6H_4$, *p*-$CH_3C_6H_4$, or 3,4-$(CH_3)_2C_6H_3$] showed that the decomposition process is described by a first order equation. The calculated activation energy for the decomposition reaction is in the range 16–30 kcal mol^{-1} and decreases with decrease in the decomposition temperature of the compound Cp_2TiR_2. Depending on R, the decomposition temperature decreases in the following sequence:[8]

$$3,4\text{-}(CH_3)_2C_6H_3 > m\text{-}CH_3C_6H_4 > p\text{-}CH_3C_6H_4 > C_6H_5 > CH_2C_6H_5.$$

In the series of isotypical compounds Cp_2MR_2 (M = Ti, Zr, or Hf), the thermal stability rises from titanium to hafnium. Among all the compounds considered, $Cp_2Hf(CH_3)_2$ is the most stable (it decomposes above 250 °C).[9,10]

An increase in the stability of the biscyclopentadienyl compound on substitution of the hydrogen atoms by deuterium in the σ-substituents at the metal atom has been noted.[7,10] A similar substitution of hydrogen atoms by deuterium in the cyclopentadienyl rings does not increase significantly the thermal stability of the compounds. This fact shows that the rate-limiting stage of the decomposition process involves the rupture of the M–R bond or the abstraction of a hydrogen (deuterium) atom from the σ-linked group.

It has also been shown that the stability of the sandwich-covalent compound increases as the hydrogen atoms in the cyclopentadienyl rings are replaced by methyl groups.[11]

When the biscyclopentadienyl derivatives Cp_2MR_2 (M = Ti, Zr, or Hf; R = alkyl or aryl) are heated *in vacuo* or in hydrocarbon solvents at the decomposition temperatures, the M–R σ-bond is cleaved with liberation of 1.4–1.9 mol of RH (Table 1).[6,7,9,10] The dimerisation products are almost absent for all the compounds. The decomposition process can be formally represented by the scheme

$$(C_5H_5)_2MR_2 \rightarrow C_{10}H_8M + 2RH.$$

The decomposition of Cp_2MR_2 results in the formation of a residue, which has the approximate empirical formula $C_{10}H_8M$ according to analytical data. The IR spectra of this residue and its alcoholysis indicate the presence in it of η^5-Cp ligands.[6,7,9] The metal-containing residues formed on decomposition of Cp_2MR_2 (M = Ti, Zr, or Hf) react differently with hydrogen chloride. Thus Cp_2TiCl_2 is not formed when the titanium-containing residue is treated with HCl, treatment of the zirconium-containing residue with HCl affords a small amount of Cp_2ZrCl_2, while treatment of the hafnium-containing residue with HCl produces a yield of Cp_2HfCl_2 of 0.7 mol per mole of the initial compound. The different yields of the metallocene dichlorides in these reactions indicate differences between the compositions of the metal-contianing thermal decomposition products formed.[10]

Table 1. Thermal decomposition of the compounds Cp_2MR_2.

Compound	Decomposition conditions	Yield of RH after decomposition of Cp_2MR_2, mol mol^{-1}	Yield of products resulting from treatment of solid residue from decomposition of Cp_2MR_2 with HCl, mol mol^{-1}		Refs.
			RH	Cp_2MCl_2	
$Cp_2Ti(CH_3)_2$	vacuum, 100 °C, 15 min	1.65	0.10	—	[6]
$Cp_2Ti(C_6H_5)_2$	vacuum, 120 °C, 60 min	1.84	0.04	—	[7]
$Cp_2Ti(C_6H_5)_2$	toluene, 110 °C, 5 h	1.90	0.07	—	[7]
$Cp_2Ti(m\text{-}CH_3C_6H_4)_2$	vacuum, 134 °C, 60 min	1.88	—	—	[7]
$Cp_2Ti(p\text{-}CH_3C_6H_4)_2$	vacuum, 125 °C, 60 min	1.98	—	—	[7]
$Cp_2Ti[3,4\text{-}(CH_3)_2C_6H_3]_2$	vacuum, 136 °C, 60 min	1.92	—	—	[7]
$Cp_2Ti[3,4\text{-}(CH_3)_2C_6H_3]_2$	toluene, 110 °C, 5 h	1.84	0.02	—	[7]
$Cp_2Ti(CH_2C_6H_5)_2$	vacuum, 120 °C, 60 min	1.64	—	—	[6]
$Cp_2Zr(CH_3)_2$	vacuum, 220 °C, 30 min	1.83	0.10	0.17	[9]
$Cp_2Zr(C_6H_5)_2$	vacuum, 160 °C, 60 min	1.61	0.06	0.09	[9]
Cp_2ZrH_2	vacuum, 230 °C, 60 min	1.55	—	not determined	[9]
$Cp_2Hf(CH_3)_2$	vacum, 290 °C, 15 min	1.37	0.14	0.67	[10]
$Cp_2Hf(C_6H_5)_2$	vacuum, 200 °C, 3 h	1.30	0.32	0.59	[10]
$Cp_2Hf(C_6H_5)_2$	toluene, 180 °C, 3 h	1.33	0.10	0.70	[10]

2. Pathways leading to formation of RH

One of the important questions arising in the study of the thermal decomposition of Cp_2MR_2 is that of the source of hydrogen atoms for the formation of RH. The cyclopentadienyl rings, the σ-linked group, or the solvent can serve as sources of this kind. In order to answer this question, studies have been made using deuterium-labelled compounds. Deuterium was introduced either into the Cp rings or into the R groups, or deuteriated solvents were used.

Table 2. Thermal decomposition of deuteriated methyl derivatives of titanium subgroup metals *in vacuo*.

Compound	Decomposition conditions		Isotopic composition of methane, %					Refs.
	T, °C	*t*, min	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4	
$Cp_2Ti(CH_3)_2\text{-}d_{10}$	90	30	54.0	41.0	4.1	0.9	—	[6]
$Cp_2Zr(CH_3)_2\text{-}d_{10}$	230	15	17.2	56.3	15.7	7.8	3.0	[9]
$Cp_2Hf(CH_3)_2\text{-}d_{10}$	290	30	48.7	33.4	14.2	2.9	0.8	[10]
$Cp_2Hf(CD_3)_2 + Cp_2Hf(CD_3)_2\text{-}d_{10}$ (1:1)	290	30	33.0	56.8	10.2	—	—	[10]

The thermal decomposition of $Cp_2M(CH_3)_2\text{-}d_{10}$ without a solvent involves the liberation of mainly CH_4, CH_3D, and CH_2D_2 (Table 2). The decomposition of the phenyl derivatives $Cp_2M(C_6H_5)_2\text{-}d_{10}$ under the same conditions affords C_6H_6, C_6H_5D, and $C_6H_4D_2$ (Table 3).

These data demonstrate unambiguously that in the decomposition of the titanium subgroup compounds there are two competing pathways leading to the formation of RH—both with participation of the hydrogen of the Cp rings and with participation of the hydrogen of the neighbouring group R.

Table 3. Thermal decomposition of deuteriated phenyl derivatives of titanium subgroup metals *in vacuo*.

Compound	Decomposition conditions		Isotopic composition of benzene, %							Refs.
	T, °C	t, min	C_6H_6	C_6H_5D	$C_6H_4D_2$	$C_6H_3D_3$	$C_6H_2D_4$	C_6HD_5	C_6D_6	
$Cp_2Ti(C_6H_5)_2$-d_{10}	140	60	37.7	32.1	30.2	—	—	—	—	[6]
$Cp_2Ti(C_6D_5)_2$	137	60	—	—	—	—	32.4	35.6	32.0	[7]
$Cp_2Zr(C_6H_5)_2$-d_{10}	160	30	65.7	12.7	11.0	6.0	3.2	1.0	0.4	[9]
$Cp_2Hf(C_6H_5)_2$-d_{10}	200	30	85.0	15.0	—	—	—	—	—	[10]

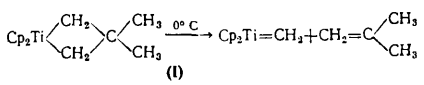
When hydrogen atoms are abstracted from the group R by an intramolecular pathway, intermediate complexes containing dehydrogenated groups R coordinated to the metal are formed:

$$Cp_2MR_2 \rightarrow RH + Cp_2M(R_{-H}). \quad (1)$$

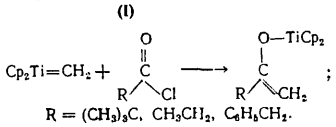
These complexes can decompose in their turn with liberation of RH as a result of the abstraction of hydrogen from the Cp or C_5H_4 groups via the reactions

$$Cp_2M(R_{-H}) \begin{cases} \rightarrow Cp(C_5H_3)M + RH \\ \rightarrow (C_5H_4)_2M + RH. \end{cases} \quad (2)$$

α-Elimination via reaction (1) from the methyl derivatives leads to the formation of carbene complexes of the type $Cp_2M=CH_2$ (I). The structural parameters of the complex (I) and the related carbene complexes have been calculated theoretically.[12] The Tebbe reagent $Cp_2Ti=CH_2AlCl(CH_3)_2$ is an example of compounds in which the methylene fragment has been stabilised by coordination to the metal. This complex participates in metathetical processes and is used to synthesise titanacyclobutanes[13–16] and other metallacycles.[17] The methylene complex (I), which is formed on decomposition of titanacyclobutanes, produces two stable titanium enolates in the presence of acid chlorides:[18,19]

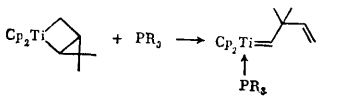


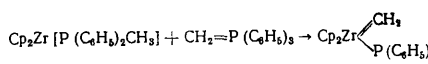
(I)



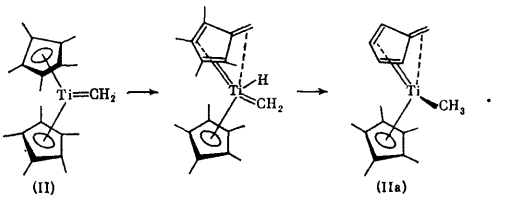
R = $(CH_3)_3C$, CH_3CH_2, $C_6H_5CH_2$.

The carbene complexes of titanocene and zirconocene can be stabilised by phosphines:[20,21]



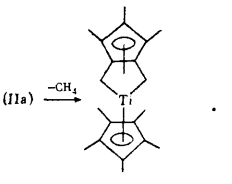


The thermal decomposition of the pentamethylcyclopentadienyl derivative $Cp^*_2Ti(CH_3)_2$ [$Cp^* = C_5(CH_3)_5$] involves the formation of the methylene complex $Cp^*_2Ti=CH_2$ (II) similar to compound (I). The methylene complex (II) is stabilised by the transfer of a hydrogen atom from a ring methyl group to the metal and then to the methylene group, which results in the formation of the complex (IIa):[22]

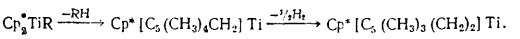


(II) (IIa)

Further heating of the complex (IIa) leads to the abstraction of a second methyl group from the metal atom, a methyl group of the cyclopentadienyl ring serving as a hydrogen donor in this process:[23]

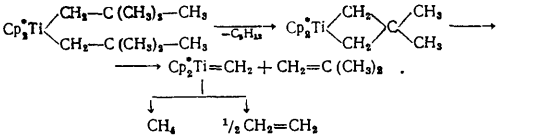


The thermal decomposition of Cp^*_2 leads to the same results:[23]



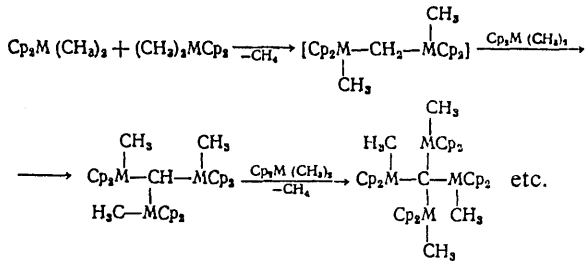
The synthesis of the ethylene complex $Cp^*_2Ti(CH_2=CH_2)$, which readily reacts with methylenecyclopropane forming the titanocyclopentane ring, has been described.[24]

γ-Elimination resulting in the formation of a metallacycle takes place in the thermal decomposition of $Cp^*_2Ti[CH_2C(CH_3)_3]_2$ in addition to the α-elimination, which leads to the liberation of neopentane and the formation of the carbene complex $Cp^*_2Ti=CH\text{–}C(CH_3)_3$ (main process). The cleavage of the bond in the metallacycle affords the carbene complex (II) and isobutene. The complex (II) generates methane as a result of the abstraction by the carbene of a hydrogen atom from the cyclopentadienyl rings or from the solvent. Ethylene is evolved on dimerisation of two carbene molecules. The unsubstituted norcarane has been detected among the decomposition products of $Cp^*_2Ti[CH_2C(CH_3)_3]_2$ in cyclohexane, which confirms the existence of compound (II):[25]



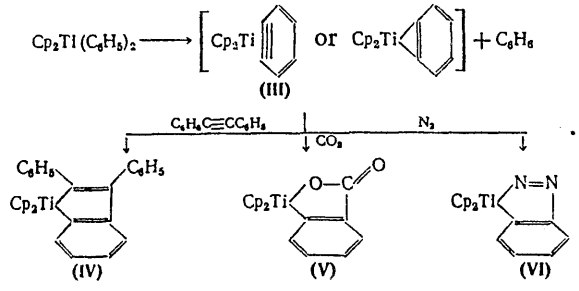
A similar γ-elimination process with formation of metallacycles takes place in the decomposition of the thorium complex $Cp^*_2Th.[CH_2Si(CH_3)_3]_2$.[26]

It has been suggested that the abstraction of hydrogen from the σ-linked ligand in the methyl derivatives $Cp_2M(CH_3)_2$ (M = Ti, Zr, or Hf) takes place also intermolecularly:

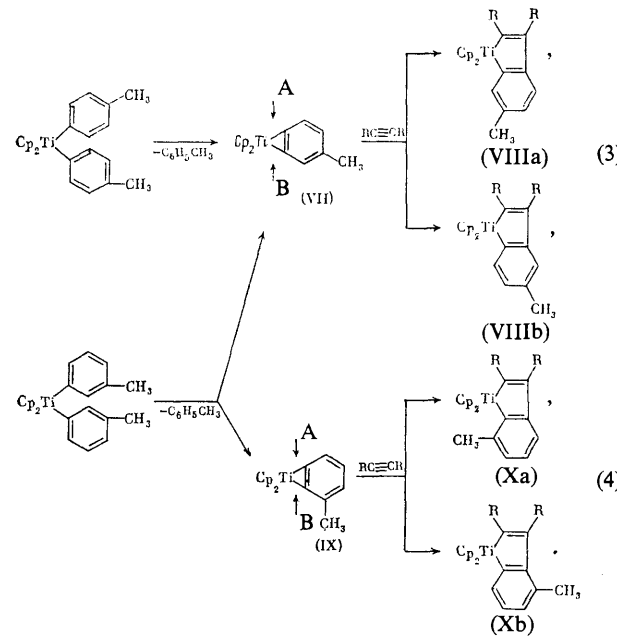


This pathway leading to the formation of RH has been confirmed by the hydrolysis of the decomposition products of $Cp_2M(CH_3)_2$ by deuteriated water. The evolution of CH_2D_2, CHD_3, and CD_4 indicates the presence of the [M–CH_2–M], [M–$\underset{\displaystyle M}{\overset{|}{C}}$H–M], and [C(M)]$_4$ groups in the decomposition products.[27]

The decomposition of the phenyl derivatives $Cp_2M(C_6H_5)_2$ via reaction (1) leads to the formation of benzene (as a result of the abstraction of the *ortho*-hydrogen atom from the neighbouring phenyl group) and of the intermediate complex (III). This decomposition mechanism has been confirmed in relation to the decomposition of $Cp_2Ti(C_6H_5)_2$ in the presence of tolane, CO_2 (80–90 °C), and N_2 (80–130 °C, 100 atm). In all three cases, the decomposition of $Cp_2Ti(C_6H_5)_2$ affords the intermediate complex (III), which then reacts with the above molecules, giving rise to the stable complexes (IV) and (V) and the unstable complex (VI) respectively:[28,29]



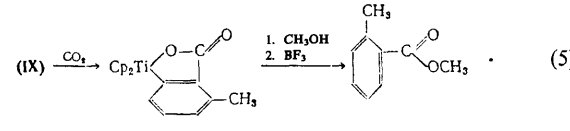
The thermal decomposition of the aryl derivatives of titanocene leads to the formation of similar intermediate complexes of titanium with substituted benzene rings, whose reactivity is determined by steric factors. The thermolysis of $Cp_2Ti(p\text{-}CH_3C_6H_4)_2$ [reaction (3)] proceeds via the formation of the intermediate complex (VII), which can react with the acetylenes RC≡CR (R = CH_3, CF_3, or C_6H_5), from the A or B side, producing the benzotitanoles (VIIIa) and (VIIIb) in approximately equal amounts:[30]



(3)

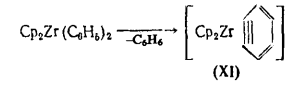
(4)

In the thermal decomposition of $Cp_2Ti(m\text{-}CH_3C_6H_4)_2$ [reaction (4)] there is in principle a possibility of the formation of the intermediate complexes (VII) and (IX). There is no doubt that the steric influence of the methyl group in the *meta*-position in the benzene ring makes the formation of the complex (IX) less preferred than that of the complex (VII). If the decomposition of $Cp_2Ti(m\text{-}CH_3C_6H_4)_2$ were accompanied by the formation of the intermediate (IX), then attack by the acetylene would be possible only from the A side, which would lead to the complex (Xa) but not (Xb).[30] However, this reaction pathway has been completely disproved[31] because, after carboxylation and alcoholysis, the orthoesters, which should have been formed via reaction (5), are absent from the products, and only the *para*- and *meta*-derivatives of benzoic acid esters are present in proportions of 1 : 3:



(5)

It has been shown[32–36] that, when $Cp_2Zr(C_6H_5)_2$ or its derivatives are heated (70–90 °C), the intermediate complex (XI) is formed:

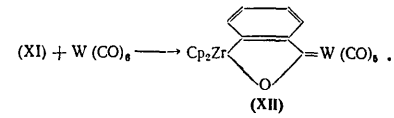


Similar complexes also serve as intermediates in the isomerisation reactions of the compound Cp_2ZrAr_2 and in the reaction with the solvent–benzene.[32]

The complex (XI) reacts with alkenes, affording high yields of zirconaindans.[33,34] The interaction of the complex (XI) with *cis*- and *trans*-stilbenes is stereospecific and gives rise to the formation of *cis*- and *trans* 2,3-diphenyl-1-zirconaindans respectively.[33] It has been shown that alkylzirconaindans decompose above 100 °C in saturated hydrocarbons with formation of phenylalkanes. It has been suggested that the decomposition proceeds via a stage involving

the formation of a phenylene complex via the transfer of a hydrogen atom from the aromatic ring to the metal. The thermolysis of 3-butylzirconaindan in the presence of an excess of norbornene entails the displacement of hexene and the formation of a zirconaindan complex containing the norbornane ring.[34]

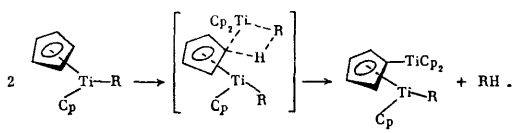
The reaction of the complex (XI) with $W(CO)_6$ yielded the carbene complex (XII):[35]



(XII)

The interaction of the complex (XI) with $CH_2 = P(C_6H_5)_3$ leads to the ylide $Cp_2Zr(C_6H_5)[CH = P(C_6H_5)_3]$.[36]

The cyclopentadienyl ligands together with the σ-linked groups R can serve as a source of hydrogen atoms in the formation of RH. The direct abstraction of hydrogen atoms by the group R from the Cp ring requires a high activation energy. Such a reaction proceeds more readily via an intermolecular pathway, in which the Cp ring is metallated by titanium, as suggested for the decomposition of trivalent titanium derivatives:[5]



However, it is more likely that hydrogen is abstracted from the Cp ring via the preliminary transfer of hydrogen to the metal. Such transfer was observed when the compounds Cp_2MR_2 (M = Ti, Zr, or Nb; R = Cl or CH_3) were treated with different reductants. Similar processes involving the transfer of hydrogen atoms to the metal occur also in the thermal decomposition of the derivatives Cp_2MR_2 (M = Ti, Zr, or Hf). One of the facts confirming such transfer is the isotopic composition of the hydrogen evolved on hydrolysis of the thermal decomposition products of Cp_2MR_2 (Table 4). When the products of the thermal decomposition of Cp_2MR_2-d_{10} are treated with HCl/H_2O, HD is formed preferentially, while treatment with DCl/D_2O leads to the preferential formation of D_2. The formation of HD in the former case and of D_2 in the latter shows that the decomposition products contain deuterium atoms which have been transferred from the Cp ligands to the metal.[10,27]

Table 4. Hydrolysis of the products of the thermal decomposition of Cp_2ZrR_2-d_{10}.[27]

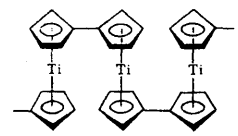
Initial compound	Agent	Isotopic composition of hydrogen
$Cp_2Zr(CH_3)_2$-d_{10}	HCl/H_2O	$H_2/HD/D_2 = 1/1.3/0.1$
	D_2O/DCl	$HD/D_2 = 1/5$
$Cp_2Zr(C_6H_5)_2$-d_{10}	HCl/H_2O	$H_2/HD/D_2 = 1/1.4/0.1$

The transfer of hydrogen to the metal takes place particularly readily after the abstraction of one group R and the liberation of a coordination site on the metal. The dehydrogenation of the cyclopentadienyl ring by the group R on formation of RH can proceed via the elimination of RH with participation of a hydrogen atom which has been transferred to the metal from the Cp ring:

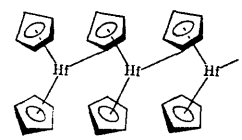
$$Cp_2MR \rightarrow Cp\,(C_5H_4)\,M\,(H)\,R \rightarrow Cp\,(C_5H_4)\,M + RH,$$
$$Cp_2MR_{-H} \rightarrow Cp\,(C_5H_4)\,M\,(H)\,R_{-H} \rightarrow Cp\,(C_5H_4)\,MR \rightarrow (C_5H_4)_2M + RH.$$

The donation of hydrogen atoms by the cyclopentadienyl ring for the formation of RH should lead to a rearrangement of the initial biscyclopentadienyl structure. The dimeric hydride forms of 'titanocene', having different structures, are known to react differently with HCl. Thus the 'titanocene' $[(\eta^5\text{-Cp})_2Ti_2(\eta^5\text{:}\eta^5\text{-}C_{10}H_8)]H_2$, having the fulvalene structure, does not afford Cp_2TiCl_2 on reaction with HCl.[37,28] However, the 'titanocene' containing the $\eta^5\text{:}\eta^1$-Cp ligands reacts with HCl to form Cp_2TiCl_2.[39]

These data permit the hypothesis that dimeric or polymeric chains with $\eta^5\text{:}\eta^5$-fulvalene ligands exist in the products of the thermal decomposition of the biscyclopentadienyl derivatives of titanium by analogy with the fulvalene form of 'titanocene':



A structure similar to the 'titanocene' with the $\eta^5\text{:}\eta^1$-cyclopentadienyl ligands is achieved in the products of the thermal decomposition of the hafnium derivatives:



The effect of the treatment of the product of the thermal decomposition of Cp_2HfR_2-d_{10} with HCl, which results in the formation (in 70% yield) of hafnocene dichloride whose isotopic composition is described predominantly by the formula Cp_2HfCl_2-d_{10}-d_7, serves as indirect proof of the existence of this structure in the hafnium products.[10] The existence of the Cp_2HfCl_2-d_9 and -d_{10} isotopic forms indicates the presence of ligands (C_5D_4) bound to the metal. The d_9 form corresponds to the $(C_5D_4)(C_5D_5)Hf$ fragments, while the d_8 form corresponds to the $(C_5D_4)_2Hf$ fragments in the decomposition products.

Thus the elimination of RH with participation of the hydrogen atoms of the Cp rings leads to a rearrangement of the initial biscyclopentadienyl structure, whose character is determined by the nature of the central atom.

3. The hydrogen exchange in the thermal decomposition of Cp_2MR_2

There exist a series of experimental data obtained in the thermal decomposition of deuteriated biscyclopentadienyl compounds of titanium, zirconium, and hafnium, which indicate the occurrence of hydrogen exchange between the groups Cp and R. The following must be included among them:

(1) The change in the isotopic composition of methane in the thermal decomposition of methyl derivatives of titanium and hafnium [it has been established that, with increase in the degree of decomposition of the compounds (after an increase in temperature and in the reaction time), the fraction of methane containing hydrogen derived from the Cp ring is found to increase[10,40,41]].

(2) The formation of protium-containing methane (CD_3H, CD_2H_2, and CH_3D) on treatment of the products of the thermal decomposition of $Cp_2M(CD_3)_2$ and deuterium-containing methane (CD_4, CD_3H, CDH_3) with DCl and on treatment of the products of the thermal decomposition of $Cp_2M(CH_3)_2$–d_{10} with HCl.[10]

(3) A clear-cut demonstration of the occurrence of hydrogen exchange has been obtained by detecting deuterium in the Cp rings in the Cp_2HfCl_2 formed on treatment of the $Cp_2Hf(CD_3)_2$ decomposition products with HCl:[10]

Isotopic forms of Cp ligands	d_0	d_1	d_2	d_3	d_4
Contents of these forms, %	85.3	12.3	1.5	0.7	0.2.

The hydrogen exchange between the Cp and R groups should entail two reactions—the reversible transfer of hydrogen from the methyl group to the metal [reaction (6)] and rapid exchange of hydride hydrogen and the hydrogen in the Cp or C_5H_4 ligands [reaction (7)]:

$$\rangle M{-}CH_3 \rightleftarrows \rangle M\langle^{CH_2}_{H}\,, \qquad (6)$$

$$Cp\,(C_5H_4)\,MH \rightleftarrows Cp\,(C_5H_5)\,M. \qquad (7)$$

The exchange is facilitated after the abstraction of one σ-linked group as a result of the liberation of a coordination site at the metal. The rate of exchange via reactions (6) and (7) must exceed the rate of elimination of the second methyl group. This in fact explains the finding that, on decomposition of $Cp_2M(CH_3)_2$, the fraction of methane containing hydrogen from the Cp rings increases with increasing reaction time. After the treatment of the $Cp_2Hf(CD_3)_2$ thermal decomposition products with HCl, Cp_2HfCl_2–d_1–d_4 compounds were isolated. These data indicate the presence in the decomposition products of the $(C_5H_5)(C_5H_3D)Hf$, $(C_5H_3D)_2Hf$, and other fragments containing one or several deuterium atoms. The dominant content of Cp_2HfCl_2-d_1 shows that the exchange involves only one ring.[10]

The transfer of the hydrogen atom from the ring to the metal takes place also via an intermolecular pathway. This is demonstrated by the composition of Cp_2MR_2 (M = Ti or Zr) in the presence of Cp_2V-d_{10}, in which there is H–D exchange between the hydride atoms of Cp_2MR_2 and vanadocene. The product of the thermal decomposition of Cp_2MR_2 also participates in the H–D exchange reaction with vanadocene. It has been shown that there exists a mobile equilibrium in which the hydrogen atoms of the Cp ligands in the initial compounds, the hydride hydrogen atoms, and the deuterium in the C_5D_5 ligands of vanadocene participate.[27]

The complexes $[Cp(C_5H_4)NbH]_2$ and Cp_2TaH_3 are known to be active catalysts of the H–D exchange in the D_2–C_6H_6 system.[42] It was found that the hydride complexes formed in the decomposition of the compounds Cp_2MR_2 are active in the hydrogen exchange of the hydrocarbons. Thus it has been established that hydrogen exchange takes place between C_6H_6 and D_2 under the conditions of the thermal decomposition of $Cp_2Ti(CH_3)_2$.[43] The thermal decomposition of $Cp_2Zr(C_6H_5)_2$-d_{10} in the presence of methane affords deuterium-containing methane. When the product of the thermal decomposition of $Cp_2Zr(CH_3)_2$-d_{10} is heated with C_2H_6, deuterium-containing propene and propane are produced (Table 5).[27] Deuteriomethane has been detected in the decomposition of $Cp_2Hf(CH_3)_2$ in C_6D_6.[10] It has been suggested that hydrogen exchange takes place under the thermal decomposition conditions between the hydride atoms of the cyclopentadienyl complex and the hydrogen atoms of the hydrocarbon.[10,27] The exchange proceeds via a stage involving the formation of σ-alkyl (or σ-aryl) intermediate transition metal complex:[44]

$$L_2M{-}H + R'D \longrightarrow \left[\begin{array}{c} R' \\ | \\ L_2M{-}D \\ | \\ R \end{array}\right] \longrightarrow L_2M{-}D + R'H\,;$$

L = Cp, C_5H_4.

Table 5. Thermal decomposition of Cp_2MR_2 in the presence of hydrocarbons (according to the results of Razuvaev and co-workers[10,27]).

System	Reaction conditions		Isotopic composition of hydrocarbons, %
	T, °C	t, min	
$Cp_2Zr(C_6H_5)_2$-d_{10} + CH_4	160	45	CH_4 96.0 CH_3D 4.0
Products of thermal decomposition of $Cp_2Zr(CH_3)_2$-d_{10} + C_3H_6	200	60	C_3H_8 17.5 C_3H_6 86.3 C_3H_7D 39.5 C_3H_5D 13.7 $C_3H_6D_2$ 26.7 $C_3H_5D_3$ 16.3
$Cp_2Hf(CH_3)_2$ + C_6D_6	200	180	CH_4 95.1 CH_3D 4.9

Thus the thermal decomposition of biscyclopentadienyl compounds is accompanied by the hydrogen exchange between the hydrogen atoms of the Cp rings, the hydride atoms, the hydrogen atoms of the σ-linked group, and the hydrogen atoms of the hydrocarbon in the presence of which the decomposition takes place:

$$H_{Cp} \rightleftharpoons H_M \rightleftharpoons H_R\,, \qquad H_M \rightleftharpoons H_{ext}$$

If a compound containing an alkyl substituent in the cyclopentadienyl ring undergoes thermal decomposition, then the hydrogen exchange involves also the atoms in the alkyl group. Thus it has been shown on the basis of ^1H NMR and EPR data as well as the results of isotope analysis that H–D exchange takes place between the hydrogen atoms of the methyl groups and molecular deuterium in the thermolysis or photolysis of $[(C_5H_4CH_3)_2ZrH_2]_2$ in a D_2 atmosphere.[45]

It has been established that hydrogen is eliminated in the first stage with formation of a trivalent zirconium derivative:

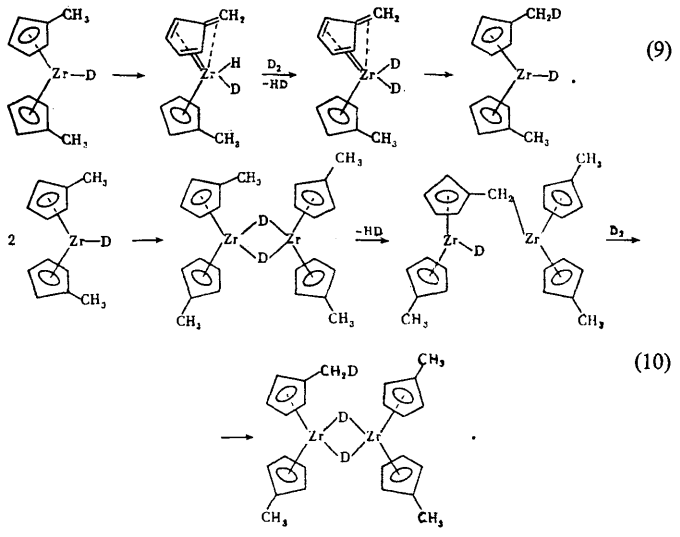
$$[(C_5H_4CH_3)_2ZrH_2]_2 \longrightarrow 2\,(C_5H_4CH_3)_2ZrH + H_2.$$

Next D_2 exchanges with hydride atoms. Such exchange can proceed via a four-centre transition state:

$$\rangle ZrH + D_2 \rightarrow \rangle Zr\langle^{H.}_{D.}\!:D \rightarrow \rangle Zr{-}D + HD. \qquad (8)$$

It has been suggested that the exchange of hydride hydrogen with the hydrogen atoms of the alkyl group takes place intramolecularly with formation of zirconium-fulvene derivatives [reaction (9)] or via

an intermolecular pathway [reaction (10)]:



(9)

(10)

If the methyl group in the cyclopentadienyl ligand is replaced by the bulky silyl group SiR_3, then hydrogen exchange proceeds only via reaction (8) without involving the cyclopentadienyl rings of the hydride complex.[45]

4. The participation of the solvent in the decomposition of Cp_2MR_2

Comparison of the products of the thermal decomposition of Cp_2MR_2 without a solvent and in solutions in hydrocarbons (benzene, toluene) shows that the decomposition processes are similar.[6,10] Two pathways leading to the formation of RH are observed in both cases—with participation of the hydrogen atoms of the Cp rings and with participation of σ-linked groups. In the thermal decomposition of deuteriated Cp_2MR_2, both in solutions and in the solid state, the isotopic composition of RH is approximately the same. In most studies on the thermal decomposition of Cp_2MR_2 in deuterium-containing hydrocarbon solvents, it has been noted that the solvents do not participate in the RH formation process.[7,40] The small amounts of RD detected in this case may indicate the occurrence of hydrogen exchange between the solvent and RH.

The participation of oxygen-containing solvents in the decomposition of the complexes Cp_2MR_2 has been established and has been confirmed by the isolation of RD [for example, in the decomposition of Cp_2MR_2 in THF-d_8 or $(C_2D_5)_2O$ [7,40]] and also by the change in the isotopic composition of RH on passing from hydrocarbon solvents to ethers in the thermal decomposition of deuteriated compounds.[10] Solvents such as tetrahydrofuran (THF) and diethyl ether readily form adducts with various transition metal compounds. It has been established that the ligand bound in the complex is an additional donor of hydrogen in the formation of RH.

The products of the thermal decomposition of Cp_2MR_2 in chlorine-containing solvents such as CCl_4 and $CHCl_3$ differ from the decomposition products in hydrocarbons (Table 6). The thermal decomposition of Cp_2MR_2 in $CHCl_3$ and CCl_4 affords a high yield of RCl and Cp_2MCl_2 together with RH.[10,46]

Experimental data show that the thermal decomposition of Cp_2MR_2 in chlorine-containing solvents includes the stage involving the decomposition proper of the compounds (both in the decomposition without a solvent and in hydrocarbon solvents) and the stages involving the interaction of the chlorine-containing solvent with the initial compound or with its thermal decomposition product. It has been suggested that, together with the radical pathway, there exists a carbene decomposition pathway. The relative contributions of these pathways depend on the nature of the metal. The contribution of the carbene pathway is insignificant for M = Ti or Zr, increasing somewhat for M = Hf.[10,46]

Table 6. Thermal decomposition of Cp_2MR_2 in chlorine-containing solvents.

Compound	Decomposition conditions			Decomposition products, mol/mol of starting material				Refs.
	solvent	T, °C	t, h	RH	RCl	Cp_2MCl_2	$(CCl_3)_2$	
$Cp_2Ti(CH_3)_2$	$CHCl_3$	70	24	1.90	Нет	0.80	not determined	[4]
$Cp_2Ti(C_6H_5)_2$	$CHCl_3$	70	24	1.80	»	0.81	»	[4]
	CCl_4	80	20	1.20	0.60	0.24; 0.68 $CpTiCl_3$	nil	[7]
$Cp_2Zr(CH_3)_2$	$CHCl_3$	150	100	1.90	0.05	0.80	»	[46]
	CCl_4	150	100	1.30	0.65	0.72	»	[46]
$Cp_2Zr(C_4H_5)_2$	$CHCl_3$	150	100	1.20	0.62	0.73	»	[46]
	CCl_4	150	100	1.30	0.60	0.65	»	[46]
$Cp_2Hf(C_6H_5)_2$	CCl_4	150	8	0.72	0.22	0.81	0.41; 0.39 $(CHCl_3)$	[10]

III. Thermal decomposition of vanadium compounds

1. Thermal stability and decomposition products

The thermal stability of the biscyclopentadienyl compounds of trivalent vanadium Cp_2VR [R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, n-C_5H_{11}, or $CH_2C(CH_3)_3$] is determined by the nature of the σ-substituent.[47] Cp_2VCH_3 is the most stable. The presence of β-hydrogen atoms in the alkyl chain reduces sharply the stability of the compounds as a consequence of the ease of the elimination reaction with participation of these atoms.

In the series of tetravalent vanadium compounds Cp_2VR_2 (R = CH_3, C_2H_5, or $CH_2C_6H_5$), the benzyl derivative has the lowest stability, the half-life in toluene at 20 °C being 30 min. The highest thermal stability is shown by $Cp_2V(CH_3)_2$. This compound is thermally stable at room temperature for a long time. According to DTA data, the decomposition of the complex $Cp_2V(CH_3)_2$ is observed above 122 °C with an exothermic heat change,[48,49] In terms of its thermal stability, $Cp_2V(CH_3)_2$ resembles the monosubstituted derivative Cp_2VCH_3. The substitution of a methyl group in $Cp_2V(CH_3)_2$ by chlorine reduces sharply the stability of the compound. The mixed derivative $Cp_2V(CH_3)Cl$ begins to decompose at 87 °C (according to DTA data).[50]

The thermal decomposition of Cp_2VR (R = CH_3 or Ar), $Cp_2V(CH_3)Cl$, and $Cp_2V(CH_3)_2$ without a solvent and in solutions in hydrocarbons or THF leads to the elimination of approximately 0.5 mol of RH per σ-linked group. The principal vanadium-containing decomposition products of these compounds are biscyclopentadienyl compounds, whose yield is 0.6–0.8 mol per mole of the initial compound. The composition of the decomposition product has been established mass-spectrometrically. The decomposition products of Cp_2VR and Cp_2VR_2 are mixtures of vanadocene and its substituted derivatives $Cp(C_5H_4R)V$ and $(C_5H_4R)_2V$. [49,51] The decomposition of $Cp_2V(CH_3)Cl$ results in the formation of Cp_2VCl and its methyl derivatives.[50]

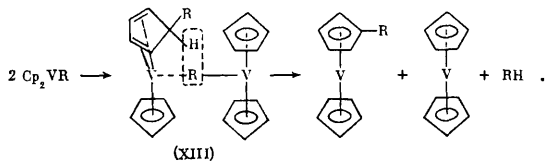
The migration of the bulky organoelemental group to the cyclopentadienyl ring has been demonstrated in the thermal decomposition of the biorganoelemental compound $Cp_2VGe(C_2H_5)_3$. The compound $Cp[C_5H_4Ge(C_5H_5)_3]V$ was isolated and characterised as a result of the reaction.[52]

2. Thermal decomposition pathways

Comparison of the compositions of the products of the thermal decomposition of the biscyclopentadienyl compounds of titanium and vanadium demonstrates a sharp difference between the decomposition pathways. In the decomposition of the vanadium compounds, the cleavage of the metal–carbon σ-bond takes place with retention of the sandwich structure, some of the σ-linked groups passing to the Cp ring.

In the thermal decomposition of vanadium compounds containing deuterium in the cyclopentadienyl rings, mainly RD and the vanadocenes $(C_5D_5)_2V$, $(RC_5D_4)(C_5D_5)V$, and $(RC_5D_4)_2V$ are formed.[49] The preferential involvement of the Cp rings as donors of hydrogen atoms in the formation of RH as well as the high yield of vanadocene and its substituted derivatives show that the formation of RH and the migration of the group R to the Cp ring are components of a single process.

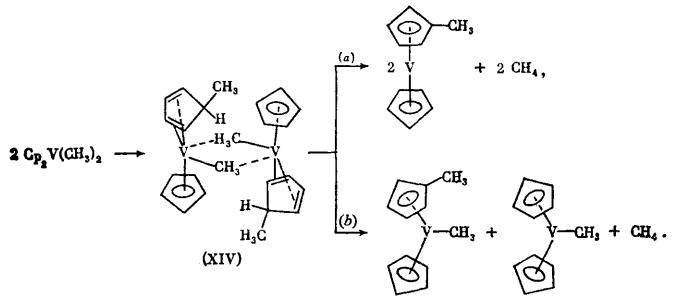
It has been suggested[49,52] that the decomposition of Cp_2VR is preceded by an intermolecular interaction leading to the dinuclear complex (XIII) with the η^4-alkyl(aryl)cyclopentadienyl ligand. The main pathway in the reaction of the complex (XIII) involves the elimination of RH, vanadocene, and its substituted derivative:



(XIII)

The isolation of small amounts of CpR indicates the occurrence of a side reaction of the complex (XIII) via a pathway involving the rupture of the V–η^4-CpR bond.

The decomposition of $Cp_2V(CH_3)_2$ is preceded by the formation of the dinuclear complex (XIV), which then decomposes via two pathways:[49]



(XIV) (XVa) (XVb)

The σ-derivatives formed via pathway (*b*) are unstable under the reaction conditions and decompose in accordance with the scheme presented above.

The formation of intermediate dinuclear complexes between the initial compounds and the vanadocene produced has also been postulated in the decomposition of Cp_2VR_n. This is indicated by the evolution of deuteriomethane in the thermolysis of an equimolar mixture of $Cp_2V(CH_3)_n$ + $Cp_2Vd\text{-}d_{10}$ and of products containing methyl groups in the deuteriated cyclopentadienyl ring.[49] The formation of di- and poly-methylvanadocenes in the thermolysis of $Cp_2V(CH_3)_n$ (n = 1,2) can be explained by the existence of the dinuclear complexes.

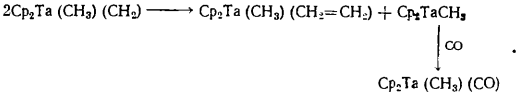
IV. Thermal decomposition of niobium and tantalum compounds

The thermal decomposition of the biscyclopentadienyl compounds of niobium and tantalum has been investigated for only a few examples. The compounds Cp_2NbR_2 (R = CH_3 or C_6H_5) decompose at temperatures close to those of the decomposition of compounds of the type Cp_2TiR_2.[53] The decomposition of Cp_2NbR_2 leads to the elimination of the σ–linked groups in the form of RH (1.3–1.8 mol). Treatment of the solid residue from the decomposition with HCl affords up to 10% of Cp_2NbCl_2.[53,54] The above products indicate the similarity of the thermal decomposition reactions of the niobium compounds and compounds of the titanium subgroup but not the vanadium subgroup elements.

The formation of C_6D_5H alone in the decomposition of $Cp_2Nb.(C_6D_5)_2$ shows that the cyclopentadienyl rings are the source of hydrogen atoms for the formation of RH. The abstraction of hydrogen from the Cp ring takes place mainly intramolecularly. This is indicated by the thermolysis of an equimolar mixture of $Cp_2Nb(C_6H_5)_2$ and $Cp_2Nb(C_6D_5)_2\text{-}d_{10}$. In contrast to the titanium analogue, the compound $Cp_2Nb(C_6H_5)_2$ does not react with tolane. This fact confirms that the decomposition of the niobium derivative does not involve the elimination of hydrogen from neighbouring phenyl groups and that a complex similar to the complex (III) is not formed.

Unfortunately there are as yet no experimental data indicating the pathway followed in the abstraction of hydrogen atoms from the cyclopentadienyl ring and in the elimination of RH. However, the existence of niobium hydride derivatives of the type $[Cp(C_5H_4)NbH]_2$ as well as the ease of the conversion of 'niobocene' into the hydride complex[55] show that in the case of titanium compounds too RH can be eliminated with participation of hydride hydrogen.

There are several examples of thermal decomposition reactions of tantalum and niobium complexes occurring with retention of the biscyclopentadienyl structure of the compounds. Thus it has been shown that the methyl complex of tantalum $Cp_2Ta(CH_3)(CH_2)$ decomposes slowly at room temperature via the mechanism



When $Cp_2Nb(C_2H_5)(C_2H_4)$ is heated, ethylene is readily split off. Subsequent β-elimination leads to the formation of $Cp_2Nb.(C_2H_4)H$.[56]

V. Photolytic decomposition of titanium and vanadium subgroup compounds

The photolytic decomposition of biscyclopentadienyl compounds of the titanium and vanadium subgroups differs from the thermal reactions already examined. EPR study of the photolysis of the methyl derivatives of titanium, zirconium, and hafnium $Cp_2M(CH_3)_2$

has led to the conclusion that the main stage of the photolysis is the homolytic cleavage of the M–CH_3 σ-bond with formation of intermediate compounds of the trivalent metal, which reacts both via the pathway involving the homolytic dissociation of a second M–CH_3 bond and via the pathway involving the intramolecular elimination of methane:[57–59]

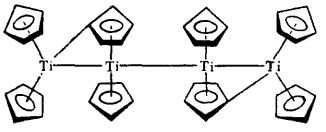
$$Cp_2M(CH_3)_2 \xrightarrow{h\nu} Cp_2MCH_3 + {}^{\cdot}CH_3 ,$$

$$\downarrow \qquad\qquad \downarrow$$

$$\text{«}Cp_2M\text{»} + {}^{\cdot}CH_3 \qquad\qquad Cp(C_6H_4)M + CH_4 .$$

This course of the process has been confirmed by the isotopic composition of the methane evolved in the photolysis of $Cp_2Ti(CD_3)_2$ in C_6H_6 ($CD_3H : CD_4 = 2.5 : 1$).[60]

The photolysis of $Cp_2M(CH_3)_2$ (M = Ti or V) results in the formation of black pyrophoric oligomeric or polymeric products containing both cyclopentadienyl rings and C_5H_4 fragments. The so called 'titanocene', obtained in the photolysis of $Cp_2Ti(CH_3)_2$, has been most thoroughly investigated. Its treatment with gaseous HCl results in the formation of Cp_2TiCl_2 as the main product. In addition, $CpTiCl_3$ and $(C_5H_4Cl)_2TiCl$ were isolated. Its reaction with Br_2 affords predominantly $CpTiBr_3$ and Cp_2TiBr. Small amounts of $Cp(C_5H_4Br)_2TiBr$ and $Cp(C_5H_4Br)TiBr_2$ were obtained. On the basis of these data, it has been suggested that the 'titanocene' formed in the photolysis has the following structure:[61]



The photolysis of $Cp_2Ti(CH_3)_2$ initiates the free-radical polymerisation of methyl methacrylate. The low-valence complex (XVI) is formed in the first stage of the polymerisation reaction (via a cryptoradical mechanism or via the preliminary transfer of hydrogen from the Cp ring to the metal). In the presence of methyl methacrylate (MMA), the complex (VI) generates a radical:

$$Cp_2Ti(CH_3)_2 \xrightarrow{-CH_4} \underset{\textbf{(XVI)}}{Cp(C_5H_4)TiCH_3} \xrightarrow{MMA} Cp(C_5H_4)Ti + CH_3\dot{M}MA \xrightarrow{n\ MMA} \text{polymer} .$$

The polymer obtained in the photolysis of $Cp_2Ti(^{14}CH_3)_2$ in MMA contains on average about one ^{14}C atom per chain. It has also been established that the tritium atoms in the cyclopentadienyl rings of $Cp_2Ti(CH_3)_2$-t_{10} enter into the composition of the polymer formed as a result of the photolysis.[62]

In contrast to $Cp_2Ti(CH_3)_2$, biphenyl is formed in the photolysis of the phenyl analogue in benzene in an amount of 1.2 mol per mole of the initial compound.[63] This finding clearly demonstrates that the solvent participates in the formation of biphenyl. The photolysis of $Cp_2Ti(C_6H_5)_2$ in C_6D_6 yielded 46% of C_6H_5–C_6H_5 and 54% of Ph–Ph-d_5. The photolysis of $Cp_2Ti(p\text{-}CH_3C_6H_4)_2$ in benzene resulted in the formation of toluene (0.11 mol), 4-methylbiphenyl (0.11 mol), and 4,4-dimethylbiphenyl (0.36 mol) together with the 'titanocene'. Under analogous conditions, toluene (0.35 mol), 3-methylbiphenyl (0.35 mol), and 3,3-dimethylbiphenyl (0.21 mol) were obtained in the photolysis of $Cp_2Ti(m\text{-}CH_3C_6H_4)_2$. The data presented show that there are two completing pathways in the photolytic decomposition of aryltitanium compounds:

$$Cp_2TiAr_2 \begin{cases} \xrightarrow{h\nu} \text{«}Cp_2Ti\text{»} + 2Ar^{\cdot} \begin{cases} \xrightarrow{\text{H donor}} Ar{-}H , \\ \xrightarrow[-H]{C_6H_6} Ar{-}C_6H_5 , \end{cases} \\ \xrightarrow{h\nu} \text{«}Cp_2Ti\text{»} + Ar{-}Ar . \end{cases}$$

The first pathway involves the homolytic cleavage of the Ti–Ar σ-bond and the generation of Ar radicals, which can abstract a hydrogen atom from the solvent or from the Cp ring or can enter into a homolytic substitution reaction with the solvent—benzene. The second pathway involves the reductive elimination reaction which leads to the formation of biaryls.[63]

In contrast to the titanium analogues, in the photolysis of diarylzirconocenes, the contribution of the reductive elimination reaction increases. This is confirmed by the high yield of 4,4-dimethylbiphenyl formed in the photolysis of $Cp_2Zr(p\text{-}CH_3C_6H_4)_2$ in benzene.[64]

The intermediate aryne complexes are not formed in the photolysis of titanium and zirconium compounds via the abstraction of an *ortho*-hydrogen atom from the aryl ligand, which is indicated by the absence of isomeric biphenyls among the reaction products.[64]

The study of the photolysis of the aryl derivatives Cp_2ZrAr_2 (Ar = C_6H_5 or $C_6H_5CH_2$) by the EPR method demonstrated the presence of a stage involving the homolytic cleavage of the Zr–Ar bond, as in the decomposition of the methyl derivatives. The compounds Cp_2ZrAr formed in this stage have been detected as complexes with phosphines.[65]

The photolysis of $Cp_2Ti(CH_3)_2$ and Cp_2TiAr_2 in the presence of CO leads to the formation of $Cp_2Ti(CO)_2$ in 50–60% yield.[63,66] The carbonyl groups in the complex $Cp_2Ti(CO)_2$ are capable of being exchanged for the molecules of gaseous carbon monoxide in hexane [reaction (11)].[67] The photolysis of $Cp_2Ti(CO)_2$ in the presence of an excess of PF_3 affords $Cp_2Ti(PF_3)_2$ [reaction (12)].

$Cp_2Ti(CO)PR_3$ is formed in the photolytic or thermal reaction of $Cp_2Ti(CO)_2$ with PR_3 (R = C_2H_5 or C_6H_5) in hydrocarbon solvents [reaction (13)]:[67]

$$Cp_2TiR_2 \xrightarrow{h\nu,\ CO} Cp_2Ti(CO)_2 \begin{cases} \underset{\longleftarrow}{\xrightarrow{h\nu,\ C^{18}O}} Cp_2Ti(CO)C^{18}O \underset{\longleftarrow}{\xrightarrow[-CO]{C^{18}O}} Cp_2Ti(C^{18}O)_2 , & (11) \\ \underset{\longleftarrow}{\xrightarrow{h\nu,\ PF_3}} Cp_2Ti(CO)PF_3 \underset{\longleftarrow}{\xrightarrow[-CO]{PF_3}} Cp_2Ti(PF_3)_2 , & (12) \\ \underset{\longleftarrow}{\xrightarrow{h\nu \text{ or } \Delta,\ PR_3}} Cp_2Ti(CO)PR_3 . & (13) \end{cases}$$

The photolysis of $Cp_2M(CH_3)_2$ and Cp_2MAr_2 (M = Ti or Zr) in the presence of diphenylacetylene leads to the metallacycles (XVII):[63,66,68]

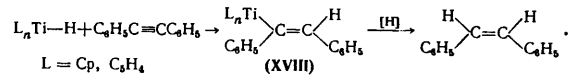
$$Cp_2MR_2 \xrightarrow[C_6H_5C\equiv CC_6H_5]{h\nu} Cp_2M(C_6H_5)_4$$

(XVII)

A similar complex can be obtained by the reaction of Cp_2TiCl_2 with metallic magnesium and tolane.[68,70] In both cases an unstable metlalocene is formed in the first stage and then reacts with an alkyne, which leads to the complex (XVII).

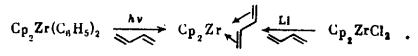
The photolysis of titanium and zirconium compounds differs from the thermal reaction, which leads to the formation of 1,1-bis-(cyclopentadienyl)-2,3-diphenylbenzotitanole or the analogous zirconole via an intermediate aryne complex.

Apart from compound (XVII), organic products such as diacetylenes and *cis*- and *trans*-stilbenes are formed in the photolysis of Cp_2TiAr_2 in the presence of diphenylacetylenes. Stilbenes are also formed in the photolysis of $Cp_2Ti(CH_3)_2$ in the presence of diphenylacetylene but in a lower yield. The formation of the reduction products, namely *cis*- and *trans*-stilbenes, indicates the presence of hydride intermediates in the photolysis process, which can be formed via the transfer of a hydrogen atom from the Cp ring to the metal:



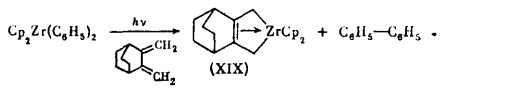
The first stage of the process involves the insertion of acetylene into the M–H bond with formation of the intermediate σ-complex (XVIII), which affords stilbene in the presence of a hydrogen donor.[63]

The stable complex $Cp_2Zr(\eta^4\text{-}trans\text{-}CH_2=CHCH=CH_2)$ is formed in the photolysis of $Cp_2Zr(C_6H_5)_2$ in the presence of *trans*-butadiene. It can also be obtained by reducing Cp_2ZrCl_2 with lithium in the presence of butadiene:[71]



When a solution of $Cp_2Zr(\eta^4\text{-}trans\text{-}CH_2\text{–}CHCH=CH_2)$ is irradiated or heated in C_6D_6, an equilibrium is established between the isomeric *trans*- and *cis*-forms of the diene complexes of zirconocene.[71]

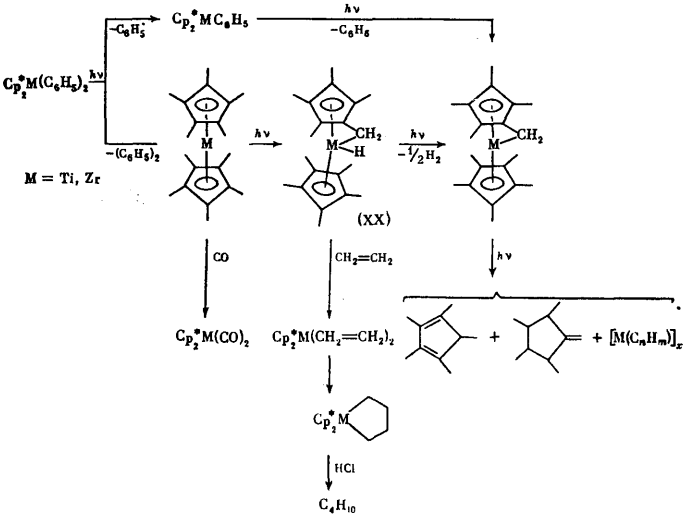
The photolysis of $Cp_2Zr(C_6H_5)_2$ in toluene in the presence of 2,3-bis(methylene)bi-cyclo[2.2.2]octane leads to the complex (XIX) in 65% yield:[72]



The photolysis of $Cp_2^*M(C_6H_5)_2$ (M = Ti or Zr)[73] as well as the unsubstituted derivatives proceeds via two main pathways: reductive elimination and homolysis. The isotopic composition of the biphenyl formed in the photolysis of $Cp_2^*M(C_6H_5)_2$ (M = Ti or Zr) in C_6D_6 established that the contribution by the reductive elimination is 97% for M = Ti and 25% for M = Zr.

The reductive elimination reaction of $Cp_2^*M(C_6H_5)_2$ leads to the unstable permethylmetallocene, which is converted into compound (XX) via the abstraction of hydrogen from the ring methyl group. Oligomeric metal-containing products as well as 2,3,4,5-tetramethylfulvene and pentamethylcyclopentadiene are formed ultimately.

A dicarbonylmetallocene is formed in the photolysis of the permethyl derivative in the presence of CO, as in the case of the unsubstituted compounds. The metallacycle is produced in the presence of ethylene (35 atm, –20 °C). The homolytic cleavage of the M–C_6H_5 σ-bond takes place to a slight extent even at low temperatures. The phenyl radicals formed have been detected by EPR as adducts with spin-trapping agents:



Comparison of the results of the photolysis of the permethyltitanocene derivatives and the unsubstituted compounds demonstrates an appreciable increase in the contribution of their reductive elimination with introduction of methyl substituents into the Cp ring. Such a change in the relative contributions of the photolytic pathways is due both to the steric influence of the bulky methyl group and to the absence from the rings of mobile hydrogen atoms capable of functioning as hydrogen donors in the homolytic decomposition. For the zirconium derivative, in which the central atom has a larger atomic radius compared with the titanium complex, the steric effect of the ligands is less significant.[73]

The photolysis of $Cp_2V(CH_3)_n$ (n = 1,2) and $Cp_2Nb(CH_3)_2$ in hydrocarbon solvents leads to the cleavage of the metal–carbon σ-bond. The main gaseous product is methane. Studies carried out with deuterium-containing compounds as well as C_6D_6 have shown that the source of hydrogen for the formation of methane may be the cyclopentadienyl rings, methyl groups, and solvents. As a result of the photolysis, the biscyclopentadienyl structure breaks down, which is indicated by the absence of vanadocene from the photolysis products.[74]

The photolysis of $Cp_2V(CH_3)_n$ (n = 1,2) and $Cp_2Nb(CH_3)_2$ in pentane in the presence of CO affords low yields of the carbonyl complexes $CpV(CO)_4$ and $CpNb(CH_3)(CO)$ respectively.[74]

VI. Exchange of cyclopentadienyl ligands

Under the conditions of photolysis in solution in toluene, the dichlorides of the biscyclopentadienyl derivatives of titanium, zirconium, and hafnium are capable of exchanging the cyclopentadienyl ligands:[75–77]

$$d_{10}\text{-}Cp_2MCl_2 + Cp_2MCl_2 \rightleftarrows 2Cp(d_5\text{-}Cp)MCl_2.$$

This process is not only photolytic but also thermal, its rate increasing with temperature.

The thermal exchange of the cyclopentadienyl ligands occurs also in the $Cp_2V\text{-}d_{10}\text{–}Cp_2M$ system:[78]

$$d_{10}\text{-}Cp_2V + Cp_2M \rightleftarrows d_5\text{-}CpVCp + d_5\text{-}CpMCp + d_{10}\text{-}Cp_2M + Cp_2V;$$
M = V, Cr, Mn.

The rate of this exchange depends on the nature of the metal in Cp_2M and increases in the sequence V < Cr < Mn.

The exchange of the cyclopentadienyl ligands can take place between metallocenes in different oxidation states. Thus the occurrence of the exchange in the Cp_2VCl–$(C_5H_4CH_3)_2VCl_2$, Cp_2V–$(C_5H_4CH_3)_2VCl_2$, and Cp_2V–$(C_5H_4CH_3)_2VCl$ systems has been demonstrated. The rate of exchange increases significantly on heating to 70 °C.[75]

Several mechanisms which can account for the exchange of the Cp ligands in metallocenes have been proposed.[75,78] In particular, a certain amount of ionic character of the bonds in the metallocenes Cp_2M (M = V, Cr, or Mn), manifested in the reactions with iron chloride and also in the rapid exchange with LiC_5D_5, indicates the possibility that the exchange reaction may proceed via an ionic pathway:

$$Cp_2M \rightleftarrows C_5H_5^- + CpM^+,$$

$$C_5H_5^- + d_{10}\text{-}Cp_2M \rightleftarrows d_5\text{-}CpMCp + C_5D_5^- .$$

The rate-determining stage of the exchange in the postulated mechanism is the dissociation into ions, whose rate is directly proportional to the amount of ionic character of the molecules. Comparison of the rates of exchange shows that the exchange process involving compounds with a more pronounced ionic character of the bonds is faster. Thus, in the systems Cp_2M-d_{10}–Cp_2M (M = V, Cr, or Mn), a faster exchange is observed in the case of manganocene, for which the ionic character of the bonding of the Cp ligands is more clearly manifested.

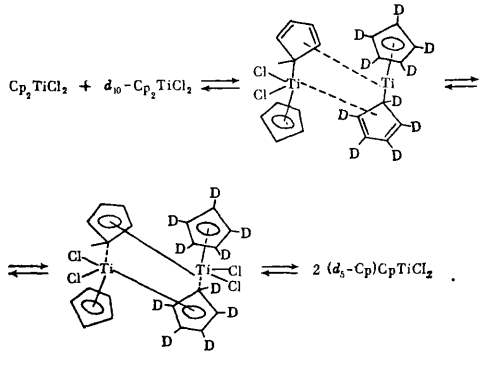
A radical pathway is possible for the photolytic ligand exchange:

$$(C_5H_5)_2V \rightleftarrows C_5H_5^{\cdot} + C_5H_5V^{\cdot},$$

$$C_5H_5^{\cdot} + (C_5D_5)_2V \rightleftarrows (C_5H_5)(C_5D_5)V + C_5D_5^{\cdot} .$$

The radical exchange of the Cp rings in Cp_2MCl_2 has been confirmed by experiments on the photolysis of Cp_2TiCl_2 by the EPR method, where the Cp radical was detected in the form of adducts with spin trapping agents.[76,80]

Together with the radical mechanism of the exchange, there exists an intermolecular bridge mechanism, which presupposes a change in the character of the bonding of the cyclopentadienyl ring during the exchange process:[77,79]



The exchange of the cyclopentadienyl ligands may be accompanied by the thermolysis of the compounds Cp_2MR_2. Such a process has been noted, for example, in the decomposition of the compounds $Cp_2V(CH_3)_n$.[49]

VII. Thermal decomposition with rupture of metal–cyclopentadienyl ring bonds

The thermal cleavage of the $(\eta^5\text{-}C_5H_5)$–M bonds occurs under more severe conditions than those leading to dissociation of the metal–carbon bond. The thermolysis of mixed sandwich-covalent titanium and vanadium derivatives takes place in the temperature range 100–200 °C. The contribution by the reactions involving the dissociation of the $M\text{–}C_5H_5$ bonds is then insignificant. The strength of this bond has also been measured thermochemically.[81] The average $M\text{–}C_5H_5$ dissociation energies in different titanium, zirconium, and vanadium compounds are in the range 63–88 kcal mol^{-1}.

The $M\text{–}C_5H_5$ bond dissociation energies of metallocenes of the 3*d* series have been estimated thermodynamically.[82] Similarly calculations have shown that dissociation in accordance with the equation

$$Cp_2M \rightarrow 2C_5H_5^{\cdot} + M \qquad (14)$$

is possible for vanadocene only at temperatures above 830 °C ($\Delta G < 0$). In a real experiment, the thermal decomposition of metlalocenes occurs at a lower temperature (350–450 °C) and not via pathway (14) alone.

The study of the kinetics of the thermal decomposition of metallocenes Cp_2M (M = V, Cr, or Mn) made it possible to establish the following catalytic series:

$$Cp_2V > Cp_2Cr > Cp_2Mn.$$

The thermal stability diminishes in parallel with the decrease in the $M\text{–}C_5H_5$ bond strength.[83]

The thermal stability of bis(cyclopentadienyl)metal dichlorides Cp_2MCl_2 (M = Ti, Zr, or Hf) also depends on the nature of the central atom and increases in the sequence

$$Cp_2TiCl_2 < Cp_2ZrCl_2 < Cp_2HfCl_2.$$

The thermal decomposition of vanadocene has been examined in greatest detail.[84] The pyrolysis of Cp_2V in a static system (450–510 °C) takes place mainly with evolution of hydrogen and cyclopentadiene. Apart from the products indicated, methane, benzene, and naphthalene are formed in the pyrolysis of vanadocene. The composition of the volatile products depends on temperature and the duration of heating. Thus at low temperatures and for short heating, the formation of an appreciable amount of cyclopentadiene is observed. With increase in temperature and heating time, the yield of C_5H_6 falls and the main volatile products of the total pyrolysis of vanadocene are hydrogen and methane. In the pyrolysis of Cp_2V in a flow system (800–900 °C), considerable amounts of acetylene and ethylene are formed in addition to the products indicated.

The data presented show that the dehydrogenation of the cyclopentadienyl and the dissociation of a C–C bond are observed in the decomposition of vanadocene together with the metal–cyclopentadienyl bond cleavage reaction. The latter can occur via radical or molecular pathways. The radical pathway is more probable when the pyrolysis is carried out at low pressures and in the bulk of the reactor. In this case, the homolysis of the bond leads to the formation of the cyclopentadienyl radical, which abstracts a hydrogen atom from the initial molecule with the consequent evolution of C_5H_6.

In the decomposition via the molecular pathway, cyclopentadiene is formed intra- or inter-molecularly with participation of the Cp ligand and the hydrogen atom which had been transferred to the metal from another Cp group beforehand:

$$Cp_2V \rightarrow Cp(C_5H_4)VH \rightarrow C_5H_6 + (C_5H_4)V.$$

The elimination of hydrogen takes place either by the direct dissociation of a ring C–H bond or via the splitting off of a hydride atom:

$$Cp_2V \rightarrow Cp(C_5H_4)VH \rightarrow H_2 + (C_5H_4)_2V.$$

The final products of such reactions are polymeric species containing the metal and the dehydrogenated rings.

Analogous reactions occur also in the decomposition of the dichlorides Cp_2MCl_2 (M = Ti, Zr, or Hf). As a result of the presence of a strong M–Cl bond in these compounds, the main reaction in the range 400–800 °C is the dehydrogenation of a cyclopentadienyl ring with evolution of hydrogen.[6,85]

It is notable that the higher rate of dehydrogenation and dissociation of the C–C ring bond compared with the rate of the reaction involving dissociation of the M–Cp bond virtually precludes the segregation of the pure metal under the conditions of the thermal decomposition of the compounds indicated. This is confirmed by thermochemical data. The calculated thermodynamic functions (ΔG, ΔH, ΔS) for the most probable reactions show that the reaction leading to the formation of a carbide is most probable for Cp_2MCl_2.[82,86] Indeed, the carbides of the corresponding metals are formed in the high-temperature (900 °C) decomposition of Cp_2MCl_2 (M = Ti or Zr) in a hydrogen atmosphere. Titanium carbides are also formed in the high temperature decomposition of the sandwich-covalent compounds Cp_2TiR_2 (R = CH_2 or C_6H_5).[85]

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Analysis of the results of studies of the thermal and photochemical reactions of the sandwich-covlent derivatives of titanium and vanadium subgroup metals permitted the conclusion that the π-cyclopentadienyl ligands play an appreciable role in the splitting of the metal–carbon σ-bond. The processes occurring in the thermal and photochemical reactions can be regarded as model processes in the study of reduction or catalytic reactions with participation of these compounds.

During the preparation of the manuscript for the press, studies were published on the intermolecular activation of the C–H bonds of the substituents in the cyclopentadienyl rings in the thermolysis of the compounds $(C_5H_4R)_2Zr(C_6H_5)_2$ [R = $C(CH_3)_2C_6H_5$],[87] $(C_5H_3R_2)_2M(CH_3)_2$ (R = t-C_4H_9, M = Ti or Zr),[88] and $Cp^*_2Zr(C_6H_5)_2$.[89] It has been established that such activation of the C–H bonds of the alkyl groups of the Cp rings can occur as a result of low-temperature reactions of decamethylmetallocenes[90,91] and on dissociative ionisation of $(C_5H_4Alk)_2ZrCl_2$.[92]

References

1. G A Razuvaev, B G Gribov, G A Domrachev, B A Salamatin *Metalloorganicheskie Soedineniya v Elektronike* (Organometallic Compounds in Electronics), Izd. Nauka, Moscow, 1972, 479 pp
2. B G Gribov, G A Domrachev, B V Zhuk, B S Kaverin *Osazhdenie Plenok i Pokrytii Razlozheniem Metalloorganicheskikh Soedinenii* (Deposition of Films and Coatings by the Decomposition of Organometallic Compound), Izd. Nauka, Moscow, 1981, 322 pp
3. G A Razuvaev, L I Vyshinskaya *Usp. Khim.*, 1983, **42**(10) 1648 [English translation in *Russ. Chem. Rev.*, 1983(10)]
4. G A Razuvaev, V N Latyaeva, L I Vyshinskaya *Khim. Khim. Tekhnol. Gor'kii*, 1973(2) 3
5. J H Teuben *J. Org. Chem.*, 1974, **69** 341
6. V N Latyaeva, L I Vyshinskaya, V P Mar'in *Zh. Obshch. Khim.*, 1976, **46** 628
7. C P Boekel, J H Teuben, H J Liefde Meiyer *J. Organomet. Chem.*, 1974, **81** 371
8. C P Boekel, J H Teuben, H J Liefde Meiyer *J. Organomet. Chem.*, 1975, **102** 161, 317
9. G A Razuvaev, L I Vyshinskaya, V P Mar'in *Dokl. Akad.Nauk SSSR*, 1975, **225** 827
10. G A Razuvaev, V P Mar'in, O N Drushkov, L I Vishinskaya *J. Organomet. Chem.*, 1982, **231** 125
11. D R Alister, D K Erwin, J E Bercaw *J. Am. Chem. Soc.*, 1978, **100** 5966
12. M M Francl, W J Pietro, R F Hout, W J Hehre *Organometallics*, 1983, **2** 281
13. F N Tebbe, G W Parshall, G S Reddy *J. Am. Chem. Soc.*, 1978, **100** 3611
14. F N Tebbe, G W Parshall, D W Ovenall *J. Am. Chem. Soc.*, 1979, **101** 5074
15. F N Tebbe, R L Harlow *J. Am. Chem. Soc.*, 1979, **102** 6149
16. R J McKinney, T N Tulip, D L Thorn, et al. *J. Am. Chem.Soc.*, 1981, **103** 5584
17. A Famili, M F Farona, S Thanedav *J. Chem. Soc., Chem. Commun.*, 1983, 435
18. J R Still, R H Grubbs *J. Am. Chem. Soc.*, 1983, **105** 1664
19. K A Brown-Wensley, S L Buchwald, L Cannizzo, et al. *Pure Appl. Chem.*, 1983, **55** 1733
20. L R Gillion, R H Grubbs *Organometallics*, 1986, **5** 791
21. J Schwartz, K L Gell *J. Organomet. Chem.*, 1980, **184** C1
22. C McDade, J C Green, J E Bercaw *Organometallics*, 1982, **1** 1629
23. A Meetsma, J H Teuben *J. Am. Chem. Soc.*, 1985, **107** 7758
24. K Mashima, H Takaya *Organometallics*, 1985, **4** 1464
25. B-H Chang, H-S Tung, C H Brubaker *Inorg. Chim. Acta*, 1981, **51** 143
26. J W Bruno, T J Mars, V W Day *J. Organomet. Chem.*, 1983, **250** 237
27. C A Razuvaev, V P Mar'in, Yu A Andrianov *J. Organomet. Chem.*, 1979, **174** 67
28. M E Vol'pin, V B Shur, V N Latyaeva, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1966, 385
29. V B Shur, E G Berkovich, M E Volpin, et al. *J. Organomet. Chem.*, 1982, **228** C36
30. M D Rausch, E A Mintz *J. Organomet. Chem.*, 1980, **190** 65
31. M Kh Grigoryan, I S Kolomnikov, E G Berkovich et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 1177
32. G Erker *J. Organomet. Chem.*, 1977, **134** 189
33. K Kropp, G Erker *Organometallics*, 1982, **1** 1246
34. G Erker, K Kropp *J. Am. Chem. Soc.*, 1979, **101** 3659
35. G Erker, U Dorf, R Mynott, et al. *Angew. Chem.*, 1985, **97** 572
36. G Erker, P Czisch, R Mynott, et al. *Organometallics*, 1985, **4** 1310

37. H Antropiusova, A Dosedlova, V Hanus, K Mach *Trans. Met. Chem.*, 1981, **6** 90
38. G J Olthof *J. Organomet. Chem.*, 1977, **128** 367
39. G P Pez, S C Kwan *J. Am. Chem. Soc.*, 1976, **98** 8079
40. G J Erskine, D A Wilson, J D McCowan *J. Organomet. Chem.*, 1976, **114** 119
41. G J Erskine, J Hartgerina, E L Weinberg, J D McCowan *J. Organomet. Chem.*, 1979, **170** 51
42. G P Pez, S C Kwan *J. Am. Chem. Soc.*, 1976, **98** 7079
43. V B Shur, E G Berkovich, M E Vol'pin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975, 1908
44. A H Janowicz, R G Bergman *J. Am. Chem. Soc.*, 1983, **105** 3929
45. C S Bajur, S B Jones, J L Peterson *Organometallics*, 1985, **4** 1929
46. G A Razuvaev, V N Latyaeva, L I Vyshinskaya, et al. *Dokl. Akad. Nauk SSSR*, 1976, **231** 114
47. H Bouman, J H Teuben *J. Organomet. Chem.*, 1976, **110** 327
48. G A Razuvaev, V N Latyaeva, L I Vishinskaya, et al. *J. Organomet. Chem.*, 1977, **129** 169
49. G A Razuvaev, V P Mar'in, S P Korneva, et al. *Dokl. Akad. Nauk SSSR*, 1976, **231** 626
50. G A Razuvaev, L I Vyshinskaya, S P Korneva, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 700
51. C P Boekel, A Jeesma, J H Teuben, H J Liefde Meijer *J. Organomet. Chem.*, 1977, **136** 211
52. G A Razuvaev, V N Latyaeva, V P Mar'in, et al. *J. Organomet. Chem.*, 1982, **225** 233
53. C P Boekel, J H Teuben, H J Liefde Meijer *J. Organomet. Chem.*, 1977, **128** 375
54. L E Mauzer *Inorg. Chem.*, 1977, **16** 525
55. D A Lemenovsky, V P Fedin *J. Organomet. Chem.*, 1977, **132** C11
56. R R Schrock *J. Am. Chem. Soc.*, 1975, **97** 6577
57. E Samuel, P Maillard, C Giannotti *J. Organomet. Chem.*, 1977, **142** 289
58. P W N M Leewen, H Heijden, C F Roobeck, J H G Frijns *J. Organomet. Chem.*, 1981, **209** 169
59. M D Rausch, W H Boon, H G Alt *J. Organomet. Chem.*, 1974, **96** 5936
60. H G Alt, M D Rausch *J. Am. Chem. Soc.*, 1974, **96** 5936
61. H G Alt *Angew. Chem.*, 1984, **96** 752
62. C H Bamford, R J Puddephatt, D M Slater *J. Organomet. Chem.*,1978, **159** C31
63. M D Rausch, W H Boon, E A Mintz *J. Organomet. Chem.*, 1978, **180** 81
64. G Erker *J. Organomet. Chem.*, 1977, **134** 189
65. A Hudson, M F Lappert, R Pichon *J. Chem. Soc., Chem. Commun.*, 1983, 374
66. J L Altwood, W E Hunter, H Alt, M D Rausch *J. Am. Chem. Soc.*, 1976, **98** 2454
67. B H Edwards, R D Rogers, D J Sikora, et al. *J. Am. Chem. Soc.*, 1983, **105** 416
68. W Skibbe, G Erker *J. Organomet. Chem.*, 1983, **241** 15
69. V B Shur, E G Berkovich, M E Volpin, et al. *J. Organomet. Chem.*, 1982, **228** C36
70. V B Shur, S Z Bernadyuk, V V Burlakov, et al. *J. Organomet. Chem.*, 1983, **243** 157
71. G Erker, J Wicher, K Engel, C Krüger *Chem. Ber.*, 1982, **115** 3300
72. G Erker, K Engel, C Krüger, et al. *Z. Naturforsch., B*, 1985, **40** 140
73. H-S Tung, G H Brubaker *Inorg. Chim. Acta*, 1981, **52** 197
74. D F Foust, M D Rausch, E Samuel *J. Organomet. Chem.*, 1980, **193** 203
75. J G S Lee, C H Brubaker *Inorg. Chim. Acta*, 1977, **25** 181
76. R W Harrigan, G S Hammond, H B Gray *J. Organomet. Chem.*, 1974, **81** 79
77. E Vitz, C H Brubaker *J. Organomet. Chem.*, 1974, **104** C16, C33
78. V P Mar'in, O N Druzhkov, Yu A Andrianov *I Vsesoyuznaya Konferentsiya po Metalloorganicheskoi Khimii: Tezisy Dokladov* (The 1st All-Union Conference on Organometallic Chemistry: Abstracts of Reports), Izd. Nauka, Moscow, 1979, Vol. 2, p. 210
79. E Vitz, P J Wagner, C H Brubaker *J. Organomet. Chem.*, 1976, **107** 301
80. P B Brindley, A G Davies, J A A Hawari *J. Organomet. Chem.*, 1983, **250** 247
81. V I Tel'noi, I B Rabinovich *Usp. Khim.*, 1977, **46**(8) 1337 [English translation in *Russ. Chem. Rev.*, 1977(8)]
82. V I Tel'noi, I B Rabinovich *Zh. Prikl. Khim.*, 1985(1) 134
83. L M Dyagileva, V P Mar'in, E I Tsyganova, G A Razuvaev *J. Organomet. Chem.*, 1979, **175** 63
84. G A Razuvaev, L M Dyagileva, V P Mar'in, et al. *Dokl. Akad. Nauk SSSR*, 1976, **231** 350
85. L I Vyshinskaya, V P Mar'in, V N Latyaeva, et al. *Izv. Akad. Nauk SSSR Neorg. Mater.*, 1976, **12** 2166
86. E V Stolyarov *Issledovanie i Primenenie Sverkhtverdykh i Tugoplavkikh Materialov* (The Study and Applications of Ultrahard and Refractory Materials), Izd. Inst. Sverkhtverdykh Mater. Akad. Nauk Ukr. SSR, Kiev, 1981, p. 58
87. G Erker, T Mühlenbernd *J. Organomet. Chem.*, 1987, **319** 201
88. I F Urazovskii, A P Moravskii, I E Nifant'ev *IV Vsesoyuznaya Konferentsiya po Metalloorganicheskoi Khimii: Tezisy Dokladov* (The IVth All-Union Conference on Organometallic Chemistry: Abstracts of Reports), Izd. Kazan. Gos. Univ., Kazan, 1988, Part 1, p. 58
89. L E Shrock, C P Brock, T J Marks *Organometallics*, 1987, **6** 201
90. I I Grinval'd, B V Lokshin, V P Mar'in, N K Rudnevskii *Dokl. Akad. Nauk SSSR*, 1988, **298** 366
91. I I Grinval'd, B V Lokshin, N K Rudnevskii, V P Mar'in *Dokl. Akad. Nauk SSSR*, 1988, **298** 1142
92. Yu A Andrianov, V P Mar'in, O N Drushkov, et al. *IV Vsesoyuznaya Konferentsiya po Metalloorganicheskoi Khimii: Tezisy Dokladov* (The IVth All-Union Conference on Organometallic Chemistry: Abstracts of Reports), Izd. Kazan. Gos. Univ., Kazan, 1988, Part 1, p. 29

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Aza analogues of organic and inorganic oxygen compounds of selenium

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ABSTRACT. In this review information is presented on the methods of synthesis and physical and chemical properties of the aza analogues of selenoxides, selenones, derivatives of seleninic and selenous acids, and selenium dioxide—compounds which formally contain selenium–nitrogen double bonds.

The bibliography includes 56 references.

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I. Introduction

For organic and organoelemental chemistry the last 20–30 years have been characterised by a rapid growth of studies into the chemistry of aza analogues of organic and inorganic oxygen compounds of elements in Groups V and VI of the Periodic Table, formed by the formal replacement of oxygen atoms in the E = O or $E(=O)_2$ group (E = P, As, Sb, Bi, S, Se, Te by an imino group (=NR). Compounds that contain E = NR, E(O) = NR, or $E(=NR)_2$ groups are of interest because they often have properties which are not typical of their oxygen analogues. Moreover, the variation in character of the radical on the imide nitrogen atom within each separate class of compounds leads not only to a wide structural diversity but also to a considerable variation in properties. Especially marked progress has been made in the chemistry of imido compounds of phosphorus and sulphur. At the present time there exist the extensive separate branches of organophosphorus and organosulphur chemistry, which have undoubtedly stimulated research into the chemistry of imido compounds of other elements, in particular, selenium.

The first examples of imido compounds of selenium—*N*-arylsulphonylselenimides—were obtained in 1962, but more intensive and systematic studies in this field were started in the 1970's.

Aza analogues of selenoxides, selenones, seleninic and selenous acid derivatives, and selenium dioxide are known at the present time. There is still no standard nomenclature for these classes of selenium compounds. In the present review we shall follow the nomenclature accepted for the analogous sulphur compounds which appear to us to correspond most closely to the IUPAC rules:

$R^1R^2Se = NR$—selenimides,
$R^1R^2Se(O) = NR$—selenoximides,
$R^1Se(=NR)Hal$—arene-*N*-R-imidoseleninyl halides,
$Hal_2Se = NR$—*N*-R-imidoselenous dihalides
N-R-imidoselenyl halides,
$RN = Se = NR^1$—selenium diimide derivatives,
RN = Se = O—selenylamines.

II. Selenimides

Among the aza analogues of selenoxides—*N*-R-selenimides—*N*-arylsulphonyl- and *N*-carbacyl-selenimides $R^1R^2Se = NR$ [R = SO_2R^3 (I), COR^3 (II)] are known at the present time. The methods of synthesis of *N*-R-selenimides and thier sulphur analogues, the corresponding *N*-R-sulphimides,[1] as a rule are similar, but there are also considerable differences between them.

A general and most simple method for the synthesis of *N*-arylsulphonylselenimides (I) is the oxidative imination of selenides with *N*-sodium-*N*-chloramides of arenesulphonic acids:[2–6]

$$R^1R^2Se + ArSO_2NNaCl \rightarrow R^1R^2Se{=}NSO_2Ar + NaCl, \quad (I)$$

R^1, R^2 = Alk, Ar, $ArCH_2$.

The reaction occurs in acetonitrile,[6] dimethylformamide,[3,5] a mixture of acetonitrile and methanol,[3] and methanol,[4] generally at 20 °C and using anhydrous arenesulphonic acid *N*-sodium-*N*-chloramides.

Selenimides (I) are also obtained by the successive treatment of selenides with t-butyl hypochlorite and *N*-sodium arenesulphonamides at –25 to –40 °C in acetonitrile or chloroform[7,8] or at 20 °C in carbon tetrachloride:[9]

$$R^1R^2Se \xrightarrow[2)\ ArSO_2NHNa]{1)\ t\text{-}BuOCl} (I) + NaCl + t\text{-}BuOH.$$

An analogous reaction is used to obtain *N*-R-sulphimides.[10] It has been proposed that a t-butoxychlorosulphurane is formed as an intermediate in this process. Treatment of diaryl or aryl alkyl selenides with t-butyl hypochlorite gives t-butoxychloroselenanes, which have been isolated and characterised:[9,11]

$$R^1R^2Se + t\text{-}BuOCl \underset{150°C}{\overset{20°C}{\rightleftarrows}} R^1R^2Se(OBu\text{-}t)Cl. \quad (III)$$

Compounds (III) are colourless crystalline products, soluble in organic solvents (benzene, chloroform, methylene chloride, 1,2-dichloroethane), and on heating to 130–140 °C in a vacuum they sublime but at atmospheric pressure at 150 °C decompose to the initial selenides and t-butyl hypochlorite. The Se–Cl bond in compounds (III) is covalent; their specific electrical conductivity in dichloroethane is virtually the same as the electrical conductivity of the solvent.[9] Compound (III), $R^1 = R^2$ = Ph, is hardly hydrolysed at all after the prolonged action of water at 20 °C, but on boiling for 2–3 h it decomposes to form a mixture of diphenyl selenoxide and

diphenylselenium dichloride (the latter is formed by the reaction of diphenyl selenoxide and hydrogen chloride):

$$Ph_2Se(OBu\text{-}t)Cl \xrightarrow[-t\text{-}BuOH]{H_2O} [Ph_2SeO + HCl] \rightarrow$$
$$\rightarrow {}^1/_2\, Ph_2SeCl_2 + {}^1/_2\, Ph_2SeO + {}^1/_2\, H_2O.$$

If hydrogen chloride is removed from the reaction mixture (by prolonged standing in a vacuum desiccator above caustic potash), only diphenyl selenoxide is obtained.[9]

Compound (III), $R^1 = R^2 = Ph$, is also formed by reaction of diphenylselenium dichloride with t-butyl hypochlorite, but this reaction is reversible and is displaced towards formation of the selenane only by removal of chlorine from the reaction mixture:[9]

$$Ph_2SeCl_2 + t\text{-}BuOCl \underset{0^\circ C}{\overset{60^\circ C}{\rightleftharpoons}} (III) + Cl_2.$$

Alkoxychloroselenanes (III) are also formed by the reaction of R^1R^2-selenium dichlorides with alkoxides in a molar ratio of 1 : 1.[12] When compounds (III) are treated with the sodium derivative of benzenesulphonamide or benzamide, the corresponding *N*-R-selenimides (I) and (II) are obtained:[9]

$$(III) + RNHNa \xrightarrow{20\ ^\circ C,\ CCl_4} \underset{(I),\ (II)}{Ph_2Se = NR} + t\text{-}BuOH,$$
$$R = PhSO_2\ (I),\ PhC(O)\ (II).$$

However, in order to prepare compounds (I) or (II) it is not necessary to isolate compounds (III) since the reaction can be carried out in one stage as shown below.

The following relatively simple and general method for the synthesis of *N*-R-selenimides (I) and (II) is the reaction of selenoxides with sulphonamides and carboxamides:[5,7,13–15]

$$R^1R^2SeO + RNH_2 \rightarrow \underset{(I),\ (II)}{R^1R^2Se{=}NR} + H_2O.$$

The reaction conditions are dependent on the nature of the amides and the substituents on the selenium atom. Dibenzyl selenoxide and methyl aryl selenoxides react with arenesulphonamides and trifluoroacetamide in chloroform, acetonitrile, or benzene on heating[5,7,13,15] or even at 20 °C when water is removed.[7,14] Acetamide or chloroacetamide do not react under these conditions. When diphenyl selenoxide is refluxed with *p*-nitrobenzamide, the corresponding *N*-*p*-nitrobenzoylselenimide is formed in low yield.[13] The reaction of diaryl selenoxide with benzamide or trichloroacetamide was carried out in the presence of acetic anhydride.[15]

When diphenyl selenoxide is heated with aromatic amines in the presence of dehydrating media, and also when diphenylselenium dichloride is reacted with aromatic amines in the presence of triethylamine, diphenyl selenide and the corresponding azobenzenes are formed.[16]

N-Arylsulphonylselenimides (I) are readily obtained by the reaction of diaryl selenoxides with bis(arylsulphonyl)diimides of sulphur or selenium[17] and also with aldimines:[18]

$$Ar_2SeO \xrightarrow[-Ar^2CHO]{\overset{(ArSO_2N{=})_2E,\ (E=S,\ Se)}{-EO_2}\quad \overset{}{Ar^1SO_2N{=}CHAr^2}} Ar_2Se{=}NSO_2Ar.$$

Arene-*N*-arylsulphonylimidoseleninyl chlorides react with styrene to form *Se*-aryl-*Se*-styryl-*N*-arylsulphonylselenimides:[19]

$$ArSe(=NSO_2Ar^1)Cl + CH_2{=}CHPh \rightarrow Ar(PhCH{=}CH)Se(=NSO_2Ar^1).$$

Se-Methyl-*Se*-aryl-*N*-phenylsulphonylselenimides are obtained by reaction of methylarylselenium dichloride with *Te*,*Te*-diaryl-*N*-phenylsulphonyltellurimides:[20]

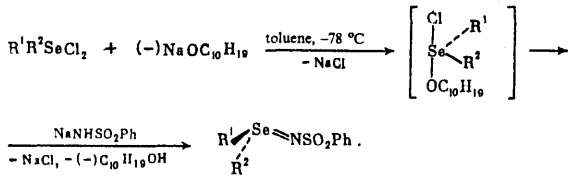
$$Ar_2Te{=}NSO_2Ph + CH_3(Ar^1)SeCl_2 \xrightarrow{benzene}$$
$$\rightarrow CH_3(Ar^1)Se{=}NSO_2Ph + Ar_2TeCl_2.$$

Selenimides (I) and (II) are relatively stable, colourless crystalline compounds. According to the data of X-ray diffraction analysis of compounds $PH_2Se = NSO_2Ph$[21] and $Ph_2Se = NSO_2C_6H_4CH_3$-*p*,[22] the length of the selenium–nitrogen bond (1.82 and 1.787 Å) is greater than the calculated length of a selenium–nitrogen double bond (1.628 Å) and also a single selenium–nitrogen with a high degree of double bond character, for example, in $Ph_3P = NSeCl_3$ (1.680 Å) and $(Ph_3P = N)_2SeCl_2$ (1.725 Å[22]), whereas the sulphur (VI)–nitrogen bond (1.60 Å[21] and 1.598 Å[22]) is shorter than a single bond (1.69 Å[22]).

From the results of X-ray diffraction analysis and the IR spectra of compounds (I) and (II) (using ^{15}N isotope exchange) the following bands were attributed to ν(Se = N): 550–590 cm^{-1},[5] 572 cm^{-1},[22] 675 cm^{-1};[23] and for ν(S(VI)–N): 930–950 cm^{-1},[5,22,23] [in two studies[14,24] ν(Se = N) in compounds (I) was assigned to the regions at 890 cm^{-1} [14] and 930–950 cm^{-1},[24] while ν(S(VI–N) was assigned to 672–677 cm^{-1}.[24] The results of these studies provide the basis for the proposal that the loss of double bond character of the Se = N bond and the considerable double bond characer of S(VI)–N in compounds (I) are due to the high contribution of resonance structures with a positive charge on the selenium atom:[5,21–24]

$$Ph_2Se{=}NSO_2Ar \longleftrightarrow Ph_2\overset{+}{S}e{-}\overline{N}SO_2Ar \longleftrightarrow Ph_2\overset{+}{S}e{-}N{=}S\begin{matrix}O^-\\ \\ O\end{matrix}$$
$$\qquad\qquad\qquad

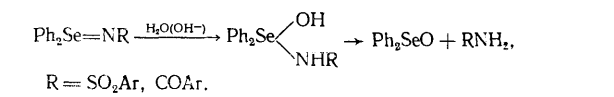
enrichment of one of the stereoisomers occurs at the stage where a compound of tetracoordinate selenium is formed:[12]



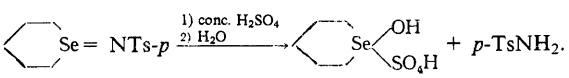
Asymmetric induction also occurs on reaction of asymmetric selenoxides with (+)- or (−)-10-camphorsulphonamides[14,18] and also with (+)- or (−)-camphorsulphonylbenzaldimine.[18]

The covalent radius of selenium (1.16 Å) is higher than the covalent radius of sulphur (1.02 Å), and the length of the Se = N bond (1.787–1.82 Å)[21,22] is greater than the length of the S = N bond (1.628–1.638 Å),[1] which is due to the greater degree of polarisation of the selenium-nitrogen bond. This is also confirmed by comparing the PMR spectra of selenimides and sulphimides with coresponding structures. The signal from the α-protons in the PMR spectra of selenimides occurs at higher field than in the corresponding sulphimides.[5]

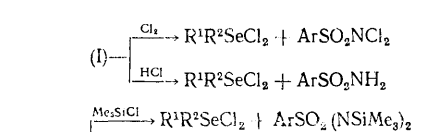
The difference in the length of E = N bonds (E = S, Se) and their degree of polarity also affect the relative reactivity of selenimides and sulphimides. In contrast to *N*-arylsulphonylsulphimides,[1] selenimides (I) are much less stable towards hydrolysis. Compounds (I) and (II) are unchanged on treatment with dilute acids and bases at 20 °C, but on heating or on treatment with concentrated alkali in alcohol they are rapidly hydrolysed to the corresponding selenoxide and arenesulphonamide.[3,4] The formation of an intermediate hydrated structure has been proposed when hydrolysis occurs or in the preparation of selenimides from selenoxides and amides.[5,6]

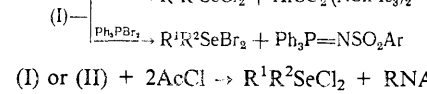


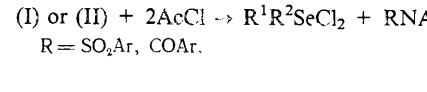
A compound with a selenurane structure was obtained by reaction of *N*-tosyl-*Se*,*Se*-pentamethyleneselenimide with sulphuric acid (−50 °C) followed by hydrolysis:[5]

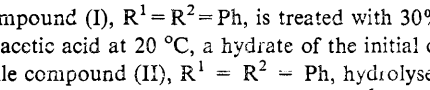


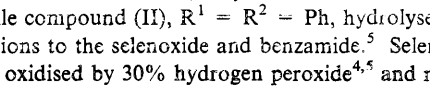
The Se = N bond in selenimides is very readily cleaved on treatment with chlorine, hydrogen chloride,[4] acetyl chloride, trimethylchlorosilane, or triphenylphosphine dibromide:[25]





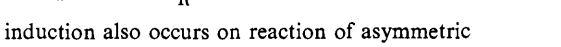




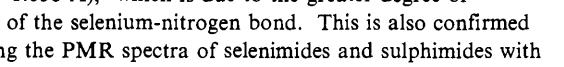


When compound (I), $R^1 = R^2 = Ph$, is treated with 30% hydrogen peroxide in acetic acid at 20 °C, a hydrate of the initial compound is formed, while compound (II), $R^1 = R^2 = Ph$, hydrolyses under these conditions to the selenoxide and benzamide.[5] Selenimides (I) and (II) are oxidised by 30% hydrogen peroxide[4,5] and nitrogen dioxide[4] at 20 °C or with an aqueous solution of potassium permanganate on boiling[5] to the corresponding selenones and amides:

When selenimides (I) are reacted with triphenylphosphine, the corresponding selenide and triphenylphosphine imide are formed in quantitative yield:[5]



Selenimides (II) decompose on heating to selenides and isocyanates[5]



In a study of the kinetics of thermolysis of selenimides and sulphimides $Ph_2Se=NCOPh$ and $Ph_2S = NCOPh$ it was established that the former decomposes 300 times faster than the latter, with the entropies of activation for these reactions being similar. This is undoubtedly due to the weaker selenium–nitrogen bond.[5]

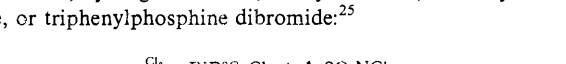
III. Selenoximides

At the present time only *Se*,*Se*-diaryl-*N*-arylsulphonylselenoximides (IV) are known among amido derivaties of hexavalent selenium. Compounds (IV) are obtained by the reaction of diaryl selenones with *N*-sulphonylarenesulphonamides,[4,26] and also with *N*,*N*′-diarylsulphonyldiimides of selenium or sulphur:[17]

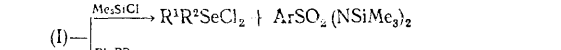
It should be noted that sulphones do not react with *N*-sulphonylarenesulphonamides.

In the IR spectra of compounds (IV), ν(Se = N) occurs in the region 930–910 cm^{-1}. It was concluded from the fine structure of the UV spectra that the fragment >Se(O)(=NSO_2−) has a rigid structure which interacts weakly with the π-system of the aromatic rings.[27]

Compounds (IV) remain unchanged on prolonged standing in air, they are stable to water at 100 °C, and are not affected by acids and bases at 20 °C. However, on prolonged heating with a 2 N solution of caustic soda they are hydrolysed to diaryl selenones and arenesulphonamides.



When treated with dry hydrogen chloride compounds (IV) decompose to form diarylselenium dichlorides, arenesulphonamides, chlorine, and water.



In contrast to selenimides (I), selenoximides (IV) do not react with elemental chlorine.[26]

IV. Arene-*N*-R-imidoseleninyl chlorides

The main method for the synthesis of arene-*N*-R-imidoseleninyl chlorides (V) is the oxidative imination of areneselenenyl chlorides or selenol derivatives with *N*-halo compounds. Compounds (V) are very readily formed by reaction of *Se*-trimethylsilyl- or *Se*-benzoylselenols with *N,N*-dichloramides of arenesulphonic acids, carboxylic, carbon, or phosphoric acids.[19,28-30] The reactions occur very readily, and trimethylchlorosilane or benzoyl chloride are easily extracted from the reaction mixture:

$$ArSeSiMe_3 + RNCl_2 \xrightarrow[-15\text{ to }5\ ^\circ C]{CCl_4} \underset{(V)}{ArSe(=NR)Cl} + Me_3SiCl,$$

$$R = SO_2Ar,\ COAr\ \ COOC_2H_5,\ (AlkO)_2P(O).$$

$$p\text{-}BrC_6H_4SeCOPh + PhSO_2NCl_2 \rightarrow p\text{-}BrC_6H_4Se(=NSO_2Ph)Cl + PhCOCl.$$

Arene-*N*-arylsulphonylimidoseleninyl chlorides are also formed by reaction of areneselenenyl chlorides with *N*-sodium-*N*-chloramides of arenesulphonic acids:[19]

$$ArSeCl + PhSO_2NNaCl \xrightarrow[10-20^\circ C]{CCl_4} (V) + NaCl.$$

When areneselenenyl chlorides are reacted with *N,N*-dichloramides of sulphonic and carboxylic acids, arylselenium trichlorides are formed together with chlorides (V):[19,29]

$$2ArSeCl + RNCl_2 \rightarrow (V) + ArSeCl_3,$$
$$R = SO_2Ar^1,\ COAr^1.$$

Diselenides also readily react with *N,N*-dichloramides to form chlorides (V) and areneselenenyl chlorides:[19,29]

$$ArSeSeAr + RNCl_2 \rightarrow (V) + ArSeCl.$$

Most likely when ArSeX reacts with *N,N*-dichloramides compounds of tetracoordinate selenium are first formed, undergoing subsequent conversion to form chlorides (V):

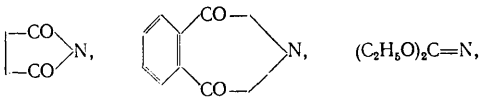
$$ArSeX + RNClZ \longrightarrow \left[\begin{array}{c} Cl \\ | \\ ArSe-X \\ | \\ R-N-Z \end{array}\right] \longrightarrow (V) + XZ,$$

$X = SiMe_3$, COR, SeR, Cl; $Z = Cl$, Na.

This is confirmed by studying the reactions of areneselenenyl chlorides with *N*-chlorimides and *N*-monochloramides of carboxylic acids, and with t-butyl hypochlorite, etc.

When areneselenenyl chlorides are reacted with *N*-chlorimides, fairly stable compounds of tetracoordinate selenium (VI) are obtained:[31]

$$ArSeCl + R_2NCl \rightarrow Ar(R_2N)SeCl_2,$$

$R_2N =$  , $(C_2H_5O)_2C{=}N$,

$PhC(OAlk){=}N$, $Ph_2C{=}N$ etc.

Compounds of tetracoordinate selenium (VII) and (VIII) are formed by reaction of areneselenenyl chlorides with carboxylic acid *N*-monochloramides[32,33] or with 6-butyl hypochlorite:[11,34]

$$ArSeCl + RCONHCl \rightarrow \underset{(VII)}{Ar(RCONH)SeCl_2},$$

$$ArSeCl + t\text{-}BuOCl \rightarrow \underset{(VIII)}{Ar(t\text{-}BuO)SeCl_2}.$$

Arene-*N*-R-imidoseleninyl chlorides (V) are very readily obtained when arylselenium trichlorides are treated with bis(trimethylsilyl)-amides of sulphonic or carboxylic acids[29] or by heating arylselenenium trichlorides with *N,N*-dichloramides.[29] However, the latter reaction is reversible and chlorides (V) are only obtained when chlorine is removed from the reaction mixture.

$$ArSeCl_3 \begin{cases} \xrightarrow{RN(SiMe_3)_2} (V) + 2Me_3SiCl \\ \xrightarrow{RNCl_2,\ \Delta} (V) + Cl_2 \end{cases}$$

$R = SO_2Ph$, COPh.

When *N*-chlorohexamethyldisilazane is reacted with areneselenenyl chloride and arylselenium trichloride in the ratio 1 : 1 : 1, compounds which apparently have the structure of arene-*N*-[aryl(dichloro)-seleno]imidoseleninyl chlorides (IX) are formed.[35] The above-mentioned reactions of areneseleninyl chlorides with *N*-chlorimides and areneselenium trichlorides with bis(trimethylsilyl)amides provided the basis for the following proposed reaction scheme:

$$ArSeCl + ClN(SiMe_3)_2 \rightarrow [Ar(Cl_2)SeN(SiMe_3)_2] \rightarrow$$
$$\xrightarrow[-2Me_3SiCl]{ArSeCl_3} \underset{(IX)}{ArSe(Cl_2)N{=}Se(Cl)Ar}.$$

The formation of isomeric chlorides (IX) as a result of the following reaction acts as confirmation of this scheme and the structure of the compounds formed.

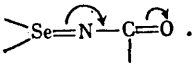
$$p\text{-}ClC_6H_4SeCl + ClN(SiMe_3)_2 \rightarrow [p\text{-}ClC_6H_4Se(Cl_2)N(SiMe_3)_2] \rightarrow$$
$$\xrightarrow{+PhSeCl_3} \underset{(IXa)}{p\text{-}ClC_6H_4Se(Cl_2)N{=}Se(Cl)Ph};$$

$$PhSeCl + ClN(SiMe_3)_2 \rightarrow [PhSe(Cl_2)N(SiMe_3)_2] \rightarrow$$
$$\xrightarrow{p\text{-}ClC_6H_4SeCl_3} \underset{(IXb)}{PhSe(Cl_2)N{=}Se(Cl)C_6H_4Cl\text{-}p}.$$

Compounds (IX) are also obtained by reaction of *N*-chlorohexamethyldisiliazane with benzeneselenenyl chloride or phenylselenium trichloride but in lower yield. The reactions are evidently more complex in these cases.[35]

N-R-Imidoseleninyl chlorides (V) and (IX) are colourless or pale yellow crystalline compounds, readily soluble in chloroform, dichloroethane, and acetonitrile; on standing in the absence of moisture they decompose after 3–5 days.[19,28,29,35]

In the IR spectra of *N*-arylsulphonylimidoseleninyl chlorides (V), $R = SO_2Ar$, $\nu(Se{=}N)$ apparently occurs in the region 910–950 cm^{-1},[24,27] while for *N*-aroylimidoseleninyl chlorides (V), R = COAr, it is in the region 845–870 cm^{-1}.[29] The shift to longer wavelength is evidently due to delocalisation of the π-electrons in the system



Chlorides (V) and (IX) are readily hydrolysed to seleninic acids and amides:[19,28,29,35]

$$(V) + 2H_2O \rightarrow ArSeOOH + RNH_2 + HCl,$$
$$(IX) + 4H_2O \rightarrow 2ArSeOOH + NH_4Cl + 2HCl.$$

When treated with dry hydrogen chloride or chlorine, compounds (V) and (IX) undergo cleavage of the Se = N bond to form arylselenium trichlorides and amides or *N,N*-dichloramides:[19,29,35]

$$(V) \begin{cases} \xrightarrow{2HCl} ArSeCl_3 + RNH_2 \\ \xrightarrow{2Cl_2} ArSeCl_3 + RNCl_2, \end{cases}$$

$$(IX)\begin{cases}\xrightarrow{4HCl} 2ArSeCl_3 + NH_4Cl\\ \xrightarrow{3Cl_2} 2ArSeCl_3 + [NCl_3]\end{cases}.$$

Chlorides (V) react with secondary amines to form the corresponding *N*-R-imidoseleninic acid amides, which are colourless crystalline or liquid, compounds that are very readily hydrolysed by atmospheric moisture and slowly decompose on standing when moisture is excluded:[19,29]

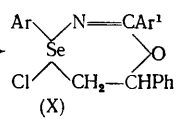
$$(V)\xrightarrow[-R_2NH.HCl\ \text{or}\ R_2NSiMe_3\ -Me_3SiCl]{2R_2NH} ArSe(=NR^1)NR_2$$

$R^1 = SO_2Ar,\ COAr;\ R_2N = (C_2H_5)_2N,$  .

Arene-*N*-arylsulphonylimidoseleninyl chlorides react with styrene to form a mixture of compounds from which *Se*-aryl-*Se*-styryl-*N*-arylsulphonylselenimides are isolated in about 50% yield:[19]

$$ArSe(=NSO_2Ar^1)Cl + PhCH{=}CH_2 \xrightarrow[-HCl]{20^\circ C} ArSe(=NSO_2Ar^1)CH{=}CHPh.$$

Arene-*N*-aroylimidoseleninyl chlorides react with styrene by a [2 + 4]-cycloaddition to form 1 : 1 adducts, which apparently have the structure of 5,6-dihydro-4-selena-1,3-oxazines (X):[29]

$$ArSe(=NCOAr^1)Cl + PhCH{=}CH_2 \rightarrow$$ 
(X)

Compounds (X) are colourless crystalline compounds, difficultly soluble in most organic solvents. In their IR spectra $\nu(C = N)$ is present at 1580 cm^{-1} and $\nu(Se-N)$ at 589 cm^{-1}, and there is no absorption in the region 840–870 cm^{-1} that is characteristic of the Se = N bond in the initial chlorides. The electrical conductivity of saturated solutions of compounds (X) in dichloroethane or methanol is higher than the electrical conductivity of the solvent by a factor of 10 or 100 respectively, which is an indication of the contribution from an ionic structure.[29]

V. *N*-R-imidoselenous dihalides

The first examples of this class of compounds—*N*-arylsulphonylimidoselenyl chlorides—were obtained in 1967 by reaction of selenium with arenesulphonic acid *N*,*N*-dichloramides.[36] It was subsequently established that oxidative imination of selenium has a wide range of application. Selenium reacts in a similar manner with the *N*,*N*-dichloramides of sulphonic and benzoic acids, and with dialkyl *N*,*N*-dichlorophosphoramidate, *N*,*N*-dichlorourethane, *N*,*N*-dichloroalkylamines, and *N*,*N*-dichloroaminopentafluorosulphur to form the corresponding *N*-R-imidoselenyl chlorides (XI):[37–41]

$$Se + RNCl_2 \xrightarrow[20^\circ C]{CH_2Cl_2\ \text{or}\ CCl_4} RN{=}SeCl_2, \quad (XI)$$

$R = SO_2Ar,\ COAr,\ C_2H_5OCO,\ (AlkO)_2PO,\ Me_2C(CN),$
$(CH_2)_5(CN),\ R_F,\ F_5S.$

In inert solvents (methylene dichloride, carbon tetrachloride, dichloroethane, etc.) the reactions generally take place at 20 °C or with slight evolution of heat.

Sulphur, as a rule, reacts with *N*,*N*-dichloramides and *N*,*N*-dichloramines in a similar manner.[42] However, it should be noted that there are some differences between the oxidative imination of sulphur and selenium. Imination of sulphur is assisted when catalysts are present (iodine, tetraalkylammonium salts, etc.).[42] In most cases selenium reacts with *N*,*N*-dichloro compounds more readily than sulphur and the reaction is unaffected by catalysts. When sulphur is reacted with sulphinic acid *N*,*N*-dichloramides, the corresponding *N*-R-imidothionyl chlorides or sulphur diimide derivatives are formed depending on the ratio of reactants and the reaction conditions.[42] When selenium reacts with these reagents only *N*-R-imidoselenyl chlorides are obtained regardless of the ratio.[37]

It was established that *N*-perfluoroalkylimidoselenyl chlorides are also formed by reaction of *N*,*N*-dichloroperfluoroalkylamines with selenium monochloride:[39,40]

$$RNCl_2 + Se_2Cl_2 \xrightarrow[-50^\circ C]{CCl_3F} (XI) + SeCl_4,$$
$$R = CF_3,\ C_2F_5.$$

It has been reported that *N*-R-imidothionyl chlorides $Cl_2 = SNCOR$, R = Ar, Alk, are obtained by reaction of sulphur with carboxylic acid *N*-monochloramides.[42] Selenium also very readily reacts with carboxylic acid *N*-monochloramides, but in this case derivatives of orthoselenous acid—bis(R-carbacylamido)selenium dichlorides (XII)—are formed:[31–33]

$$2RCONHCl + Se \rightarrow (RCONH)_2SeCl_2, \quad (XII)$$
$$R = Ar,\ Alk.$$

When selenium is reacted with *N*,*N*-dichloroperfluoroaryl- or *N*,*N*-dichlorotetrafluoropyridyl-4-amines, the corresponding azo compounds and selenium tetrachloride are formed:[39]

$$Se + 2RNCl_2 \rightarrow RN{=}NR + SeCl_4,$$
$$R = C_6F_5,\ p\text{-}CF_3C_6F_4,\ 4\text{-}C_5F_4N.$$

The reaction schemes for the oxidative imination of both selenium and sulphur have not yet been established. It has been proposed that sulphur or selenium on reacting with *N*,*N*-dichloro compounds by a radical or ionic mechanism form the intermediates RN(Cl)ECl, which, depending on the nature of R (the state of the E–Cl bond), undergo conversions by three different routes—to form *N*-R-imidothionyl chlorides (*N*-R-imidoselenyl chlorides), azo compounds, or derivatives of sulphur diimides (the latter conversion is not typical for selenium):[39]

$$RNCl_2 + E \rightarrow [RN(Cl)ECl]\begin{cases}\xrightarrow{E=S,\ Se} RN{=}ECl_2\\ \xrightarrow{-ECl_2} [RN{:}] \rightarrow {}^1/_2RN{=}NR\\ \xrightarrow{E=S,\ -Cl_2} [RN{=}S] \rightarrow {}^1/_2RN{=}S{=}NR + {}^1/_2S_8\end{cases}$$

N-R-Imidoselenyl chlorides and fluorides are very readily formed by the reaction of selenium tetrachloride or tetrafluoride with *N*,*N*-bis-(trimethylsilyl)amides:[43,44]

$$RN(SiMe_3)_2 + SeHal_4 \rightarrow RN{=}SeHal_2 + 2Me_3SiHal,$$
$$R = MeSO_2,\ PhSO_2,\ PhCO;\quad Hal = Cl,\ F.$$

N-Pentafluorotelluroimidoselenyl fluoride is obtained by reaction of selenium tetrafluoride with *N*-trimethylsilylpentafluorotellur-amine:[44]

$$F_5TeNHSiMe_3 + SeF_4 \rightarrow F_5TeN{=}SeF_2 + Me_3SiF + HF.$$

On heating pentafluorotelluramine with selenium tetrachloride, *N*-pentafluorotelluroimidoselenyl chloride is formed:[44]

$$F_5TeNH_2 + SeCl_4 \xrightarrow{CH_2Cl_2,\ \Delta} F_5TeN{=}SeCl_2 + 2HCl.$$

Selenium tetrachloride reacts on heating with *N,N*-dichlorobenzenesulphonamide to form *N*-phenylsulphonylimidoselenyl chloride:

$$PhSO_2NCl_2 + SeCl_4 \rightarrow PhSO_2N{=}SeCl_2 + 2Cl_2.$$
(XI)

However, this reaction is reversible and goes to the right only when chlorine is removed from the reaction mixture.[37]

N-R-Imidoselenyl chlorides and fluorides are colourless or pale yellow crystalline compounds with low stability. Their stability improves when the electronegativity of the radical R is increased. Out of the compounds of this class that are known at the present time the most stable are *N*-pentafluorotelluroimidoselenyl chlorides[44] and *N*-arylsulphonylimidoselenyl chlorides.[36,37] *N*-Perfluoroalkylimidoselenyl chlorides start to decompose immediately after preparation or distillation according to the scheme:[41]

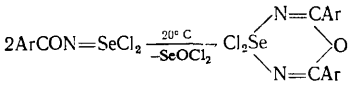
$$6R_FN{=}SeCl_2 \rightarrow 3R_FN{=}NR_F + 2SeCl_4 + 2Se_2Cl_2.$$

It is very likely that *N*-perfluoroarylimidoselenyl chlorides cannot be obtained because of their extremely low stability and not because there is a different pathway for the reaction between selenium and *N,N*-dichloroperfluoroarylamines.[39]

N-Pentafluorothioimidoselenyl chloride undergoes the following conversions even at room temperature:[40,41]

$$2F_5SN{=}SeCl_2 \xrightarrow{20^\circ C} 2F_3S{\equiv}N + SeCl_4 + SeF_4.$$

N-Aroylimidoselenyl chlorides slowly decompose at 20 °C with the elimination of selenyl chloride and giving compounds which apparently have the structure of 4-dichloro-4,1,3,5-selenaoxadiazines:



In the IR spectra of imidoselenyl chlorides (XI) the absorption due to ν(Se = N) varies over a quite broad region (Table 1). The lowest value of ν(Se = N) is that in *N*-aroylimidoselenyl chlorides; ν(C = O) (1600 cm^{-1}) is also decreased in these compounds at the same time, which is probably due to delocalisation of electron density in the group[38]

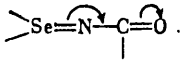


Table 1. Frequencies of the stretching vibrations of the Se = N bond in the IR spectra of *N*-R-imidoselenyl chlorides.

R	ν (Se=N)·см⁻¹	Refs.	R	ν (Se=N), см⁻¹	Refs.
F_5S	1045	[40]	C_2F_5	933	[41]
F_5Te	965	[44]	$(CH_3)_3C$	960	[37]
$ArSO_2$	980—975	[24, 37]	$(CH_2)_4C(CN)$	950	[37]
CF_3	962	[41]	ArCO	765—750	[38]

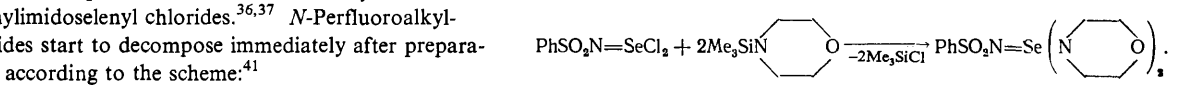
Compounds (XI) are very reactive. They are hydrolysed even by moist air to form amides and amines, selenous acid, and hydrogen chloride.[37] Acidolysis of *N*-phenylsulphonylimidoselenyl chlorides with formic acid results in the formation of benzenesulphonamide and selenyl chloride:[37]

$$PhSO_2N{=}SeCl_2 + 2HCOOH \rightarrow PhSO_2NH_2 + SeOCl_2 + 2CO.$$

Compounds (XI) very readily undergo cleavage of the Se = N bond when treated with hydrogen chloride or chlorine:[37,38]

$$(XI) \begin{cases} \xrightarrow{2HCl} RNH_2 + SeCl_4 \\ \xrightarrow{2Cl_2} RNCl_2 + SeCl_4 \end{cases}$$
R = $ArSO_2$, ArCO, Alk.

When *N*-phenylsulphonylimidoselenyl chloride is reacted with *N*-trimethylsilylmorpholine, the dimorpholide of *N*-phenylsulphonylimidoselenous acid is obtained:[37]

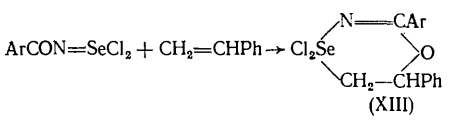


When compounds (XI) are reacted with *N,N*-bis(trimethylsilyl)-amides, selenium diimide derivatives are formed,[38,45] (see below).

N-R-Imidoselenyl chlorides react very readily with unsaturated compounds. The course of the reaction depends on the nature of the acyl residue. For example, *N*-phenylsulphonylimidoselenyl chloride reacts with styrene in the ratio 1 : 2 to form *Se,Se*-[bis(2-chloro-2-phenylethyl)]-*N*-phenylsulphonylselenimide:[37]

$$PhSO_2N{=}SeCl_2 + 2PhCH{=}CH_2 \rightarrow PhSO_2N{=}Se(CH_2CHClPh)_2.$$

N-Aroylimidoselenyl chlorides react with ethylenic hydrocarbons in the ratio 1 : 1 by a [4 + 2]-cycloaddition mechanism to form 4,4-dichloro-5,6-dihydro-4,1,3-selenaoxazines (XIII):[38,46]


(XIII)

Compounds (XIII) are colourless crystalline compounds which are difficultly soluble in most organic solvents. When compound (XIII), Ar = COPh, is treated with methanol, (2-phenyl-2-benzoyloxyethyl)-(methoxyl)selenium dichloride is obtained:[38]

$$(XIII) + MeOH \rightarrow PhC(O)OCH(Ph)CH_2Se(OMe)Cl_2.$$

For other properties of compounds (XIII), see below.

VI. Aza analogues of selenium dioxide

Out of the aza analogues of oxygen compounds of sulphur, the nitrogen analogues of sulphur dioxide—thionylamines and thionylamides RN = S = O and sulphur diimide derivatives RN = S = NR—have attracted particular attention. The high reactivity and preparative availability of these classes of compounds have offered considerable potential for their use in organic synthesis, which is suggested by the large number of publications, review articles, and monographs (see bibliograph of Bussas et al.[47]). This has undoubtedly stimulated interest in the aza analogues of selenium dioxide—derivatives of selenium diimide and selenylamines or selenylamides.

1. Selenium diimide deriatives

One of the main methods of synthesising symmetrical deriatives of selenium diimide (XIV) is the reaction of selenium tetrafluoride or tetrachloride with bis(trimethylsilyl)amides of sulphonic or carboxylic acids:[43,45,48–50]

$$SeHal_4 + 2RN(SiMe_3)_2 \xrightarrow[-4Me_3SiHal]{15-20^\circ C} RN{=}Se{=}NR, \quad (XIV)$$
$$R = ArSO_2,\ ArCO,\ AlkCO;\quad Hal = Cl,\ F.$$

Symmetric and asymmetric derivatives of selenium diimide are obtained by the reaction of hexamethyldisilylamides with *N*-acylimidoselenyl chlorides or fluorides[43,45,49]

$$RN{=}SeHal_2 + R^1N(SiMe_3)_2 \xrightarrow[-2Me_3SiHal]{\text{ether, } 0-20\ ^\circ C} RN{=}Se{=}NR^1,$$
$$R = ArSO_2,\ PhCO,\quad R^1 = ArSO_2,\ ArCO,\ AlkCO;$$
$$Hal = Cl,\ F.$$

Selenium bis(sulphonyl)diimides are unexpectedly obtained by reaction of *N*,*N*-bis(trimethylsilyl)amides with selenyl fluoride or chloride.[43,51] By analogy with the reaction of thionyl chloride[47] formation of the corresponding *N*-R-selenylamides RN = Se = O would be expected.[47] However, only selenium diimide derivatives are formed as a result of this reaction, whatever the ratio of reactants:

$$SeOHal_2 + RN(SiMe_3)_2 \xrightarrow{-Me_3SiHal} [RN{=}Se{=}O] \xrightarrow[-(Me_3Si)_2O]{RN(SiMe_3)_2} (XIV),$$
$$R = PhSO_2,\ MeSO_2,\ CF_3CO,\ CF_3SO_2;\quad Hal = Cl,\ F.$$

When *N*-phenylsulphonylimidoselenyl fluoride is reacted with hexamethyldisiloxane, selenium bis(phenylsulphonyl)diimide is obtained in place of the expected *N*-selenylbenzenesulphonamide. It has been proposed that in this reaction, as in the previous one, *N*-selenylamides are formed as intermediates:[43]

$$PhSO_2N{=}SeF_2 + (Me_3Si)_2O \xrightarrow{-2Me_3SiF} [PhSO_2N{=}Se{=}O] \xrightarrow[-SeOF_2]{PhSO_2N{=}SeF_2} (PhSO_2N{=})_2Se.$$

Selenium *N*,*N*-bis(trimethylsilyl)diimide is obtained by reaction of Li hexamethyldisilazane with selenyl chloride:[51]

$$2(Me_3Si)_2NLi + SeOCl_2 \rightarrow (Me_3SiN{=})_2Se + Me_3SiCl + LiCl.$$

Reaction of selenium tetrachloride with t-butylamine gives selenium bis(t-butyl)diimide:[52,53]

$$SeCl_4 + 6\ t\text{-}BuNH_2 \xrightarrow[-4\ t\text{-}BuNH_2HCl]{\text{ether, } 25\ ^\circ C} (t\text{-}BuN{=})_2Se.$$

Selenium diimide derivatives (XIX) are light yellow crystalline compounds that are fairly readily soluble in methylene dichloride and dichloroethane. They have low thermal stability—at 20 °C they can be kept for 2–3 days in the absence of moisture while on heating they rapidly decompose.[18,43,45,48–52] Selenium bis(t-butyl)diimide is a liquid which decomposes at room temperature to form *N*,*N*′-di(t-butyl)-2,4,5-triselena-1,3-diazolidine, which a yellow crystalline product:[52]

$$3(t\text{-}BuN{=})_2Se \xrightarrow[-(t\text{-}BuN{=})_2]{} \begin{array}{c} Se \\ /\ \backslash \\ t\text{-}Bu-N \quad N-Bu\text{-}t. \\ |\quad\ | \\ Se-Se \end{array}$$

Selenium bis(trifluoromethylseleno)diimide is stable only up to 80 °C. Above that temperature the compound decomposes:[51]

$$(F_3CSeN{=})_2Se \rightarrow CF_3SeSeCF_3 + Se + N_2.$$

Selenium bis(trimethylsilyl)diimide decomposes even at −48 °C. The structure of this compound has been demonstrated from its chemical reactions.[51]

In the IR spectra of selenium diimide derivatives, the intense absorption bands in the region 1000–900 cm^{-1} are due to the Se=N bond frequencies.[45,49] In the IR spectrum of selenium bis(t-butyl)-diimide two absorption bands at 998 cm^{-1} (*as*) and 650 cm^{-1} (*s*) have been attributed to stretching vibrations of the Se = N bond.[52] In the PMR spectrum of this compound (in $CDCl_3$ in the presence of shift reagents) at −30 °C there are two signals (δ 1.38 and 1.40) which coalesce at 5 °C. On the basis of this it was proposed that at low temperature selenium bis(t-butyl)diimide has a (*Z*/*E*)-configuration:[52]

$$\begin{array}{c} Bu\text{-}t \\ / \\ N{=}Se{=}N \\ | \\ t\text{-}Bu \end{array} .$$

Selenium diimide derivatives (XIV) are very reactive compounds. They are readily hydrolysed by atmospheric moisture to the corresponding amides or amines and selenous acid.[45,49] When treated with dry hydrogen chloride selenium diimides undergo cleavage of the Se = N bond to form the corresponding amides and selenium tetrachloride:[45]

$$(PhSO_2N{=})_2Se + 4HCl \rightarrow 2PhSO_2NH_2 + SeCl_4.$$

The reaction of selenium bis(arylsulphonyl)diimide with chlorine occurs in two stages. Firstly, when the reagents are reacted in the ratio 1 : 2, *N*,*N*-dichlorobenzenesulphonamide and *N*-phenylsulphonylimidoselenyl chloride are obtained, the latter decomposing on further treatment with chlorine to give *N*,*N*-dichlorobenzenesulphonamide and selenium tetrachloride:[45]

$$(PhSO_2N{=})_2Se \xrightarrow{2Cl_2} PhSO_2NCl_2 + PhSO_2N{=}SeCl_2 \xrightarrow[-SeCl_4]{2Cl_2} PhSO_2NCl_2.$$

Selenium bis(arylsulphonyl)diimides react with compounds containing an X=O group (aldehydes, dimethylformamide, diphenyl selenoxide, triphenylphosphine oxide, etc.) to form compounds with an X = NSO_2Ar group:[17]

$$(PhSO_2N{=})_2Se + 2X{=}O \rightarrow 2X{=}NSO_2Ph + SeO_2,$$
$$X = ArCH,\ Me_2NCH,\ Me_2S,\ Ph_2S,\ Ph_2Se,$$
$$Ph_3P,\ Ph_2Se(=O),\ (C_2H_5)_2NC_6H_4N.$$

Selenium bis(benzoyl)diimide (XIV), R = PhCO, reacts with dimethyl sulphoxide in a similar manner:[17]

$$(PhCON{=})_2Se + 2Me_2SO \rightarrow 2Me_2S{=}NCOPh + SeO_2.$$

Selenium bis(benzoyl)diimide does not react with aromatic aldehydes. However, in the presence of benzamide reaction occurs very readily and *N*,*N*′-dibenzoylamidals are formed.[17] Apparently in this case selenium bis(benzoyl)diimide acts as a dehydrating agent in the reaction between benzamide and aldehyde, and the rate of this reaction, which is a source of benzamide, is much higher than the rate of reaction between the selenium diimide and aldehydes. The overall equation for the reaction is as follows:

$$2ArCHO + 2PhCONH_2 + (PhCON)_2Se \rightarrow 2ArCH(NHCOPh)_2 + SeO_2.$$

Selenium bis(phenylsulphonyl)diimide initially reacts with triphenylphosphine to give a 1 : 1 adduct, which on treatment with a further mole of triphenylphosphine forms triphenylphosphine selenide and a compound which probably has the structure of *N,N'*-bis(phenylsulphonyl)-*N*-triphenylphosphoniohydrazinate:[17]

$$(PhSO_2N{=})_2Se + Ph_3P \rightarrow [PhSO_2N{-}Se{-}\overline{N}SO_2Ph] \rightarrow \underset{\overset{|}{{}^+PPh_3}}{} \xrightarrow[-Ph_3PSe]{Ph_3P} PhSO_2N{-}\overline{N}SO_2Ph.$$
$$\underset{\overset{|}{{}^+PPh_3}}{}$$

Triphenylphosphine oxide, benzonitrile, and selenium are formed from selenium bis(benzene)diimide on reacting with triphenylphosphine:[17]

$$(PhCON{=})_2Se + 2Ph_3P \rightarrow 2Ph_3PO + 2PhCN + Se.$$

Reaction of selenium bis(trimethylsilyl)diimide with benzenesulphonyl chloride gives the corresponding bis(phenylsulphonyl)diimide:[51]

$$(Me_3SiN{=})_2Se + PhSO_2Cl \rightarrow (PhSO_2N{=})_2Se + 2Me_3SiCl.$$

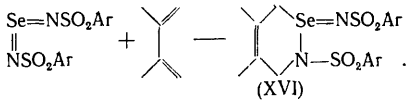
Selenium diimide derivatives react very readily with unsaturated compounds. The course of the reaction depends on the structure of the initial reagents. Disubstituted selenium diimides that contain just one acyl group on the nitrogen atom react with unsaturated compounds (styrene, cyclohexene, 1,1-diphenylethylene, etc.) by a [4 + 2]-cycloaddition mechanism to form 4-imino-5,6-dihydro-4,1,3-selenaoxazines, which are colourless crystalline compounds.[46,49] In particular, when selenium *N*-benzoyl-*N'*-phenylsulphonyldiimide is reacted with styrene, 4-phenylsulphonylimino-5,6-dihydro-2,6-diphenyl-4,1,3-selenaoxazine (XV) is formed, being identical to the compound obtained by reaction of compound (XIII), Ar = Ph, with bis(trimethylsilyl)benzenesulphonamide (see Section V):

$$\left.\begin{array}{l} PhSO_2N{=}Se{=}NCOPh + CH_2{=}CHPh \\ (XIII) + PhSO_2N(SiMe_3)_2 \end{array}\right\} \rightarrow PhSO_2N{=}Se \underset{CH_2{-}CHPh}{\overset{N{=}CPh}{\diagdown\!\!\diagup O}} \quad (XV)$$

On hydrolysis of both compound (XIII) and compound (XV) the same 2-phenyl-2-benzoyloxyethaneseleninic acid is obtained:[38,49]

$$\left.\begin{array}{l} (XIII) \xrightarrow[-HCl,\ -NH_4Cl]{3H_2O} \\ (XV) \xrightarrow[-PhSO_2NH_2,\ -NH_3]{3H_2O} \end{array}\right\} \rightarrow PhC(O)OCH(Ph)CH_2SeOOH.$$

Selenium bis(arylsulphonyl)diimide reacts with hydrocarbon dienes by a [2 + 4]-cycloaddition mechanism to form 1 : 1 adducts, which apparently have the structure of 3,6-dihydro-1-arylsulphonyl-2-arylsulphonylimino-2,1-selenazines (XVI):[50]



(XVI)

Compounds (XVI) are colourless crystalline compounds, stable on standing at 20 °C when moisture is excluded.

In 1976 Sharpless et al.[53,54] reported the synthesis of selenium *N,N'*-ditosyldiimide by reaction of chloramine-T with selenium or selenium tetrachloride with *p*-toluenesulphonamide. In fact, chloramine-T and chloramine-B readily react with selenium in methylene dichloride or dichloroethane in the ratio 2 : 1. However, the compounds formed in this process differ in composition and physical and chemical properties from the coresponding selenium bis(arylsulphonyl)diimides described above.[45,49,50] The compounds obtained from chloramine-B or chloramine-T and selenium by the method of Sharpless[53,54] are colourless, finely crystalline compounds with quite a sharp melting point. In contrast to the corresponding selenium bis(arylsulphonyl)diimides, they are insoluble in methylene dichloride, dichloroethane, and other organic solvents. On the basis of this it was proposed that when chloramine-B or chloramine-T react with selenium, the *N,N'*-disodium salts of bis(arylsulphonylamido)selenium dichloride (XVII) are formed:[50]

$$Se + 2ArSO_2NNaCl \rightarrow \underset{(XVII)}{[ArSO_2N(Na)]_2SeCl_2},$$
$$Ar = Ph,\ p\text{-}MeC_6H_4.$$

Indirect evidence for the structure of the "Sharpless products" is given by the reaction of selenium with carboxylic acid monochloramides, resulting in the formation of bis(aroylamino)selenium dichlorides (XII) (see Section V).[32,33]

When selenium tetrachloride is reacted with arenesulphonamides in the presence of triethylamine in dichloroethane (see the study of Sharpless[53]) selenium bis(arylsulphonyl)diimide is also possibly obtained. In fact, on mixing the reactants an orange-yellow colour characteristic of selenium diimides immediately appears. However, after 5–10 min the reaction mixture darkens and selenium separates out almost quantitatively. It was established by independent experiments that when triethylamine hydrochloride is added to selenium bis(arylsulphonyl)diimide in dichloroethane, the reaction mixture darkens after 1–3 min, selenium separates out, and a mixture of oily products of indeterminate structure is formed. It cannot be ruled out that selenium bis(arylsulphonyl)diimide forms a bis(triethylammonium) salt, which then decomposes:[50]

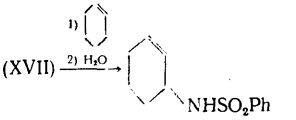
$$(ArSO_2N{=})_2Se + 2Et_3N{\cdot}HCl \rightarrow (ArSO_2NH{\cdot}Et_3N)_2SeCl_2.$$

This proposal is indirectly supported by the reaction of triethylamine hydrochloride with selenium bis(benzoyl)diimide, which results in the formation of bis(benzoylamino)selenium dichloride (XII) (see Section V):

$$(PhCON{=})_2Se + 2Et_3N{\cdot}HCl \rightarrow \underset{(XII)}{(PhCONH)_2SeCl_2} + 2Et_3N.$$

Compound (XII) has been isolated and identified; but if it is not immediately isolated from the reaction mixture, the latter gradually darkens (after 10–15 min) and selenium separates out.[50]

A difference between the properties of selenium diimide derivatives and "Sharpless products" is also revealed in reactions with unsaturated compounds. When (XVII) is reacted with olefins, products derived from allylic amidation[50] are obtained (cf. the studies of Sharpless[53,54]), for example:

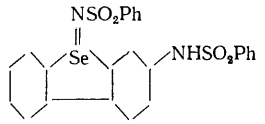


Selenium bis(arylsulphonyl)diimide also react with olefins, but the course of the reaction depends on the nature of the olefin. When α-methylstyrene is reacted with selenium bis(phenylsulphonyl)-

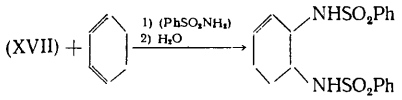
diimide, as also with compound (XVII), 2-phenyl-3-phenylsulphonylaminopropene is obtained[50] (cf. Sharpless[53,55]):

$$(PhSO_2N{=})_2Se \text{ or } (XVII) \xrightarrow[2)\ H_2O]{1)\ PhC(Me){=}CH_2} PhC(CH_2NHSO_2Ph){=}CH_2.$$

However, these compounds react in different ways with cyclohexene. Compound (XVII) gives *N*-benzenesulphonamido-2-cyclohexene, while from the products of the reaction between selenium bis(phenylsulphonyl)diimide and cyclohexene a product is isolated, which apparently has the structure of 1-phenylsulphonylamino-9-phenylsulphonylimino-9-selenaperhydrofluorene:[50]



When compounds (XVII) are reacted with cyclohexadiene in the presence of sulphonamide followed by hydrolysis, 1,2-bis(phenylsulphonylamino)-3-cyclohexene (XVIII) (cf. Sharpless[54]):



(XVIII)

When the products (XVI) of the reaction between disubstituted selenium diimides and hydrocarbon dienes were hydrolysed (Sharpless et al. suggested that these compounds were intermediates), it was not possible to obtain arylsulphonamidation compounds of the type (XVIII).[50]

2. Selenylamines

There is very little information about N = R-selenylamines and N = R-selenylamides. It was reported in 1932 that when aromatic amines are reacted with selenyl chloride, *N*-selenylarylamines (XIX) are formed:[56]

$$3ArNH_2 + SeOCl_2 \xrightarrow[-2ArNH_2\cdot HCl]{} ArN{=}Se{=}O, \quad (XIX)$$

$Ar = Ph,\ o\text{-}MeC_6H_4.$

Compounds (XIX) are orange-yellow oils which can be distilled under vacuum and decompose when heated at atmospheric pressure. On heating with aniline in the presence of zinc chloride, compounds (XIX) give difficultly soluble, dark green pigments containing selenium.

Reaction of t-butylamine with selenyl chloride gives *N*-t-butylselenylamine, which is a brown liquid that is extremely susceptible to hydrolysis:

$$3\ t\text{-}BuNH_2 + SeOCl_2 \xrightarrow[-2\,t\text{-}BuNH_2HCl]{\text{ether},\ -10\ ^\circ C} t\text{-}BuNSeO.$$

When traces of moisture are present the product is converted to a colourless crystalline compound with mp 145 °C, which apparently has the structure of a selenous acid amide $t\text{-}BuNH_2.SeO_2$.[52] The NMR spectrum of t-butylselenylamine confirms the presence of t-butyl groups. In the IR spectrum of this compound the intense absorption and at 1110 cm^{-1} has been attributed to ν_{as}(NSeO) and the band at 625 cm^{-1} to ν_s(NSeO).[52]

As was indicated above, attempts to obtain *N*-selenylamide derivatives RNSeO, where R = $ArSO_2$, $AlkSO_2$, PhCO, AlkCO, Me_3Si, were not successful.[43,49] Evidently these compounds are extremely unstable and undergo further conversions.

References

1. T L Gilchrist, C J Moody *Chem. Rev.*, 1977, **77** 409
2. D Spinelli, G Monako *Boll. Sci. Fac. Chim. Ind. Bologna*, 1962, **20** 56 *Chem. Abs.*, 1963, **58** 4457
3. D Hellwinkel, G Farbach *Liebigs Ann. Chem.*, 1968, **715** 68
4. N Ya Derkach, T V Lyapina, N A Pasmurtsvea *Zh. Org. Khim.*, 1974, **10** 807
5. S Oae, M Fukamura, N Furukawa *Phosphorus Sulfur*, 1981, **10** 153
6. M Hori, T Kataoki, H Shinuzu, K Tomimatsa *Tetrahedron Lett.*, 1982, **23** 901
7. S Tamagaki, S Oae, K Sakaki *Tetrahedron Lett.*, 1975, 649
8. V I Naddaka, V P Krasnov, V I Minkin, L P Popova *Zh. Org. Khim.*, 1982, **18** 259
9. N Ya Derkach, N P Tishchenko, V G Voloshchuk *Zh. Org. Khim.*, 1978, **14** 958
10. D Swern, J Ikedo, G F Whiterfild *Tetrahedron Lett.*, 1972, 2635
11. N Ya Derkach, T V Lyapina *Zh. Org. Khim.*, 1974, **10** 1991
12. V P Krasnov, V I Naddaka, V I Minkin *Zh. Org. Khim.*, 1981, **17** 445
13. V I Nsddaka, V P Gar'kin, I D Sadekov, et al. *Zh. Org. Khim.*, 1979, **15** 896
14. F A Davis, J M Billmers, O D Stringer *Tetrahedron Lett.*, 1983, **24** 3191
15. V I Naddaka, V P Krasnov, V I Minkin *Zh. Org. Khim.*, 1985, **21**
16. V I Naddaka, V P Gar'kin, V I Minkin *Zh. Org. Lhim.*, 1976, **12** 2481
17. N Ya Derkach, G G Barashenkov, E I Slyusarenko *Zh. Org. Khim.*, 1982, **18** 70
18. F A Davis, O D Stringer, J P McCouley *Tetrahedron*, 1985, **41** 4747
19. N Ya Derkach, N A Pasmurtseva, T V Lyapina, E S Levchenko *Zh. Org. Khim.*, 1974, **10** 1873
20. V I Naddaka, V P Gar'kin, K V Avanesyan *Zh. Org. Khim.*, 1986, **22** 1102
21. I G Furmanova, R G Gerr, V P Krasnov, V I Naddaka *Zh. Strukt. Khim.*, 1984, **25** 166
22. H W Roesky, K-L Weber, U Seseke, et al. *J. Chem. Soc. Dalton Trans.*, 1985
23. V I Naddaka *Zh. Org. Khim.*, 1985, **21** 716
24. Yu A Nuzhdina, Yu P Egorov, N Ya Derkach, et al. *Teor. Eksp. Khim.*, 1974, **10**
25. V I Naddaka, V P Krasnov, V I Minkin *Zh. Org. Khim.*, 1983, **19**
26. N Ya Derkach, N A Pasmurtseva, E S Levchenko *Zh. Obshch. Khim.*, 1972, **42**
27. Yu A Nuzhdina, Yu P Egorov, L V Mironyuk, N Ya Derkach *Teor. Eksp. Khim.*, 1975, **11** 605
28. N Ya Derkach, N A Pasmurtseva, E S Levchenko *Zh. Org. Khim.*, 1971, **7**
29. N Ya Derkach, T V Lyspina, E S Levchenko *Zh. Org. Khim.*, 1980, **16** 33

30. N Ya Derkach, N P Tishchenko *Zh. Org. Khim.*, 1977, **13** 100
31. N Ya Derkach, T V Lyapina *Zh. Org. Khim.*, 1981, **17** 529
32. N Ya Derkach, T V Lyapina *Zh. Org. Khim.*, 1974, **10** 139
33. N Ya Derkach, T V Lyapina, E S Levchenko *Zh. Org. Khim.*, 1978, **14** 280
34. N Ya Derkach, N P Tishchenko, E S Levchenko *Zh. Org. Khim.*, 1977, **13** 96
35. N Ya Derkach, T V Lyapina, E S Levchenko *Zh. Org. Khim.*, 1981, **17** 622
36. Ya G Bal'on, E S Levchenko *Zh. Org. Khim.*, 1967, **3** 777
37. N Ya Derkach, N A Pasmurtseva *Zh. Org. Khim.*, 1973, **9** 1414
38. N Ya Derkachh, T V Krasnyanskaya, E S Levchenko, T G Zabolotnaya *Zh. Org. Khim.*, 1984, **20** 2377
39. A V Zibarev, G I Dolenko, S A Kru[oder, et al. *Zh. O4g. Khim.*, 1980, **16** 390
40. J S Thrasher, K Seppelt *Z. Anorg. Allg. Chem.*, 1983, **507** 7
41. J S Thrasher, C W Bauknight, D D DesMarteau *Inorg. Chem.*, 1985, **24** 1598
42. A W Kirsanov, E S Levchenko, L N Markowski *Organic Sulfur Chemistry, IUPAC* (Edited by R Friedland), Pergamon Press, Oxford–New York, 1984, p. 109
43. N Ys Derkach, G G Barashenkov, E S Levchenko *Zh. Org. Khim.*, 1982, **18**
44. H Hartl, P Hauppmann, D Lentz, K Seppelt *Inorg. Chem.*, 1983, **22** 2183
45. N Ya Derkach, G G Barashenkov, E S Levchenko *Zj. Org. Khim., 1979,* **15**
46. N Ya Derkach, T V Lyapina, G G Barashenkov *Zh. Org. Khim.*, 1979, **15** 879
47. R Bussas, G Kresza, H Münsterer, A Schwöbel *Sulfur Reports*, 1983, **2** 215
48. N Ys Derkach, G G Barashenkov *Zh. Org. Khim.*, 1976, **12** 2484
49. N Ys Derkach, G G Barashenkov, E S Levchenko *Zh. Org. Khim.*, 1983, **19** 1622
50. N Ya Derkach, G G Barashenkov *Zh. Org. Khim.*, 1986, **22** 1189
51. F Fockenberg, A Haas *Z. Naturforsch. B*, 1986, **41** 413
52. M Herberhold, W Jelien *Z. Naturfforsch. B*, **41** 144
53. K B Sharpless, T Hori, L K Truesdale, C O Dietrich *J. Am. Chem.Soc.*, 1976, **98** 269
54. K B Sharpless, S P Singer *J. Org. Chem.*, 1976, **41** 2504
55. K B Sharpless, T Hori *J. Org. Chem.*, **41** 176
56. A Baroni *Atti. R. Accad. Naz. Lincei Rend [6]*, 1932, **16** 253; *Chem. Zentralbl.*, 1933, **1** 1767

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The influence of electric fields on the chemisorption and catalytic properties of semiconductor catalysts

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ABSTRACT. Studies of the influence of electric fields on the chemisorption and catalytic properties of semiconductor catalysts, carried out in order to test the principal postulates of the electronic theory of catalysis, are examined. It is shown that, because of the high density of the surface states, the possibility of the electronic control of the surfaces of polycrystalline catalysts by the field effect method is extremely limited. Possible ways of regulating the chemisorption and catalytic activities of solid catalysts with the aid of an external electric field are discussed: (1) the change in the concentration of polar molecules in strong inhomogeneous local fields near the surface; (2) the activation of surface compounds by "hot" electrons; (3) the modification of the defective structure when the concentration of cations in the surface layers of oxide catalysts is altered; (4) surface doping of film catalysts by alkali metals from the dielectric support during their electrolytic deposition.

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Introduction

In chemical thermodynamics the external electric field is considered, like pressure and temperature, as an additional thermodynamic parameter influencing the rate and equilibrium constants for a chemical reaction. The principal aspect of the utilisation of electric fields in catalysis is at the junction between catalysis and electrochemistry and has been the subject of a special branch of chemistry—electrocatalysis. The need to solve practical problems—the creation of highly effective hydrogen and oxygen electrodes, the search for low-temperature hydrocarbon oxidation catalysts, the intensification of various reactions involved in the electrosynthesis of organic and inorganic compounds, and also the additional possibilities for the investigation of the mechanism of catalysis by electrochemical methods—have stimulated a large number of studies in the field of electrocatalysis, the principal results of which have been surveyed in a series of reviews[1–4] and monographs.[5,6]

Very strong fields are used in the study of surfaces by the autoelectronic and autoionic microscopic methods. These methods make it possible to obtain an image of the surface and the use of an atomic probe or a mass spectrometer also permits the study of the chemical composition of the surface and of a wide variety of reactions occurring in extremely strong electric fields at the tip of the emitter. The field-stimulated surface reactions have been analysed in a series of reviews.[7–10]

Finally, as the electronic ideas have developed, yet another aspect of catalysis has arisen—the employment of the field effect method in the study of the chemisorption and catalytic properties of semiconductors.

The idea that free carriers are involved in chemisorption and catalytic properties appeared in connection with the experimental observation of the dependence of the electrophysical parameters of semiconductors (electrical conductivity, electron work function, and the Hall constant) on the gaseous and environment. The theoretical foundations of the electronic theory of catalysis were laid in the studies of Vol'kenshtein [Wolkenstein],[11] Hauffe,[12] German,[13] and other workers. The use of quantum-statistical methods for the description of surface phenomena made it possible to discover the role of the Fermi level as a "collective" factor influencing the chemisorption and catalytic properties of semiconductors. Hence follows directly the possibility of regulating the activity of catalysts via external influences such as the introduction of heterovalent additives[14–16] and the application of an external electric field, which shifts the position of the Fermi level on the semiconductor surface.

The change in the chemisorption and catalytic properties of semiconductors following the application of an external electric field was predicted theoretically by Vol'kenshtein as early as 1955.[17] The electroadsorption effect was first observed experimentally in a study[18] where an increase in the hydrogen and carbon monoxide pressure was noted when a positive potential was applied to a germanium film specimen. At the present time the influence of the field on chemisorption and catalytic properties has been observed also in other studies. In view of the fundamental importance of these results for the confirmation of the electronic theory of catalysis, they have been described in many monographs and review articles devoted to the physical chemistry of the surfaces of semiconductors.[11,19–21]

In semiconductor physics, the field effect method has been given a theoretical justification. It has found technical applications in connection with the use of sufficiently perfect single crystals with the lowest concentration of surface states at the semiconductor–dielectric interface. However, the majority of the adsorption and catalytic studies in which the field effect method was applied have been carried out on polycrystalline specimens with a high concentration of surface states, which exceeds by several orders of magnitude the

density of the field-induced charge. Under such conditions, it is impossible to expect any appreciable shift of the position of the Fermi level or a change in the charge state of the catalytic reactive centres. In most studies, qualitative results concerning the effect of the field on adsorption and catalysis were presented without a comparison of the orders of magnitude of the observed effect with the concentration of the field-induced charge and the possible shift of the surface potential. It is striking that, despite the entire wide variety of the condenser designs and conditions (temperature, pressure, electric field strength, material of the dielectric) used, different secondary influences by the field on the heterogeneous catalytic system were as a rule not taken into account.

The aim of the present review is a critical examinaion of the results of studies of the chemisorption and catalytic properties of semiconductors by the field effect method with allowance for the physicochemical phenomena arising in systems when an external field is applied and the discussion of the possible mechanisms of the observed effects and the ways in which the electric field influences the adsorption and catalytic processes.

Henceforth the terms "electroadsorption" and "electrocatalysis" will be understood to imply the influence of an external field on the chemisorption and catalytic processes regardless of the mechanism involved in the action of that field. The electric field strength used in the field effect method is determined by the breakdown strength of the dielectric and does not exceed 3×10^8 V m^{-1}, but, owing to the roughness of the relief, near the surface the field strength may greatly exceed the average value calculated from the geometry of the condenser. We shall therefore consider briefly below the mechanisms of the influence of a very strong field on a heterogeneous gas–solid catalytic system.

II. The possible mechanisms of the influence of a very strong electric field ($>10^8$ V m^{-1}) on a heterogeneous gas–solid catalytic system

The electroadsorption and electrocatalytic effect in a gas-solid system may be determined both by the change in the state of the gas and solid molecules in the external field and by the influence of the field on their interaction. The effect of the field on a heterogeneous catalytic system is based on the following physical phenomena.

1. The change in the potential energy of the electrons of the atoms, molecules, and ions formed in the autoionisation process in a very strong external field (5×10^9–5×10^{10} V m^{-1}).
2. The formation of a system of dipoles oriented by the field.
3. The change in the electron work function of the solid as a consequence of the influence of the field on the electrostatic image forces.
4. The appearance of a mechanical stress, directed at right angles to the surface of the solid, when the electric field is applied.

We shall consider the mechanisms of the influence of the field on adsorption and catalysis determined by these phenomena.

The possibility of altering the properties of a heterogeneous catalytic system under the influence of very strong fields ($>5 \times 10^9$ V m^{-1}), comparable to intraatomic fields, is not open to doubt. Quantum-mechanical calculation performed for a series of gas molecules have shown[22,23] that, for $E > 5 \times 10^9$ V m^{-1}, the electron density is redistributed and this is accompanied by a change in the effective charges on atoms, in the bond lengths and angles, and in the ionisation potentials and electron affinities and hence by a change in the reactivity of the molecules. A simple diatomic adsorbate–support model in an external electric field has been calculated[24] by the LCAO method. An effect of the field on the bond energy, the equilibrium position, and the vibration frequencies of the adsorbate has been observed for $E > 10^9$ V m^{-1}. The energies of the bonds formed on chemisorption of the H_2O and CO molecules on NaCl and MgO(001) have been given[25] as a function of the adsorbate–support distance in the presence of an external field. It has been shown that the field alters not only the electrostatic but also the exchange energy of the interaction of the adsorbed molecules with the surface of ionic crystals.

In the strong electric field ($\sim 10^{10}$ V m^{-1}) arising at the tip of the ion emitter, atoms and molecules are ionised due to the quantum-mechanical tunnel electron transfer through the barrier generated by the field and the image forces in the metal.[8–10,26] The change in the form of the potential curve for the ion near the surface of the solid when an external $\sim 10^{10}$ V m^{-1} field is applied can lead (depending on the sign of the field) either to the stabilisation of the surface ionic structures or to the desorption of the ion by the field. Analysis of the chemical composition of the surface by the method involving the desorption of ions by the field using a time of flight atomic probe or an ionic field mass spectrometer have made it possible to observe various reactions occurring in the presence of strong electric fields. The following types of reactions have been quoted in a review.[9]

(a) Proton or cation exchange in the ionisation of gas molecules near the surface.

(b) The formation of complex ions on interaction of various gases with metallic emitters.

(c) The decomposition of molecules into fragments under the influence of the field.

(d) The ion–molecule reactions which can be initiated by radicals, radical-ions, or molecules in ionised states.

The study of the elementary processes occurring under the influence of very strong fields is of definite interest also for catalysis in the absence of an external field, because fields with $E \simeq 10^9$ V m^{-1}, generated by the ionic lattice of the solid, are then present over the surface of catalysts.[27]

For $E < 5 \times 10^9$ V m^{-1}, where the changes in the quantum-mechanical parameters of the molecules under the influence of the field become insignificant, the influence of the field on the adsorption and catalytic processes can be determined by polarisation effects. On polarisation in an external electric field, molecules with a dipole moment μ and a polarisability α receive an additional energy $\mathscr{E} = \mu E + {}^1/_2 \alpha E^2$, which results in their preferential orientation in space in the direction of the field, which cannot fail to affect the energy of the bond between the adsorbed species and the catalyst surface.

The dependence of the coverage of the tungsten tip of an [field ion] emission microscope by oxygen and alkali metal atoms on the field strength near the tip has been investigated.[28–30] The state of the surface before and after adsorption and also the change in the degree of adsorption under the influence of fields of different polarity were characterised by the electron work function of the tip determined from the Fowler–Nordheim relation between the emission current and the applied potential. It was observed that the degree of surface coverage by metal atoms under the influence of a field having a positive polarity increases and that under the influence of a field with a negative polarity diminishes. In relation to oxygen, the electron adsorption effect has the opposite sign—additional adsorption of oxygen on the tungsten tip is observed when a field with a negative polarity is applied. The results

obtained make it possible to represent the metal and oxygen atoms adsorbed in a charged form as dipoles with effective dipole moments μ^* and polarisabilities α^*, the heat of adsorption of which changes in the presence of the field E by an amount $\Delta q = \mu^* E + {}^1/_2 \alpha^* E^2$. With increase in the degree of coverage and hence with decrease in the proportion of the charged form of the chemisorbed species, the influence of the field on the chemisorption weakens and the effective values of μ^* and α^* diminish in the general case.

The changes in the state of the gas phase after the application of an external field can also be described by means of a thermodynamic approach[31] taking into account the influence of polarisation and spatial orientation processes on the entropy and the internal and free energies of the reactants and products of the chemical reaction and hence on its rate and equilibrium constants. The change in free energy per unit volume of the dielectric after the application of a field E is $\Delta \mathscr{F} = {}^1/_2 \varepsilon_0 \varepsilon_D E^2$. If the dielectric constants ε_D of the reactants and products are not the same, there is a possibility of a shift of the thermodynamic equilibrium in the system. According to the data of Block and Moentack,[32] the change in the equilibrium constant K as a function of the electric field strength E is determined by the relation

$$\partial \ln K / \partial E = \Delta M / kT,$$

where ΔM is the difference between the field energies of all the species in the field E before and after the reaction:

$$\Delta M = \left[\sum \mu_p - \sum \mu_r\right] E + {}^1/_2 \left[\sum \alpha_p - \sum \alpha_r\right] E^2.$$

(The subscripts r and p refer to the reactants and products of the reaction respectively).

The change in the reaction rate constant as a result of the decrease in the entropy of the dipolar molecules in the gas phase or in the adsorption layer, caused by the freezing of the rotational degrees of freedom in the electric field, has been estimated.[33] For a limited rotational freedom of the activated complex, this increases the reaction rate constant in the field $E = 9 \times 10^9$ V m^{-1} by a factor of 10^2–10^4. Evidently the polarisation effect can have an appreciable influence on the thermodynamic state of the gas phase and on the rate of chemical processes in a field $E > 10^9$ V m^{-1}, where the field energies of the species exceed kT. For example, $\mathscr{E} \simeq kT$ for a water molecule with $\mu = 1.8$ D and $\alpha = 1.46$ Å when $E = 3 \times 10^9$ V m^{-1}. When $E < 10^8$ V m^{-1}, the polarisation effects may be neglected.

Another thermodynamic parameter which changes in the presence of an inhomogeneous electric field is the pressure exerted by a gaseous dielectric on the surface of the solid catalyst. In the space near the electrode, the polarised gas molecules are acted upon by the force

$$\mathscr{F} = (\mu + \alpha E)\, dE/dr,$$

which is proportional to the electric field strength gradient dE/dr and which varies as the density of the flux of species incident per unit area per unit time and of the momentum given up by the molecules to the solid.[7] The multilayer adsorption of water vapour ($\sim$100 monomolecular layers) on a tungsten tip has been observed[34] at high electric field strengths ($E > 10^9$ V m^{-1}) and a low vapour pressure ($p_{H_2O} = 10^{-3}$ Pa) in the chamber of an ion emitter. The condensation of water vapour under such conditions can be explained by the increase in the pressure p_{H_2O} by several orders of magnitude near the tip as a result of the force acting on the dipolar H_2O molecules in the field direction. The sharp increase in surface coverage of a germanium cathode by oxygen in a field with the autoionic sign whose strength exceeds 1.39×10^{10} V m^{-1} has been noted.[35] The authors attribute this threshold effect to the possibility that the oxygen molecule may overcome the activation barrier in adsorption on a germanium tip as a result of the energy aquired in the inhomogeneous electric field. The increase in the surface coverage of the catalyst by the reactants under the influence of the electric field can alter the kinetics and mechanism of the catalytic process.

The external electric field can act both on the local properties of the solid catalyst and on the electron work function as a consequence of the Schottky effect. The decrease in the electric image forces in the presence of the external field reduces the overall electron work function by an amount $\Delta\chi = e^{3/2} E^{1/2}$ and is observed from the increase in the thermal electron and autoelectron emission currents and also from the increase in the degree of surface ionisation.[36] The surface ionisation and ion adsorption and desorption processes induced by the field can influence the rate of homogeneous-heterogeneous catalytic reactions. As an example, one may quote the decomposition of ammonia on the Pt–Rh–Pd catalyst in an electric field.[37] When a negative potential was applied to the catalyst, an increase in the rate of decomposition of NH_3 by a factor of 1.5–2 was observed with a simultaneous decrease in temperature and the conductivity of the specimen. The mechanism of the action of the field was attributed by the authors to the field-induced desorption of the negatively charged species, which accelerates the gas-phase processes. The field thereby prevents the species recombination processes on the surface, as a result of which the temperature on the catalyst surface decreases.

The changes $\Delta\chi$ become appreciable for fields with $E > 10^8$ V m^{-1} and should have a significant influence on the rates of reactions in which the electronic transitions between the solid and the surface species constitute the rate-limiting stage of the reaction. The study of the dependence of the activation energy for the decomposition of formic acid and of the rate of the latter on the electron work function of the catalyst, altered by an external electric field, has been undertaken.[38] A silver wire 2.5×10^{-5} m in diameter, serving as the internal electrode of a cylindrical condenser, was used as the catalyst. The changes in the electron work function $\Delta\chi$ after the application of the field were detected reliably by measuring the autoelectron emission currents. In conformity with earlier results,[39] it was assumed that the catalytic decomposition of formic acid should be accelerated by a field with a positive polarity of the silver catalyst and should be inhibited by one with a negative polarity. However, experiments showed that an irreversible decrease in the rate of reaction takes place in both cases. The authors explained this result by an increase in the roughness of the catalyst surface and a change in its structure when the reaction takes place in the presence of the field.

The mechanism of the change in the structure of the catalyst surface in an external field is apparently complex, but, when $E > 10^9$ V m^{-1}, the mechanical stress $\sigma_E = {}^1/_{8\pi} \varepsilon_0 E^2$, arising under the influence of mechanical forces and directed at right angles to the electrode surface, plays an important role. In fields with $E = (3$–$5) \times 10^9$ V m^{-1}, whereupon the energy imparted by the field to the gas molecules is comparable to kT, the mechanical stress $\sigma_E = 10^6$–10^7 Pa can induce the plastic deformation of the surface layers of the solid.[40]

Thus, despite the wide variety of the mechanisms of the action of fields with $E > 10^9$ V m^{-1} on the catalytic system (the rearrangement of the molecular and surface structures, the change in the energy of the bond between the adsorbate and the surface, the dependence of the rate and equilibrium constants for a chemical reaction on the field, the increase in the gas pressure near the catalyst-electrode, and the influence of the field on the electronic transitions between the solid and the adsorbed species, and the desorption of ions by the field), the possibility of using very strong fields in catalytic studies is limited as a consequence of the degradation of the catalyst surface by the field.

III. The influence of the electric field on the chemisorption and catalytic processes occurring on semiconductor catalysts

1. The mechanism of the influence of the electric field on chemisorption and catalysis from the standpoint of the electronic theory

In the case of a semiconductor catalyst, the influence of the field on chemisorption and catalytic processes can be associated with the shift of the position of the Fermi level on the semiconductor surface when an additional surface charge is induced by the field. This possibility has been examined in the electronic theory of catalysis.[11,41,42] According to the electronic theory,[11] the gas molecules are adsorbed on the surface of the semiconductor catalyst in neutral and charged forms, between which transitions are possible. The probability that a species exists in the charged or neutral state and also the degree of surface coverage of the adsorbent under the conditions of thermodynamic equilibrium, when adsorption equilibrium between the gas phase and the surface and the electronic equilibrium between the bands and the surface state have been attained, is determined by the position of the Fermi level at the surface of the semiconductor catalyst.[11] The species chemisorbed in the donor, acceptor, and neutral forms differ in their reactivities. The Fermi level, by determining the concentration of the active form, is thus a regulator of the rate of the catalytic reaction. The rate of reaction may depend on the position of the Fermi level also in the case where the intermediate surface compounds are formed with participation of the conductivity electrons of the solid.[43] Hence follows the possibility of a change in the adsorption capacity and catalytic activity of the semiconductor catalyst after the application of an external field, which alters the concentration of the free carriers in the surface region of the semiconductor and hence the level of the chemical potential of the electrons.

The relative changes in the chemisorption capacity and catalytic activity induced by the electric field are defined by the following relations according to the data of Baru and Vol'kenshtein:[42]

$$\Delta N/N_0 = (N - N_0)/N_0 = \eta_0^{\mp} \{\exp[\mp (V_s - V_{s0})] - 1\}, \quad (1)$$

$$\Delta g/g_0 = (g - g_0)/g = \exp[\mp (V_s - V_{s0})] - 1, \quad (2)$$

where N and N_0 are the total numbers of species of the given kind chemisorbed on a unit surface under the conditions of equilibrium in the gas phase when the field is applied and in its absence, $\eta_0^{\mp} = N_0^{\mp}/N_0$ is the relative content of the charged form on the surface for $E = 0$, g and g_0 are the rates of reaction when the field is applied and in its absence, and $V_s - V_{s0}$ is the change in the surface potential (in units of kT) equal to the shift of the position of the Fermi level on the surface of the specimen following the application of the field; $(V_s - V_{s0}) > 0$ corresponds to an increase in the electron work function after the induction of a positive charge in the semiconductor and $(V_s - V_{s0}) < 0$ corresponds to its decrease after the introduction of a negative charge into the semiconductor.

It follows from Eqns. (1) and (2) that the field inducing a negative charge in the semiconductor and shifting the level of the chemical potential on the specimen surface upwards relative to the edge of the band increases the degree of adsorption of acceptors (and also accelerates the acceptor reaction) and diminishes the degree of adsorption of donors (inhibits the donor reaction). The field inducing a positive charge in the semiconductor acts in the opposite way. The form of the functional dependence of $\Delta N/N_0$ and $\Delta g/g_0$ on $V_s - V_{s0}$ shows that the positive effect increases with increase in the displacement of the surface potential, while the negative effect is expressed by the asymptotic approach of $\Delta N/N_0$ to $\eta_0^{\mp}$ and of $\Delta g/g_0$ to -1. Consequently the electrodesorption effect is limited by the relative contribution of the charged form of chemisorption before the application of the field.

2. The change in the bending of the bands of on the surfaces of semiconductors under the influence of an external electric field

The conclusion arising from the electronic theory that the chemisorption and catalytic activities of semiconductors can be regulated by an electric field has been tested experimentally. The change in the concentration of free carriers in the surface region of the semiconductor catalyst was achieved by applying a potential difference to a condenser one of the plates of which consisted of the semiconductor investigated. The wide variety of condenser designs employed is striking (Fig. 1) A plane-parallel condenser has been used in a number of studies[44–49] (Figs. 1*a*, 1*c*, and 1*e*), while the role of the dielectric plate was assumed by a vacuum (gas) or a mica plate. The principal deficiency of condensers having this design is the presence of a field in the gas phase at the surface of the adsorbate, which requires special precautions to avoid their discharge and the ionisation of the gas.

A condenser design free from this disadvantage has been proposed[18] (Figs. 1*b* and 1*f*). A thin film specimen, whose thickness d is smaller than the Debye shielding length L, is sputtered onto a support which serves simultaneously as the dielectric plate of the condenser; a metallic electrode is deposited on the other side of the support. Condensers having this design have been used in a number of studies[18,50–71] and it has been shown[72] that, when the condition $d < L$ holds, the application of the field should alter the position of the Fermi level and the degree of filling of the surface states by electrons not only from the inner side of the film but also from its outer side directed towards the gas phase.

Cylindrical condensers with a gap above the catalyst surface have been used to investigate the influence of the field on chemisorption and catalytic processes at elevated temperatures and pressures (from 2×10^3 to 10^5 Pa)[73–77] (Figs. 1*g* and 1*h*). In order to avoid discharge processes in the gas phase and the electrical breakdown of the dielectric, the field strength between the condenser plates was kept at a value not exceeding 10^6 V m^{-1} and the charge induced in the semiconductor was $e\Delta n_v \leqslant 5 \times 10^{13}$ el. charge m^{-2}. In a number of studies,[44–46,50–54] electroadsorption has been investigated at room temperature and low adsorbate pressures (0.5 Pa), which made it possible to increase the field strength to 2×10^7–2×10^8 V m^{-1} and the induced charge to 10^{15}–10^{16} el. charge m^{-2}.

A quantitative comparison of the experimental results for the influence of the field on chemisorption and catalytic processes with theoretical data derived from Eqns. (1) and (2) of the electronic theory is possible, provided that the dependence of the shift of the surface potential (V_s–V_{s0}) on the electric field strength E is known. The dependence of V_s on E cannot be obtained purely theoretically from the solution of the Poisson equation because a large part of the charge induced by the field is captured by the surface state of the semiconductor and the shift of the surface potential is much smaller than the theoretically possible value. The field effect method has been developed in detail for germanium and silicon single crystals.[78–80] This method makes it possible to calculate from the experimental field effect curve the bending of the bands on the surface and the charge captured by the surface state as a function of the field-induced charge.

Most of the studies of the influence of the field on chemisorption and catalytic processes have been carried out on polycrystalline semiconductor specimens, an exact calculation of the electrophysical parameters of the surface of which as a function of the electric field strength is impossible. The relation obtained by Many et al.[80] has been used by Deren and Mania[75] to estimate the order of magnitude of the bending of the bands after the application of the field:

$$V_s - V_{s0} = eLE \tag{4}$$

where L is the Debye shielding length:

$$L = (\varepsilon_0 \varepsilon_n kT/2\pi e^2 n_0)^{1/2}, \tag{5}$$

where ε_n and ε are the dielectric constants of the semiconductor and the dielectric, n_0 is the concentration of free carriers in the semiconductor, and e is the charge of the electron. The field strength in the semiconductor E_n is linked to the field strength in the dielectric E by the electrostatic relation

$$E_n = (\varepsilon/\varepsilon_n) E. \tag{6}$$

One should bear in mind that such a shift of the surface potential is established in the first instant after the field has been switched on and then, as the charge is captured by surface states, the quantity V_s–V_{s0} can decrease appreciably. Virtually all the semiconductors investigated are characterised by a high density of surface states.

On a germanium single crystal, the density of fast and slow states is 10^{16} m^{-2}, but increases after the adsorption of water, *p*-benzoquinone, and diphenylamine vapours to 10^{18} m^{-2} and above.[81,82] On epitaxial PbS films, the concentration of slow states *in vacuo* is 10^{17} m^{-2}.[83] Evidently the density of surface states on polycrystalline specimens should be even higher. The shift of the Fermi level on the outer side of the film after the application of an electric field to its reverse side has been determined by the conductimetric and the contact potential difference methods in a study[57] carried out on polycrystalline TiO_2 films deposited on mica supports (the condenser illustrated in Fig. 1*b*). It was shown that a thin film of reduced TiO_2 (~500 A) provides an almost complete shield against the field and the change in the contact potential difference is much lower than the theoretical value, which indicates a transfer of a considerable proportion of the induced charge to the surface states.

A large proportion of studies of the influence of the field on the chemisorption and catalytic properties of semiconductors have been carried out on polycrystalline zinc oxide specimens.[48,50,51,66–68,76] The field effect on ZnO single crystals and polycrystalline film specimens *in vacuo* has been observed by a number of workers.[84–91] Estimating the mobility of the field effect with different initial conductivities of the specimen, Heiland[85] calculated the density of surface states per unit energy range in the vicinity of the Fermi level: $S_{EF} = 10^{18}$ m^{-2} eV^{-1}. Later S_{EF} was regarded[92,93] as the "effective" density of capture centres taking into account the fact that a proportion of the states undergoing charge transfer after the application of an electric field or on illumination exist not on the surface but in the region of the space charge. The nature of the capture centres for the free carriers is apparently immaterial for the estimation of the shift of the Fermi level following the application of the external field. Bearing in mind that the field-induced charge $e\Delta n_V$ is equal to the sum of the charges $e\Delta n_{ss} + e\Delta n_c$ ($e\Delta n_{ss}$ and $e\Delta n_c$ are respectively the density of the charge transferred to the capture centres and the charge participating in the conduction by the

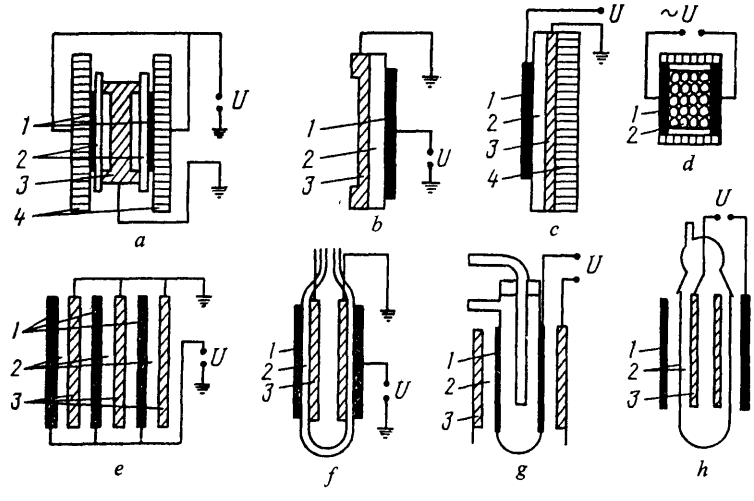


Figure 1. Design of the condensers used in the study of the influence of an external electric field on the chemisorption and catalytic properties of semiconductors: *1*, field electrodes; *2*, layers of dielectric; *3*, test specimens; *4*, support or holder.

specimen) and that we have $e\Delta n_c \ll e\Delta n_{ss}$ so that $e\Delta n_V \simeq e\Delta n_{ss}$, it is possible to estimate the shift of the Fermi level provided that the density of states S_{EF}, per unit energy range, is known:

$$V_s - V_{s0} = \Delta n_V / S_{EF}. \quad (7)$$

Henceforth, in order to discriminate between the mechanisms of the effect of the field on the chemisorption and catalytic properties of polycrystalline semiconductors, the observed effects will be compared with the changes in the surface potential $V_s - V_{s0}$ (possible for the field strengths E and the concentrations of the field induced charge $e\Delta n_v$ employed) calculated with the aid of Eqns. (4) and (7).

3. The electroadsorption of gases on semiconductor adsorbents

(a) The electroadsorption of oxygen and methanol and water vapours on a germanium single crystal

The classical field effect method[78–80] has been used to investigate the influence of the field on the adsorption of oxygen and methanol and water vapours on a germanium single crystal.[44–46] It is noteworthy that the surface properties of germanium, studied by many investigators,[21,78–80] are by no means described by the simple ideal crystal model with a local level of the adsorbed molecule, which has served as the basis of Vol'kenshtein's electronic theory. On a "real", i.e. oxidised, surface of the germanium single crystal[78] one observes a high concentration of fast and slow states of adsorption or biographical origin. By virtue of the cooperative character of the local fields, the curves for the charge capture by both fast and slow surface states, which depend on the surface potential, are monotonic.

In the adsorption of different molecules, the local surface levels are not manifested, but the energy spectrum shifts smoothly towards an increase in the concentration of slow surface states. Kiselev[94–97] proposed a donor–acceptor mechanism of the charging of the surface in adsorption, which is based on the idea that the adsorbed molecules interact with "defective" surface atoms. When an adsorption complex is formed, the electrophysical parameters of the defect change, as a result of which it is converted into a hole or electron capture centre and the localisation of the charge influences in its turn the character and strength of the bond. The chemisorption of the charged form alters the bending of the bands on the semiconductor surface, which entails a redistribution of the charge between the levels of the chemisorbed species and the levels of the biographical defects. The redistribution of the charge between the fast and slow surface states of biographical and adsorption origin and the continuous character of the energy spectrum complicate the observation and interpretation of the electroadsorption effect.

Since the surface of the germanium single crystal (2×10^{-4} m^2) is small, manometric adsorption measurements were not performed and the electroadsorption effect was estimated from the sign and magnitude of the change in the surface charge after the adsorption of the gas in the presence of the field.[44–46] The condenser illustrated in Fig. 1*a* was used in these studies. It is striking that the electroadsorption depended on the method used for the preliminary treatment of the surface of the germanium single crystal. By varying the etching conditions, two types of surface were obtained. For the same geometry of the condenser, gas pressure, and electric field strength, the electroadsorption of oxygen was observed on a type II surface but was absent on a type I surface. On the other hand, methanol vapour was adsorbed in the presence of the field only on the type I surface. This must be regarded as proof that the electroadsorption of gases is not associated with the discharge in the gas phase but is determined by phenomena occurring on the surface of germanium in the presence of the field.

The influence of a field with negative polarisation, which increases the number of electrons on the surface, on the adsorption of O_2 was observed on incompletely oxidised type II germanium specimens with a high density of slow acceptor states (there were no slow donor states on these specimens). After the field had been switched off in an oxygen atmosphere, the steady relaxation of the reverse electron transition to the bulk of germanium from the slow acceptor states, which are apparently centres for the adsorption of O_2, increased (compared with a vacuum). This induced an increase in the negative surface charge (Fig. 2). An increase in the positive surface charge has been detected on type I specimens, having the structure of the "real" surface and a high density of slow donor states, in the adsorption of methanol vapour under conditions involving the application of a field with positive polarity to the specimen.

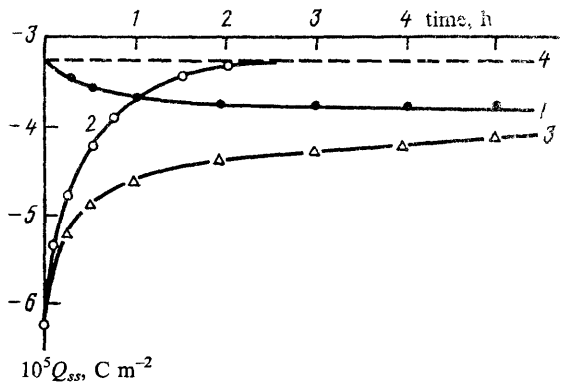


Figure 2. Relaxation of the surface charge: *1*, in the adsorption of O_2; *2*, when the field is switched off *in vacuo*; *3*, when the field is switched off in an oxygen atmosphere; *4*, the charge on the surface conditioned *in vacuo*.

A quantitative comparison of the change in the positive charge of the surface with the shift of the Fermi level has been carried out[46] in relation to the electroadsorption of water vapour using a pulse method, which is free of the disadvantages of the field effect method at a constant potential such as the inconstancy of the shift of the Fermi level as a function of time, the filling of surface states of non-adsorption origin, and appreciable changes in the surface potential of the opposite sign when the field is switched off. The amplitude, duration, and Q-factor of the pulses were chosen so that the switching on of the pulse field *in vacuo* did not change the surface charge of the specimen heated at 450 K. When a pulsed field with a positive polarity is applied to germanium in the presence of water vapour, the positive surface charge accumulates, the accumulation effect increasing with increase in the amplitude of the pulses. In a pulsed field with the opposite polarity, a decrease in the positive surface charge was observed with a tendency towards saturation as the amplitude of the pulses rose.

The experimental dependence of the change in the positive surface charge ΔQ_V in the adsorption of water vapour on germanium in a field with a positive polarity applied to the specimen (measured after the completion of the rapid relaxation process) on the change in the bending of the bands (V_s–V_{s0}) is described by the relation[46]

$$\Delta Q_V = \text{const} \cdot \exp(V_s - V_{s0}). \quad (8)$$

The results of the study of the electroadsorption of water and methanol vapours on germanium have been examined by Kiselev[94–96] from the standpoint of the donor–acceptor model. According to these data,[94,95] the CH_3OH and H_2O vapours are adsorbed on an oxidised germanium surface via a coordination mechanism in the vicinity of surface defects, which serve as capture centres for holes from the bulk of the semiconductor. The localisation of a hole near a coordinated water molecule should result in the unshared electron pair being pulled even further to the adsorption centre and in an increase in bond strength. A field increasing the concentration of holes on the semiconductor surface should promote the adsorption of water molecules, while a field with the opposite polarity should induce their desorption.[94–97] In later studies,[98,99] the accumulation of the positive surface charge was explained by the protonation of H_2O. According to Kiselev and co-workers,[98,99] the localisation of a hole in a slow state increases the effective dipole of the adsorbed complex, increases the amount of ionic character of the bond, and decreases the activation energy for the heterolytic dissociation of H_2O. These processes can be regulated by altering the electronic state of the surface with the aid of an external electric field. The number of protonated water molecules increases exponentially with increase in the shift of the surface potential (V_s–V_{s0}) in the presence of the field.

(b) The electroadsorption of O_2 on polycrystalline ZnO films

The influence of field on the adsorption of oxygen has been investigated on β-HgS films[47] and polycrystalline ZnO specimens.[48,50,51,56] A condenser with a mica plate, illustrated in Fig. 1*c*, where the maximum field strength was 10^7 V m^{-1}, has been used.[47] In order to observe the effect, measurements were made of the resistances of the specimens in the adsorption of O_2 with the field applied to the specimen. The adsorption of oxygen ($p_{O_2} = 5 \times 10^{-1}$ Pa) was accompanied by an increase in the resistance of the β-HgS film exhibiting *n*-type conductivity. When a field increasing the concentration of electrons in the semiconductor was subsequently switched on, the resistance of the specimen σ fell and, after it had been switched off, the resistance acquired a value appreciably exceeding σ before the application of the field. This result has been explained[47] by the transition from the neutral form of chemisorption to the charged form as a consequence of the additional capture of electrons by centres with chemisorbed oxygen.

The additional increase in the resistance of the specimens after the adsorption of oxygen with the field applied to the specimen has been observed by Hoenig and Lane[48] and Constantinescu et al.[56] Hoenig and Lane[48] used a condenser with an air gap (Fig. 1*c*), low field strengths $E_{max} = 5.6 \times 10^5$ V m^{-1}, and an induced charge concentration $E\Delta n_V = 2 \times 10^{13}$ el. charge m^{-2}. Under these conditions, the shift of the Fermi level, estimated according to Eqn.(7), is $\sim 2 \times 10^{-5}$ eV and the influence of the collective factor on the adsorption of gases may be disregarded because it is insignificant.

The fact that the additional increase in the resistance of the ZnO film in the presence of oxygen occurred following the application of a field with a negative polarity to the semiconductor is also striking (Fig. 3*a*). This result is an argument against the discharge mechanism of the electroadsorption of oxygen, since in a discharge negative charging of the surface is attained after the application of a positive potential to the specimen. However, the data obtained by the field effect method on ZnO single crystals and polycrystalline specimens (with the exception of one study[100] carried out on a ZnO single crystal freshly cleaved in an ultrahigh vacuum at low temperatures) indicate the absence of surface conductivity of the inversion type; the negative charge induced by the electric field increases the conductivity of the specimen by an amount $\Delta\sigma_V$. It has been shown[88] that in an oxygen atmosphere the quantity $\Delta\sigma_V$

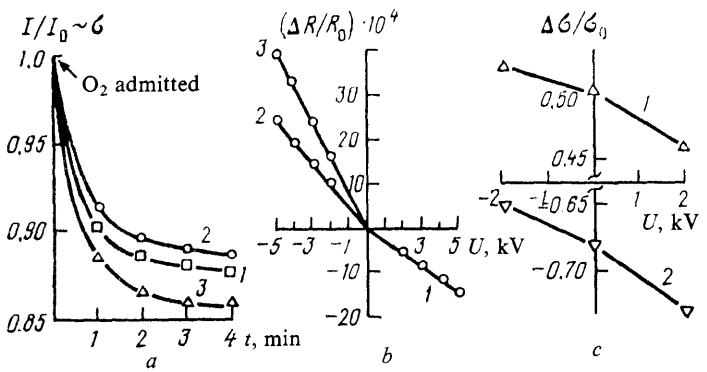


Figure 3. The influence of the field on the adsorption of oxygen and hydrogen on polycrystalline ZnO films. *a*, Variation of the conductivity of the specimen in a stream of the N_2 + O_2 mixture: *1*, in the absence of the field; *2*, on application of a field having the – sign to the specimen; *3*, on application of a field having the + sign to the specimen; *b*, The relative changes in resistance $\Delta R/R_0$ as a function of the applied potential: *1*, on application of a field having the – sign to the specimen (the changes $\Delta R/R_0$ *in vacuo* and in a O_2 atmosphere are the same); *2*, on application of a field having the + sign to the specimen *in vacuo*; *3*, ditto in a O_2 atmosphere ($p_{O_2} = 1.3 \times 10^2$ Pa); *c*, the relative changes in the conductivity of the film $\Delta\sigma/\sigma_0$ in the adsorption of hydrogen (curve *1*) and oxygen (curve *2*) atoms as a function of the magnitude and sign of the potential applied to the field electrode ($p_{O_2} = p_{H_2} = 1.33$ Pa).

diminishes (whilst retaining the positive sign) as a result of the additional capture of electrons by the oxygen-generated acceptor traps. The increase in the resistance of the ZnO films when a negative-polarity field is applied to the semiconductor is apparently associated with some kind of additional mechanism of capture of free carriers by the adsorbed oxygen.

The field effect is usually considered in the literature from the standpoint of the breakdown of the electronic equilibrium between the surface and the bulk of the semiconductor when a transverse electric field is applied. However, under conditions where a field acts on defective structures such as those of polycrystalline oxide films, there is apparently a shift of not only the electronic but also of the electronic-ionic equilibrium in the surface region of the semiconductor. In particular, on reduced ZnO films with a high concentration of interstitial Zn^+ ions, there is a possibility of the relaxation polarisation of the specimen under the influence of the external field penetrating the specimen over a distance equal to the Debye shielding length. The characteristic features of the variation of the electrical conductivity of ZnO following the adsorption of oxygen have been explained by the migration of the interstitial zinc in the region of the space charge.[101] In another study,[102] this phenomenon was regarded as an additional mechanism for the discharge of a surface subjected to the action of a corona discharge. The relaxation polarisation of ZnO following the application of a positive potential to the field electrode of the condenser (Fig. 1*c*) should lead to the diffusion of Zn^+ into the bulk of the specimen and of electrons to the ZnO surface. The increase in the resistance of the film observed in electroadsorption of O_2 can be explained by the capture of these electrons by the chemisorbed oxygen.[48]

The relaxation polarisation of the film in an external field apparently determines the mechanism of the electroadsorption of O_2, which has been observed[56] from the additional increase in the resistance of the ZnO film in a O_2 atmosphere following the application of a positive-polarity field to the specimen (Fig. 3*b*), which seemingly conflicts with the ideas of the electronic theory of adsorption. ZnO films with a thickness of (3–5) $\times$ 10^4 nm, comparable to the Debye shielding length, and the condenser illustrated in Fig. 1*f* were used in the above study. The authors suggest that oxygen is adsorbed mainly on the outer side of the film adjoining the gas phase and explain the observed effect by a change in the potential within the Zn film as a result of the accumulation of electrons at the oxide film–gas interface. The mechanism of such electron accumulation is apparently associated with the migration of mobile interstitial zinc ions Zn^+ to the glass–semiconductor interface when a negative potential is applied to the field electrode.

A somewhat different result was obtained on ZnO films 5×10^3 nm thick, sputtered onto a mica support (the condenser illustrated in Fig. 1*b* was used) under conditions where there was no field over the semiconductor surface.[50] The character of the change in the film resistance agrees with the electronic theory of adsorption: the negative-polarity field applied to the semiconductor increases the concentration of negatively charged adsorbed oxygen atoms and reduces the degree of adsorption of positively charged hydrogen atoms (Fig. 3*c*), the relative increase in the concentration of the charged forms of the chemisorbed species amounting to 7–9%. In the study of Ryl'tsev et al.,[50] the electroadsorption effects were investigated at the field-induced charge concentrations $e\Delta n_V$ = 1.6×10^{16} el. charge m^{-2}, which are the maximum possible in the field effect method, whereas in other investigations[48,56] these concentrations were lower by 2–3 orders of magnitude. The shift of the Fermi level, estimated with the aid of Eqn. (7), is $\sim 1.6 \times 10^{-2}$ eV and the values of ΔN^- observed by Ryl'tsev et al.[50] do not exceed those calculated by Eqn. (1).

Consequently the influence of the field on adsorption processes, investigated by Ryl'tsev et al.,[50] is probably due to the "collective" factor. The discrepancy between the results obtained in the above studies[50,56] can be accounted for bearing in mind that Ryl'tsev et al.[50] used several times thinner films, which were "transparent" to the gas, on which adsorption occurred not only on the outer side but also over the entire surface of crystallites, including the space charge region modified by the external field. Furthermore, relaxation polarisation should influence to a lesser extent the results obtained by Ryl'tsev et al.[50] because they used films characterised by a narrow space charge region whose specific resistance was lower by 2–3 orders of magnitude than that of the films used by Constantinescu et al.[56]

The adsorption of atomic hydrogen and oxygen on ZnO[50] and TiO_2 [51] films deposited on quartz supports and subjected to a thermal field treatment has also been investigated. Despite the sevenfold enrichment of the TiO_2 specimen in electrons, the effects observed[51] were small: the rate of adsorption of oxygen atoms increased by 15% and the rate of adsorption of hydrogen atoms diminished by 25%. The authors explained the appreciable change in the conductivity of the semiconductor films after they have been acted upon by a field with a strength of 5×10^6 V m^{-1} at 500–650 K by the electret state of the quartz support. However, according to Kovalenko's data,[103] quartz does not possess the properties of a very effective electret, its surface charge amounting to 5×10^{14} el. charge m^{-2}, which cannot ensure a change in the resistance of the oxide films by an order of magnitude. The type of spectroscopic composition of the quartz was not indicated in the above studies[50,51] and no data were given concerning the electret charging and discharging processes, which precludes a definite conclusion about the mechanism of the action of the field on the electrical conductivity and chemisorption properties of the films.

(c) The desorption of gases by the field using a metal–dielectric–semiconductor system

One of the difficulties in the interpretation of the electroadsorption effects observed from the change in the resistance of the specimen as a result of the action of the field in a gas atmosphere is associated with the impossibility of separating the charges captured by the adsorbed molecules and by the "slow" surface states of non-adsorption origin, whose electrophysical parameters change as a result of adsorption. Studies in which electroadsorption was observed directly by the manometric method are therefore of great interest.[18,52–54] The shift of the adsorption equilibrium after the application of the field was first investigated on polycrystalline *p*-type germanium films $\sim 10^3$ nm thick.[18,52] The condenser illustrated in Fig. 1*b*, with the maximum values E_{max} = 7×10^7 V m^{-1} and $e\Delta n_V = 4 \times 10^{15}$ el. charge m^{-2}, was used in the investigation. The desorption of H_2, CO, and hydrocarbons was observed after the application of a positive-polarity field to the germanium film; the amount of desorbed gas corresponds to thousandths of a monolayer. The application of a field having the opposite sign did not result in the observation of the electrodesorption effect. The authors explain the results[18,52] by a change in the occupancy by electrons of the adsorption centres located on the outer side of the film, directed towards the gas phase, when the field is applied to the inner side. Theoretically this is possible if the film thickness d is smaller than the Debye shielding length L;[72]

according to the authors,[18,52] this conditions holds for $d \simeq 10^3$ nm. The electrophysical parameters of the germanium films used were not indicated in the above studies,[18,52] but according to other data[104,105] thin ($< 10^4$ nm) germanium films have *p*-type conductivity and a high concentration of free carriers [$n_p = (6\text{–}8) \times 10^{24}$ m^{-3}] regardless of the type of conductivity of the single crystal used for the sputtering, which is due[105] to the high density of surface acceptor states. However, in this case $L = 10^2$ nm according to Eqn. (5) and the condition $d < L$ cannot be fulfilled.

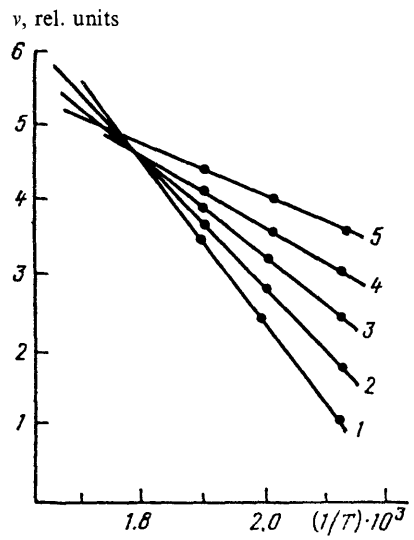


Figure 4. The Arrhenius relations for the rate of decomposition of formic acid at different currents flowing through the Ni–Al_2O_3–Au structure; *i*(A): *1*, 0; *2*, 0.25; *3*, 0.5; *4*, 1.0; *5*, 1.5.

The influence of the field on the desorption of gases as well as catalytic reactions has also been observed in other systems metal–dielectric–thin film involving a semiconductor or a metallic catalyst, but this happened after the application of a field of only one sign, namely one with a positive polarity, to the catalyst.[53–55,106] An appreciable increase in the steady-state rate of decomposition of formic acid and ammonia and also a change in the selectivity of the oxidation of propene on a gold film deposited on a nickel disc with an intervening Al_2O_3 layer has been observed[55] after the application of a negative potential to the nickel disc which performed the role of a field electrode (the condenser illustrated in Fig. 1*b* was used). For different currents flowing through the metal–oxide–metal (MOM) structure, a compensation effect was observed: with increase in temperature, the influence of the field on the rate of decomposition of formic acid was weakened (Fig. 4). The authors[55] explain these results by a change in the rates of the elementary processes in the interaction of the surface compounds with the stream of "hot" electrons arising in the MOM and MDS (metal–dielectric–semiconductor) structures when the electron gas in the dielectric is heated by a strong electric field.[107]

Various mechanisms for the scattering of the kinetic energy of electrons by the surface of the solid and the species adsorbed on it have been detected by the spectroscopy of the characteristic losses of low energy electrons (EELS).[108] The possibility of the vibrational excitation of the molecules adsorbed on the surface of a solid in processes involving the capture of free carriers by deep electron traps has been demonstrated.[109] The resonance adsorption of the excess kinetic energy of the "hot" electrons during scattering by surface states of adsorption origin can apparently be accompanied by both desorption and by the appearance of chemically active species. After the electrodesorption of H_2 and switching off the field at room temperature, the sorption of oxygen and the evolution of methane on germanium films were observed, which may be associated with the activation of the surface hydrocarbon compounds. Unfortunately the leakage currents in the condenser and their dependence on the electric field strength were not indicated in the above studies,[18,52] which makes it difficult to discuss the mechanism of the effect of the field.

(d) Gravimetric study of the influence of the field on the adsorption of oxygen and methanol on a silver catalyst

In order to test the proposed electronic mechanism of the oxidation of methanol, the influence of the field on the adsorption of oxygen and methanol on a silver catalyst coated by an oxide film was investigated gravimetrically[73] at $T = 723$ K and $P = 10^5$ Pa. A result discouraging from the standpoint of the electronic theory was obtained—oxygen was adsorbed for both negative and positive polarity of the external field on the catalyst. A similar result had been obtained earlier[48] on ZnO films using a plane-parallel condenser (Fig. 1*c*). When a field increasing the concentration of electrons in the semiconductor was switched on, the gas pressure in the system fell, which indicated additional adsorption of O_2. When a field with the opposite polarity was switched on, increasing the concentration of holes in the semiconductor, the desorption of oxygen was observed initially at low field strengths, changing subsequently to the adsorption of O_2 with increase in field strength. These results indicate that vacuum insulation conditions are maintained for the mica-free condensers used by Hoenig and Lane,[48] since the occurrence of a gas discharge should have been accompanied only by an increase in pressure.

The fact that the concentration of oxygen adsorbed due to the effect of the field (N-N_0) exceeds by several orders of magnitude the concentration of the induced charge $e\Delta n_V$ is striking.[48,73] The quantity N-N_0 calculated[48] from the change in pressure is 10^{17} molecules m^{-2}, whereas $e\Delta n_V = 10^{13}$ el. charge m^{-2}. The adsorption of oxygen under the influence of fields of both polarities has been explained[72] by the polarisation of non-polar O_2 molecules and the attraction of the induced dipoles to the surface of the cylindrical electrode. An electrostatic mechanism of the field effect on adsorption can also be proposed to account for the results of Hoenig and Lane[48] bearing in mind that the strength of the inhomogeneous electric field near the catalyst greatly exceeds the value calculated from the geometry of the condenser because of the roughness of the surface and is defined by the relation $E = U/Ar$,[9] where U is the external potential difference and r is the radius of individual crystallites or surface rugosities. For $U = 500$V and $r = 10^3$ nm, the energy imparted by the field to the polarised O_2 molecules exceeds their average kinetic energy in the absence of the field. As a result of this, the gas pressure in the inhomogeneous field over the catalyst surface and the degree of coverage of the latter by the adsorbate increase when an external potential is applied.

In the case of polar methanol molecules, the electroadsorption effect has different signs for different polarities of the external field in contrast to oxygen.[73] In a negative-polarity field on a silver catalyst, the degree of coverage by adsorbed methanol increases by 50%, while in a positive-polarity field it diminishes by approximately the same amount. Bearing in mind the clear discrepancy between the low field-induced charges ($e\Delta n_V = 10^{12}$ el. charge m^{-2}) and the large electroadsorption effect, the electroadsorption of methanol, like that of oxygen, must be explained by the electrostatic attraction of the dipolar alcohol molecules to the surface of the charged catalyst and not by the influence of the electronic factor. The orientation of the methanol molecules with the positive end towards the surface (the "hydrogen" orientation) apparently promotes the formation of various surface compounds of methanol, which have been detected by IR spectroscopy.[110] The increase in the partial pressure of the molecules with the "hydrogen" orientation both as a consequence of the dipolar polarisation and the attraction of the dipoles in the inhomogeneous field explains the increase in the amount of adsorbed gas in the presence of a negative-polarity field on a silver catalyst.

4. The influence of the field on catalytic reactions

Examination of the experimental data for the influence of the field on the adsorption of O_2, H_2, and methanol and water vapours on semiconductor adsorbents has shown that in some cases the observed effects can be explained by a shift of the Fermi level and a change in the concentration of free carriers under the influence of the external electric field, while in others they can be explained by secondary effects such as the relaxation polarisation of the solid and the polarisation of the gas in the vicinity of the catalyst surface. A secondary process of this kind must be taken into account also in the interpretation of the results obtained in the study of the influence of the field on the reactions occurring on semiconductors.

a) Dehydrogenation of ethanol on ZnO and the oxidation of methanol on a silver catalyst

In the study of catalytic reactions in the presence of an external field, cylindrical condensers with an air gap and a low field strength E between the plates are most often used. An exception is the study of Ivankiv et al.,[49] where a plane-parallel condenser with a mica plate, illustrated in Fig. 1*c*, permitting the attainment of $E_{max} = 3.5 \times 10^7$ V m^{-1} and $E\Delta n_V = 10^{15}$ el. charge m^{-2}, was used to investigate the influence of the field on the dehydrogenation of ethanol. The study was performed at 523 K on pressed and polished discs prepared from ZnO + 1% CuO powder. Copper oxide is apparently added to achieve a satisfactory conductivity and catalytic activity of the specimens. When a positive-polarity field was switched on, the rate of dehydrogenation of ethanol increased on the catalyst and the yield of aldehyde rose, while for a negative polarity the rate of reaction fell. The authors attribute these effects to a change in the concentration of the electron and hole gas on the surface of the semiconductor when a transverse electric field is applied. The results obtained agree with the idea that electron-accepting surface centres participate in the alcohol dehydrogenation reaction.[111] It is noteworthy that the curve relating the electrocatalytic effects to the electric field strength obtained in the above study[49] reaches a plateau (saturation) at $E = 1.5 \times 10^7$ V m^{-1} and does not change when E is increased to 3×10^7 V m^{-1}. The insignificant leakage currents (3×10^{14} electrons s^{-1}) when the rate of the catalytic reaction in the presence of the field changes (2×10^{17} molecules s^{-1}) is also evidence against a discharge mechanism of the electrocatalytic effect.

The influence of the field on the selectivity of the oxidation of methanol on a silver catalyst covered by an oxide film has been observed[74] at $T = 750$ K and very low concentrations of the field-induced charge ($e\Delta n_V = 10^{12}$ el. charge m^{-2} is smaller by three orders of magnitude than in the study of Ivankiv et al.[49]). A condenser with a cooled field electrode, illustrated in Fig. 1*g*, was used.[74] When a negative-polarity field was switched on, the yield of formaldehyde on the catalyst increased by 7–8%, while in the presence of a positive-polarity field the yield of formaldehyde fell but that of CO_2—the product of the total oxidation of CH_3OH—increased (Fig. 5). The authors explain the observed effect by a change in the concentration of free carriers on the catalyst surface. However, bearing in mind the very low concentration of the induced carriers and the results for the influence of the field on the adsorption of O_2 and CH_3OH, it would probably be more reasonable to attribute the observed electrocatalytic effects to the different reactivities of the surface compounds formed in the adsorption of methanol, with the "hydrogen" and "oxygen" types of orientation, in the partial and total methanol oxidation reactions.

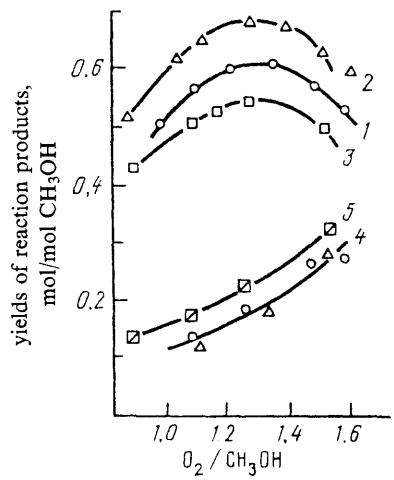


Figure 5. Dependence of the yield of methanol oxidation products on the electric potential applied to the catalyst: *1*, the yield of formaldehyde in the absence of the field; *2*, ditto on application of a field having the – sign to the specimen; *3*, ditto for a field with a + sign applied to the specimens; *4*, the yield of CO_2 in the absence of the field and on application of a field having the + sign to the specimen; *5*, ditto with the – sign of the field applied to the specimen.

(b) The oxidation of CO on NiO, ZnO, and Cu_2O

When different metal oxide films, grown on the surface of a foil by oxidation in oxygen at elevated temperatures were used, a change in the rate of oxidation of CO to CO_2 was observed in the presence of an external electric field.[75–77] In these studies, the external potential was applied between the field electrode and the metallic foil, which ensured the uniformity of the distribution of the potential along the oxide film (the design of the condenser is shown in Fig. 1*h*).

An increase in the rate of oxidation of CO by a factor of 1.5–2 and a decrease in the activation energy for the reaction by 0.21 eV after a positive-polarity field had been applied to the catalyst were observed[75] on nickel oxide obtained by heating nickel foil at 1300 °C in a stream of oxygen. A quantitative comparison of the relative changes in the rate of reaction $\Delta g/g_0$ as a function of the electric field strength, according to Eqns. (2) and (4), has been carried out.[75] Expressing the effective shielding length in terms of a series of semiconductor characteristics of NiO, the authors found that the experimental data agreed quantitatively with the theoretical relation between $\Delta g/g_0$ and E. However, it becomes clear from the comparison of the data presented[75] that the electric field strength in the vacuum gap near the catalyst surface was used as the value of E, whereas Eqn. (4) has been obtained for the electric field strength in the semiconductor at the interface with the vacuum E_n. The quantities E_n and E are linked by the relation $E_n = E/\varepsilon_n$, where ε_n is the dielectric constant of the semiconductor. Bearing in mind that $\varepsilon_{NiO} = 10$ for the field strength $E_{max} = 10^6$ V m^{-1} and $L = 3 \times 10^3$ nm employed,[73] we obtain from Eqn. (4) $V_s V_{s0} = 3 \times 10^{-3}$ eV. The experimentally observed increase in the rate of reaction by a factor of 1.5–2 as well as the decrease in the activation energy for the reaction after the application of the field by 0.21 eV do not correspond to the maximum possible shift of the surface potential, which could also be much smaller as a consequence of the transfer of the charge to surface states.

Deren and Mania[76] studied the influence of the field on the rate of oxidation of CO to CO_2 on the oxide coating of a zinc foil under the conditions of an electrode working in a non-stationary regime, whose activity gradually fell with time. After the application of a positive potential to the field electrode, a sharp increase in the rate of reaction was observed initially, but after several minutes it fell to the value corresponding to the rate of oxidation in the absence of the field. A field with the opposite polarity induces a temporary decrease in the activity of ZnO. These results led to the conclusion that there exists a limiting acceptor stage in the oxidation of CO to CO_2. The increase and then the decrease in the rate of oxidation of CO after the application of a negative-polarity field to the catalyst to values corresponding to a zero external potential is evidence against the discharge mechanism of the electrocatalytic effect. The authors explain the observed time variation by the transfer of the induced electrons to slow surface states.

The electrocatalytic effect occurs also when Cu_2O is used as the catalyst.[77] In order to elucidate the mechanism of the field effect on the catalytic activity of Cu_2O, a study was made of the possibility of the structural modification of the Cu_2O film during its growth on a copper plate at 1050 °C in the presence of a 10^6 V m^{-1} field. When a positive potential was applied to the copper plate, the layer of the Cu_2O scale acquired an increased resistance, in contrast to the copper(I) oxide formed in the absence of the field, which is associated, according to the authors,[77] with the formation of an interstitial solid solution of the excess copper ions. When a field with the opposite polarity was applied, layers of Cu_2O with an excess of oxygen, exhibiting a reduced resistance, were formed. The influence of the field on the oxidation of copper also affects the interplanar spacings in the specimens and the thickness of the oxide films. The copper(I) oxide obtained in the absence and presence of the field exhibited different catalytic properties. The Cu_2O films formed on application of a negative potential to the specimen had an increased activity in the oxidation of CO to CO_2 compared with the films oxidised with application of a positive potential. This difference increased when the reaction was carried out in the presence of a field having the same sign as that used in the formation of the film.

Thus the authors have shown that the enrichment or depletion of the oxide surface in the metal cations under the influence of the electric field may be the cause of the modification of its catalytic activity. A similar change in the defective structure of the surface may occur on NiO and ZnO specimens as a result of the migration of the cations into the region of the space charge modified by the external field. The movement of Ni^{2+} in NiO as well as that of the interstitial zinc in ZnO under conditions where the surface potential is modified by the adsorbed oxygen has been considered.[101,112] It is noteworthy that, when NiO and ZnO films were used as the catalysts, the acceleration of the oxidation of CO to CO_2 was observed for different signs of the external potential: after the application of a positive-polarity field to NiO on a foil and after the application of a negative-polarity field to ZnO. A catalytic study of oxides was carried out in the low-temperature region (180–400 °C), where the CO oxidation reaction probably has an associative mechanism.[113] According to the data of Sokolovskii et al.,[114] the decomposition of surface carbonates on ZnO proceeds with participation of the O_2^- radical-anions. The sharp rise in the catalytic activity of ZnO for a negative potential on the specimen can apparently be explained by the additional adsorption of oxygen in a charged form, which is observed (as described in the previous Section) when the field-induced charge is transferred to the surface adsorption states and also as a consequence of the relaxation polarisation of the oxide in the region of the space charge. According to Gravel',[115] the rate-limiting stage of the oxidation of CO on the NiO catalyst is the interaction of CO_3^- with the adsorbed carbon monoxide. The enrichment of the surface layers of nickel oxide in the Ni^{2+} and Ni^{3+} cations promotes the formation of carbonyl complexes and an increase in the catalytic activity of NiO.

(c) The reversible chemical modification of ZnO, TiO_2, and Pt/TiO_2 film catalysts by the electric field

A series of studies[58–71] have been devoted to the mechanism of the effect of the field on the adsorption and catalytic properties of thin ZnO, TiO_2, and Pt/TiO_2 films deposited on the inner surface of a Pyrex reactor (see the condenser illustrated in Fig. 1*f*). The influence of the field on the rate of decomposition of isopropyl alcohol,[58] the oxidation of CO by NO and O_2,[60] the decomposition of NO[60] and water vapour,[61] and the adsorption of O_2,[59,62] H_2,[61] and CO[62] has been observed. The results have been explained from the standpoint of the electronic theory of catalysis with participation of charged intermediate compounds in the catalytic processes.

In order to test the mechanisms of the field effect, the above reactions were reproduced in a quartz reactor (Fig. 1*f*) and also in experiments using a plane-parallel condenser with a mica plate as the dielectric (Fig. 1*b*). For comparable field-induced charges, the changes in the conductivity of the film ($\Delta\sigma_V$) deposited on mica did not exceed several per cent of the initial conductivity of the specimen, the shift of the Fermi level was less than $0.1kT$, and the influence of the field on the adsorption of oxygen and on the rate of oxidation of CO and of the decomposition of NO were not observed.[57]

In a glass reactor at temperatures in the range 130–160 °C, changes in the conductivity of the ZnO, TiO_2, and Pt/TiO_2 films, which were anomalously high for the field effect method, were obtained for a positive potential applied to the field electrode. For

an initial specific conductance $\sigma_0 = 10^{-11}$–10^{-10} Ω, referred to a unit surface of the specimen, the relative changes $\Delta\sigma_V/\sigma_0$ reached 10^4–10^5 and the activation energy for electrical conduction fell from 0.7–0.9 to 0.1–0.2 eV.[67] The ZnO, Pt/TiO_2, and TiO_2 films retained a low resistance state for several tens of hours after the field had been switched off, exhibiting at the same time a "memory effect" with respect to the action of the field on chemisorption and catalytic processes. However, their transition to the low resistance state was reversible. The application of a negative potential to the field electrode as well as heating to a high temperature resulted in the return of the resistance of the films and of their chemisorption and catalytic properties to the initial values. The results of the measurements of the condenser charging and discharge currents under conditions of the application of fields with the opposite polarity and thermally stimulated depolarisation, also confirming the reversibility of the change in the state of the film catalyst after thermal field treatment, have provided a basis for explaining the observed effects in terms of the relaxation polarisation of the Pyrex glass, which has the properties of a thermoelectret.[63] The thermoelectrisation of the dielectric[116] may be caused both by the formation of dipoles and by the separation of charges in the electret during the migration of current carriers (for example, Na^+ ions in Pyrex glass).

In order to elucidate the possibility of the transfer of sodium from the support to the semiconductor film, the electron diffraction and oxygen absorption methods as well as the method involving the titration of the absorbed oxygen with carbon monoxide were used. It was shown that the passage of a charge through the condenser is accompanied by the electrolytic migration of sodium from the dielectric glass support and its deposition on the surface of a semiconductor film as a finely dispersed metallic phase.[64–66] Thus the earlier results for the influence of the field on adsorption and catalysis can be explained by the surface doping of the oxide films with sodium. The adsorption of oxygen with application of a positive potential to the field electrode takes place as a consequence of the interaction of oxygen with sodium accompanied by the formation of the compounds NaO_2, Na_2O_2, and Na_2O. When sodium superoxide and peroxide are heated, they decompose with evolution of oxygen, the maxima in the thermal desorption spectrum being observed at 370 and 520 K.[65] The decrease in the adsorption capacity of the oxidised TiO_2 film relative to hydrogen after the preliminary application of a positive-polarity field to the field electrode[61] can be explained by the blocking of the hydrogen adsorption centres by sodium atoms.[117] The cause of the evolution of hydrogen when water vapour is admitted into the system after the latter had been exposed to the field is evident:[71] hydrogen is displaced from H_2O by sodium, which binds strongly to the oxygen of the water molecule.

The increase in the rate of absorption of a stoichiometric mixture of O_2 and CO and the simultaneous inhibition of the CO oxidation reaction on ZnO films on application of the field[68] can be explained by the interaction of CO and CO_2 with sodium oxides and the formation of Na_2CO_3. The blocking of part of the ZnO surface by these compounds reduces the steady-state rate of oxidation of CO by a factor of 2–3, while the activation energy and the reaction orders remain unaltered. At the same time, the electrophysical parameters of the ZnO film working under stationary conditions differ greatly from the initial values after the application of the field as a result of the interaction of part of the sodium with the oxygen of the crystal lattice (the activation energy for electrical conduction diminishes from 0.65 to 0.17 eV). Hence it is concluded that the concentration of the conductivity electrons is not the parameter controlling the rate of oxidation of CO on ZnO films.

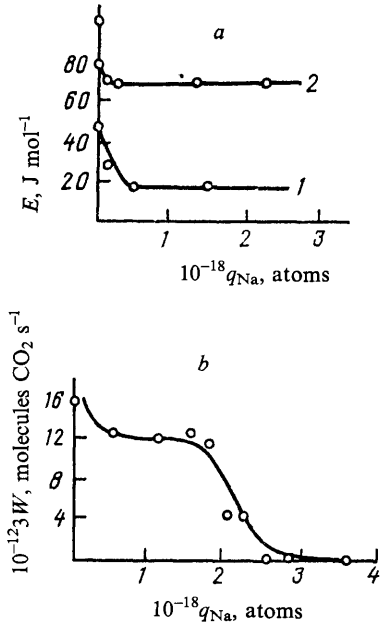


Figure 6. Dependence of the activation energy for electrical conduction in the Pt/TiO_2 film on the amount of Na introduced (*a*) and dependence of the rate of oxidation of CO on the Pt/TiO_2 film (~4 wt.% Pt) on the amount of electrodeposited Na (*b*): *1*, *in vacuo*; *2*, in the presence of the $2CO + O_2$ stoichiometric mixture ($p_{2CO+O_2} = 0.72$ Pa).

In order to elucidate the role of the contact fields between the active phase and the carrier in chemisorption and catalytic processes, the effect of the field on a deposited Pt/TiO_2 catalyst was investigated.[69,70] The transfer of sodium from the support to the surface of the Pt/TiO_2 film is accompanied, as in the case of TiO_2, by a sharp decrease in the activation energy for the electrical conduction of the film at low levels of doping. The activation energy does not change on further increase in the concentration of the added sodium (Fig. 6*a*, curves *1* and *2*). The change in the catalytic properties of the Pt/TiO_2 system on doping with sodium is not correlated with the change in the activation energy for electrical conduction (Fig. 6*b*) and is observed at higher concentrations of added sodium where, according to the conditions in the preparation of the sodium-modified deposited platinum catalyst, the chemical interaction between sodium and platinum becomes possible.[70] This permits the conclusion that the position of the Fermi level in the carrier and the associated contact phenomena at the metal–semiconductor interface do not play an appreciable role in the catalytic process on platinum.

When quartz is used as the dielectric, a similar pattern in the variation of the electrical conductivity and in the catalytic and chemisorption properties of TiO_2 film is observed, but with the

electric field applied at a higher temperature (~530 K) than for Pyrex (430 K), this being associated with the reduced sodium content in quartz.[71]

It is of interest to note that, when a field with a positive polarity is applied to the field electrode during the oxidation of CO to CO_2 on ZnO and Pt/TiO_2 films, the catalysts are not poisoned irreversibly by compounds formed by sodium with O_2, CO, CO_2, and Pt. For standard conditioning at 750 K, these compounds decompose with evolution of CO and CO_2 to the gas phase and the sodium oxide particles remaining on the surface react chemically with the glass, fusing with the latter, as a result of which the catalytic activity of the film returns to its initial value (before the application of the field). The reversible character of the interaction of sodium with the oxides ZnO, TiO_2, and Pt/TiO_2 makes it possible to return the catalytic and adsorption characteristics of these catalysts to the initial values by applying a field with the reverse polarity. This makes it possible to use an external electric field to regulate the rates of catalytic processes in which metallic sodium exhibits a satisfactory activity or is a promoting additive.

At elevated temperatures (from 670 to 720 K), glass begins to play the role of a solid electrolyte and the metal–glass–conducting catalyst film system, in which the metal is exposed to air and the catalyst is placed in the gas investigated, constitutes an electrochemical cell. As a result of adsorption and absorption processes on the metal, glass, and the catalyst, electrode potentials arise between the gas electrodes. They depend on the nature of the catalyst and the gas investigated.[118,119]

The influence of polarisation on the rates of catalytic hydrogen oxidation and ammonia synthesis reactions has been investigated.[120,121]

(d) The influence of an alternating field on the oxidation of CO on NiO and the hydrogenation of ethylene on ZnO

It has been suggested[122] that an alternating external field be used as the basis of a method for the investigation and regulation of heterogeneous catalytic reactions on semiconductors. The possibility of the adsorption of gas molecules for one polarity of the alternating field and of their desorption for the other as a function of the donor–acceptor properties of the gas has been considered.[122] The author[122] called this phenomenon alternosorption. The use of an alternating field makes it possible to control the time during which the species are present on the catalyst surface. Whilst studying the dependence of the rate of reaction on the frequency of the external field, it is possible to determine the optimum time for the elementary step in the oxidation-reduction catalytic process.

The influence of a sinusoidal 2.2×10^6 V m^{-1} external field on the rate of oxidation of CO to CO_2 has been investigated at 123 °C.[123] Nickel discs coated by a layer of NiO 10^3 nm thick, separated from one another by ceramic plates, were used as the catalyst. In the frequency range from 50 to 300 Hz, the rate of oxidation of CO increases severalfold and passes through a maximum located between 100 and 200 Hz. Hence it was concluded that the time during which the adsorbed species are present on the catalyst surface is between 5 and 10 ms.

The influence of the alternating electric field was investigated in greater detail in the hydrogenation of ethylene on a ZnO specimen.[124] A polycrystalline zinc oxide powder was placed between two field electrodes to which an alternating potential was applied (see the condenser illustrated in Fig. 1*d*). When a 1.2×10^5 V m^{-1} sinusoidal potential was switched on in the temperature range from 60° to 146 °C, a change in the reaction orders with respect to hydrogen and ethylene and a decrease in the activation energy from 71 to 48 kJ mol^{-1} were observed. The authors were unable to establish the mechanism of the action of the field, but noted that it may be associated with induction heating or a discharge, because the rate of reaction decreased in the presence of the field.

This study is of interest because of the methodological approach to the selection of the condenser design. A design was selected which does not require specially prepared film catalyst specimens and ohmic terminals on them, the longitudinal alternating field being applied directly to the polycrystalline powdered semiconductor, (Fig. 1*d*). The polycrystalline specimens consisted of a multiplicity of crystallites loosely adjoining one another and having a large number of contacts. The equivalent electric circuit of such specimens consists of a combination of a series of active resistances and capacitances. A theoretical model of the barrier conductivity of polycrystalline films taking into account the change in the filling of the surface states at the boundary between the crystallites, when the height of the barrier was altered by application of an external electric field, was examined.[125] The application of an alternating field to the polycrystalline semiconductor entails an alternation of the charges of the contact capacitances accompanied by the filling and emptying of the surface traps located in the boundary regions of the crystallites.

According to the donor–acceptor mechanism of adsorption and charging, the role of the effective electron and hole traps on the surface of the semiconductor is assumed by electron-accepting and electron-donating centres forming surface complexes with the molecules adsorbed on them. The participation of the main centres and also of the ion pair, consisting of a coordinatively unsaturated cation and an oxygen ion, in the activation of adsorbed ethylene and hydrogen during the hydrogenation of the former was examined by Minachev et al.[126] Apparently the mechanism of the influence of the alternating field on the kinetics of the hydrogenation of ethylene is determined by the change in the filling of these centres by free carriers.

IV. Conclusion

This review has examined studies in which changes were observed in the concentration of the charged form of the chemisorbed species, in the coverage of the surface by the adsorbent, and in the rates of catalytic reactions on application of an electric field at right angles to the surface of the catalyst using various methods: conductimetric, field effect, gravimetric, volumetric, and mass-spectrometric analysis of the gas.

Various designs of the condensers, in which the field strength and hence the charge induced in the semiconductors varied within wide limits (from 10^{12} to 10^{16} el. charge m^{-2}), were used for this purpose. The estimates of the change in the surface potential following the application of the field, obtained in the present review, show that even at the highest concentration of the induced charge, amounting to 10^{16} el. charge m^{-2}, the quantity $V_s - V_{s0}$ on polycrystalline specimens does not exceed tenths of kT. In almost all the studies of the influence of the field on catalytic reactions, the induced charge $e\Delta n_V = 10^{12}$–10^{13} el. charge m^{-2} and the corresponding shifts of the surface potential are negligible ($\ll kT$). Thus, owing to the high density of the surface states, the possibilities of the field effect method for discovering the role of the collective factor in semiconductor catalysis are extremely limited.

The authors explained the results obtained in terms of a change in the filling of the active surface centres by free carriers. Under conditions where almost all the field-induced charge passes to the surface states and the shift of the Fermi level is negligible, the changes in the local properties of the surface under the influence of the captured charge carriers come to the fore. In Vol'kenshtein's theory, the electrons and holes on the semiconductor surface play the role of free valences; their direct involvement in the formation of a bond converts the adsorbed molecules into radicals with an increased reactivity. In the donor–acceptor model of adsorption and charging,[21] the more probable and general case of the deformation of the adsorbed complex in the Coulombic field of the captured charge carrier is considered. This increases the amount of ionic character of the bond and the probability of the dissociation of the molecule. It has been shown[109] that the capture of free carriers by adsorbed states is accompanied by the evolution of the excess energy, which is dissipated in the vibrational modes of the adsorbed molecules, which can also stimulate their dissociation or desorption.

Various secondary effects, i.e. effects not associated directly with a change in the concentration of the free carriers, introduce some uncertainty into the interpretation of the results for the influence of the field on adsorption and catalysis. Essentially, only the change in the chemisorption and catalytic properties of semiconductors following the application of the electric field has been established in the majority of studies, while the question of the mechanism of the action of the field remained open. In the review much attention has therefore been devoted to the most probable mechanisms of chemisorption and catalysis in the presence of the field for the given catalytic systems and associated with the occurrence of a series of physicochemical processes, among which the influence of the relaxation polarisation of the dielectric and of the surface layers of the semiconductor must be specially emphasised.

It is suggested in the electronic theory of catalysis that the field effect method can shift the Fermi level and can alter the concentration of electrons and holes on the semiconductor surface without changing the chemical composition of the catalyst. This point of view is in general incorrect because the application of an external field to defective structures such as polycrystalline semiconductor films and dielectric supports at elevated temperatures (>400 K) is accompanied by the migration of weakly attached ions through space and the establishment of a new electronic–ionic equilibrium. The defective structure and the chemical composition of the catalyst surface are modified as a consequence of this.

It has been established[64–66] that the surface doping of film catalysts with sodium atoms deposited electrolytically from a sodium-containing glass support having the ionic type of conductivity can be achieved with the aid of an external field. The alkali metals sodium and potassium on a carrier exhibit a satisfactory catalytic activity,[127,128] but they are of even greater interest as promoting additives to deposited metallic catalysts.[129,130]

Electrodeposited sodium is introduced onto the surface in the atomic form and exists on it in a finely dispersed metallic state.[65,66] It is of interest to investigate in reducing media the catalytic activity of finely dispersed metallic sodium and of the intermetallic compounds formed when sodium interacts with the active metallic phases of the deposited catalyst. Bearing in mind that, as a consequence of the reversibility of the interaction of sodium with oxides, its surface content can be varied smoothly in either direction and that the amount of electrodeposited metal can be easily evaluated coulometrically, the doping method proposed[64–71] must be recognised as a convenient procedure for the preparation of model film catalysts. The use of other metal-containing glasses makes it possible to extend the class of metallic doping additives.

A series of other physicochemical phenomena, which are apparently responsible for the mechanisms and may be used to regulate adsorption and catalytic processes, have been considered in this review. They include the following.

1. The change in the concentration of polar molecules with a definite type of orientation in strong inhomogeneous local fields near the catalyst surface. The inhomogeneous fields arising as a result of the greater curvature and roughness of the catalyst surface relief may alter both the rate and the selectivity of the catalytic process.

2. The involvement in the catalytic processes of the "hot" electrons arising when a current flows in MOM and MDS structures. As a result of the excess kinetic energy of the "hot" electrons, there is a possibility of the activation of the reactants chemisorbed on the catalyst or of the desorption of the reaction products and hence of the acceleration of the catalytic reaction.

3. The change in the chemical composition of the surface layers of the catalyst in an external electric field. The modification of the defective structure as a result of the increase or decrease in the concentration of cations near the catalyst surface alters the probability of the formation of different surface compounds and can be used in the study of the mechanisms of catalytic processes.

The study of the influence of an alternating field on catalytic reactions is promising. When an alternating field is employed, there is no need to assemble a special condenser, since there are many contact capacitances in the polycrystalline specimen itself at the boundary between the crystallites. When a sinusoidal potential is switched on, the contact capacitances undergo alternating changes in charge and there is a multiplicity of steps involving the capture of free carriers by the surface states arising in the interaction of the adsorbed molecules with the electron-accepting and electron-donating centres on the semiconductor surface, which may entail the deformation of the intramolecular bonds and a change in the reactivity of the adsorbed molecules. Additional physicochemical methods (IR spectroscopy, thermal desorption) can be used to investigate the adsorption and catalytic processes occurring in the presence of an alternating field.

In conclusion one must say that, although the prediction of the electronic theory that the field effect method would prove promising in the study of the elctronic factor in catalysis has not come true, nevertheless an external electric field can be used effectively for the regulation of the chemisorption and catalytic activities of semiconductor catalysts. The different physicochemical processes occurring when an electric field is switched on may stimulate adsorption and catalytic reactions.

References

1. M Ya Fioshin, I A Avrutskaya *Usp. Khim.*, 1975, **44** 2067 [English translation in *Russ. Chem. Rev.*, 1975(11)]
2. R W Murray *Philos. Trans. R. Soc., London, A*, 1981, 302(1468) 2253
3. A M Skudin Elektrokhimiya (Electrochemistry), Izd. VINITI, Moscow, 1982, Vol. 18, p. 228 [Itogi Nauki i Tekhniki (Advances in Science and Engineering)], 1982, **18** 228

4. S D Varfolomeev, I V Berezin Fizicheskaya Khimiya: Sovremennye Problemy (Physical Chemistry: Modern Problems), Izd. Khimiya, Moscow, 1982, p. 68
5. B B Damaskin, O A Petrii, V V Batrakov *Adsorbtsiya Organicheskikh Soedinenii na Elektrodakh* (Adsorption of Organic Compounds on Electrodes), Izd. Nauka, Moscow, 1968, 333 pp
6. V S Bagodskii (Editor) *Problemy Elektrokataliza* (Problems of Electrocatalysis), Izd. Nauka, Moscow, 1980
7. R S Hansen, N C Gardner *Experimental Methods for the Investigation of Catalysis* (Translated into Russian), Izd. Mir, 1972, p. 173
8. A Van Oostrom *Advances in the Study of the Surfaces of Solids* (Translated into Russian), Izd. Mir, Moscow, 1977, p. 40
9. J Block, A W Ganderna *Methods for the Analysis of Surfaces* (Translated into Russian), Izd. Mir, Moscow, 1979, p. 464
10. E Muller *Methods for the Analysis of Surfaces* (Translated into Russian), Izd. Mir, Moscow, 1979, 401
11. F F Vol'kenshtein *Fizikokhimiya Poverkhnosti Poluprovodnikov* (The Physical Chemistry of the Surfaces of Semiconductors), Izd. Nauka, Moscow, 1973, 399 pp
12. K Hauffe *Catalysis. Electronic Phenomena [Reaktionen in und an Festen Stoffen?]* (Translated into Russian) Inostr. Lit., Moscow, 1958, p. 241
13. J E German *J. Chim. Phys.*, 1954, **51** 691
14. S Z Roginskii Poverkhnostnye Svoistva Poluprovodnikov (Surface Properties of Semiconductors), Izd. Akad. Nauk SSSR Moscow, 1962, p. 5
15. O V Krylov *Kataliz Nemetallami* (Catalysis by Non-Metals), Izd. Khimiya, Moscow, 1967, 240 pp
16. N P Keier *Issledovanie Poverkhnosti Katalizatorov Izotopnymi Metodami* (The Study of the Surfaces of Catalysts by Isotopic Methods), Izd. Nauka, Moscow, 1984, 135 p
17. F F Vol'kenshtein *Problemy Kinetiki i Kataliza*, 1955, **8** 201
18. V I Lyashenko, O A Serba, I I Stepko *Dopov. Akad. Nauk Ukr. RSR*, 1962, (3) 350
19. F F Vol'kenshtein *Usp. Khim.*, 1966, **35** 1277 [English translation in *Russ. Chem. Rev.*, 1966(7)]
20. V L Bonch-Bruevich, V B Sandomirskii *Zh. Fiz. Khim.*, 1978, **52** 3009 [English translation in *Russ. J. Phys. Chem.*, 1978(12)]
21. V F Kiselev, O V Krylov *Elektronnye Yavleniya v Adsorbtsii i Katalize na Poluprovodnikakh i Dielektrikakh* (Electronic Phenomena in Adsorption and Catalysis on Semiconductors and Dielectrics), Izd. Nauka, Moscow, 1979, 234 pp
22. J Panciz, I Hasligerova *Collect. Czech. Chem. Commun.*, 1980, **45** 2474
23. E N Korol' (Editor) *Fizicheskie Osnovy Polevoi Mass-Spektroskopii* (The Physical Principles of Field Mass Spectrometry), Izd. Naukova Dumka, Kiev, 1978, p. 82
24. A Bennett *J. Surf. Sci.*, 1975, **50** 77
25. E N Korol, I Yu Posudievsky *Surf. Sci.*, 1986, **169** 104
26. J Block *Chemistry and Physics of Solid Surface. IV* (Springer Series in Chemical Physics). (Edited by R Vanselow, R Howe), Springer Verlag, Berlin etc., 1982, Vol. 20, p. 407
27. B V Il'in *Priroda Adsorbtsionnykh Sil* (The Nature of Adsorption Forces), Gostekhizdat, Moscow–Leningrad, 1952, 124 pp
28. M Domke, J Block, M Drechler *Surf. Sci.*, 1975, **51** 451
29. E V Klimenko, A G Naumovets *Surf. Sci.*, 1969, **14** 141
30. E V Klimenko, A G Naumovets *Fiz. Tverd. Tela*, 1971, **13** 33
31. G Fröhlich *Theory of Dielectrics* (Translated into Russian), Inostr. Lit., Moscow, 1960, 252 pp
32. J Block, B L Moentack *Z. Naturforsch. A*, 1967, **22** 711
33. R Copeland *J. Phys. Chem.*, 1971, **75** 2967
34. A R Anway *J. Chem. Phys.*, 1969, **50** 2012
35. V G Ivanov, T P Smirnova, G N Fursei *Poverkhnost': Fizika Khimiya, Mekhanika*, 1986, (12) 128
36. L N Dobretsov, M V Gomoyunova *Emissionnaya Elektronika* (Emission Electronics), Izd. Nauka, Moscow, 1966, 564 pp
37. D Vladov, Vl Dyakovitch, Sh Dinkov *J. Catal.*, 1966, **5** 412
38. J Block, H Kral *Z. Phys. Chem. (Munich)*, 1960, **24** 66
39. G M Schwab, J Block, G Shultze *Naturwissenschaften*, 1957, **44** 482; *Angew Chem.*, 1959, **71** 101
40. W Pohl, D Warschauer (Editors) *Solids Under High Pressure* (Translation into Russian), Izd. Mir, Moscow, 1966, 524 pp
41. F F Vol'kenshtein, V B Sandomirskii *Dokl. Akad. Nauk SSSR*, 1958, **118** 980
42. V G Baru, F F Vol'kenshtein *Dokl. Akad. Nauk SSSR*, 1966, **167** 1314
43. G K Boreskov *Dokl. Akad. Nauk SSSR*, 1959, **127** 591
44. E P Mikheeva, N P Keier *Kinet. Katal.*, 1964, **5** 748
45. N P Keier, E P Mikheeva *Kinet. Katal.*, 1969, **10** 288
46. E P Mikheeva, N P Keier *Dokl. Akad. Nauk SSSR*, 1974, **218** 906
47. L I Ivankiv, A M Muzychuk *Zh. Fiz. Khim.*, 1968, **42** 424 [English translation in *Russ. J. Phys. Chem.*, 1968(2)]
48. S A Hoenig, J R Lane *Surf. Sci.*, 1968, **11** 163
49. L I Ivankiv, M V Miliyanchuk, A K Filatova *Glubokii Mekhanizm Kataliticheskikh Reaktsii* (Detailed Mechanism of Catalytic Reactions), Izd. Nauka, Moscow, 1968, Vol. 12, p. 327 [Problemy Kinetiki i Kataliza (Problems of Kinetics and Catalysis)]
50. N V Ryl'tsev, E E Gutman, I A Myasnikov *Zh. Fiz. Khim.*, 1981, **55** 986 [English translation in *Russ. J. Phys. Chem.*, 1981(4)]
51. N V Ryl'tsev, I A Myasnikov, E E Gutman *Zh. Fiz. Khim.*, 1983, **57** 381 [English translation in *Russ. J. Phys. Chem.*, 1983(2)]
52. V I Lyashenko, A A Serba, I I Stepko *Kinet. Katal.*, 1966, **7** 1095
53. L I Ivankiv, V V Solyanik *Ukr. Fiz. Zh.*, 1968, **13** 852
54. L I Ivankiv, A M Muzychuk, V V Solyanik *Ukr. Fiz. Zh.*, 1969, **14** 12
55. W Haidinger, J Figer *The Physical Basis for Heterogeneous Catalysis: Proceedings of the 9 Battie Colloquium in the Materials Sciences Held in Gstaad, Sept. 2–6, 1974* (Edited by E Drauglis, R I Jaffee), Plenum Press, New York–London, 1975
56. M Constantinescu, E Segal, M Vass *Rev. Roum. Chim.*, 1976, **21** 503
57. V G Devyatov, E P Mikheeva, L M Usol'tseva *Kinet. Katal.*, 1982, **23** 1022
58. N P Keier, E P Mikheeva, L M Usol'tseva *Dokl. Akad. Nauk SSSR*, 1968, **182** 130
59. N P Keier, E P Mikheeva, L M Usol'tseva *Kinet. Katal.*, 1970, **11** 1009
60. L M Usol'tseva, E P Mikheeva, N P Keier *Kinet. Katal.*, 1973, **14** 1350
61. L M Usol'tseva, E P Mikheeva, N P Keier *Kinet. Katal.*, 1979, **20** 161

62. V G Devjatov, E P Mikheeva, N P Keier *React. Kinet. Catal. Lett.*, 1978, **9** 199
63. E P Mikheeva, V G Devyatov, V M Kolchanova, L M Usol'tseva *Trudy V Sovetsko-Yaponskogo Seminara po Katalizu* (Tashkent, 1979) [Proceedings of the V Soviet–Japanese Seminar on Catalysis (Tashkent, 1979)], Izd. Fan, Tashkent, 1979, p. 188
64. E P Mikheeva, V G Devyatov, V M Kolchanova *Kinet. Katal.*, 1983, **24** 418
65. V M Kolchanova, E P Mikheeva, L M Usol'tseva, et al. *Kinet. Katal.*, 1983, **24** 667
66. V G Devyatov, E P Mikheeva, N P Keier *Kinet. Katal.*, 1983, **24** 671
67. V G Devyatov, V M Kolchanova, E P Mikheeva, L M Usol'tseva *Izv. Akad. Nauk SSSR. Neorg. Mater.*, 1984, **20** 1983
68. V G Devyatov, E P Mikheeva, N P Keier *Kinet. Katal.*, 1984, **25** 239
69. V M Kolchanova, E P Mikheeva *React. Kinet. Catal. Lett.*, 1984, **26** 339
70. V M Kolchanova, E P Mikheeva *React. Kinet. Catal. Lett.*, 1984, **26** 15
71. E P Mikheeva, V G Devyatov, V M Kolchanova *IV Vsesoyuznaya Konferentsiya po Mekhanizmu Kataliticheskikh Reaktsii. Moskva, 1986: Tezisy Dokladov* (The IV All-Union Conference on the Mechanisms of Catalytic Reactions. Moscow, 1986: Abstracts of Reports), Inst. Khim. Fiz. Akad. Nauk SSSR, Moscow, 1986, Part II, p. 406
72. V E Lashkarev *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1952, **16** 203
73. P M Stadnik, V P Fentsik, G K En'ko *Kataliz i Katalizatory*, 1970, **6** 149
74. V P Fentsik, P M Stadnik *Poverkhnostnye i Kontaktnye Yavleniya v Poluprovodnikakh* (Surface and Contact Phenomena in Semiconductors), Izd. Tomsk. Univ., Tomsk, 1964, p. 190
75. J Deren, R Mania *J. Catal.*, 1974, **35** 369
76. J Deren, R Mania *Rocz. Chem.*, 1974, **48** 1565
77. P M Stadnik, S G Kuznetsova *Ukr. Khim. Zh.*, 1970, **36** 117
78. A V Rzhanov *Elektronnye Protsessy na Poverkhnosti Poluprovodnikov* (Electronic Processes on the Surfaces of Semiconductors), Izd. Nauka, Moscow, 1971, 480 pp
79. V I Lyashenko (Editor) *Elektronnye Yavleniya na Poverkhnosti Poluprovodnikov* (Electric Phenomena on the Surfaces of Semiconductors), Izd. Naukova Dumka, Kiev, 1968, 397 pp
80. A Many, G Golstein, N B Grover *Semiconductor Surfaces*, North-Holl. Publ., Amsterdam, 1965, 496 pp
81. S N Kozlov, Yu F Novototskii-Vlasov, V F Kiselev *Fizika i Tekhnika Poluprovodnikov*, 1972, **6** 2102
82. V D Kazarnitskii, S N Kozlov, V F Kiselev, Yu F Novototskii-Vlasov *Dokl. Akad. Nauk SSSR*, 1970, **195** 115
83. A M Murtazin, Yu A Zarif'yants *Fizika i Tekhnika Poluprovodnikov*, 1973, **7** 2041
84. G J Heiland *Phys. Chem. Solids*, 1958, **6** 155
85. G Heiland *Discuss. Faraday Soc.*, 1959, (28) 168
86. H J Krusemeyer *J. Chem. Solids*, 1962, **23** 767
87. H J Krusemeyer *Phys. Rev.*, 1959, **114** 655
88. H J Van Hove *Surf. Sci.*, 1967, **7** 474
89. H J Van Hove *Surf. Sci.*, 1970, **22** 76
90. T I Povkhan *Zh. Nauchn. Prikl. Fotogr. Kinematogr.*, 1974, **19** 221
91. A Many *Crit. Rev. Solid State Sci.*, 1974, **4** 515
92. J Haifdanarson, K Hauffe, J Range *Phys. Status Solidi, A*, 1975, **31** 47
93. G Heiland, D Kohl *Phys. Status Solidi, A*, 1978, **49** 27
94. V F Kiselev *Kompleksoobrazovanie v Katalize* (Complex Formation in Catalysis), Izd. Nauka, Moscow, 1968, Vol. 13, p. 249 [*Problemy Kinetiki i Kataliza* (Prolems of Kinetics and Catalysis)]
95. V F Kiselev *Khemosorbtsiya i Ee Rol' v Katalize* (Chemisorption and Its Role in Catalysis), Izd. Nauka, Moscow, 1970, Vol. 14, p. 25 [*Problemy Kinetiki i Kataliza* (Problems of Kinetics and Catalysis)].
96. V F Kiselev *Dokl. Akad. Nauk SSSR*, 1967, **176** 124
97. V F Kiselev *Kinet. Katal.*, 1970, **11** 403
98. V F Kiselev, V A Matveev, A S Petrov *Kinet. Katal.*, 1980, **21** 523
99. V F Kiselev, V A Matveev *Vestn. Mosk. Univ., Ser. 3: Fizika Astronomiya*, 1985, **26** 82
100. G Heiland *Current Problems in Electrophotography* (Edited by W F Berg, K Hauffe, G de Walter), de Gruyter, Berlin–New York, 1972, p. 73
101. R Glemsa, R J Kokes *J. Phys. Chem.*, 1965, **69** 3254
102. S R Morrison *Current Problems in Electrophotography* (Edited by W F Berg, K Hauffe, G de Walter), de Gruyter, Berlin–New York, 1972, p. 61
103. G M Kovalenko *Kratkie Soobshcheniya po Fizike: Sbornik* (Brief Communications on Physics: Collected Volume), Izd. FIAN, Moscow, 1970, No. 9, p. 15
104. B W Slooper, C O Tiller *J. Appl. Phys.*, 1967, **38** 140
105. R R Humphris, A Catlin *Solid State Electronics*, 1965, **8** 957
106. O S Frolov, O V Snitko, G F Romanova *Ukr. Fiz. Zh.*, 1969, **14** 585
107. M I Elinson (Editor) *Nenakalivuemye Katody* (Non-incandescent Cathodes), Izd. Sov. Radio, Moscow, 1974, p. 69
108. H Lüth *Surf. Sci.*, 1983, **126** 126
109. V F Kiselev, S N Kozlov *Poverkhnost': Fizika, Khimiya, Mekhanika*, 1982, (2) 13
110. A A Davydov *IK-Spektroskopiya v Khimii Poverkhnostnykh Okislov* (IR Spectroscopy in the Chemistry of Surface Oxides), Izd. Nauka, Novosibirsk, 1984, 245 pp
111. V I Yakerson, L I Lafer, A M Rubinshtein *Poverkhnostnye Soedineniya v Geterogennom Katalize* (Surface Compounds in Heterogeneous Catalysis), Izd. Nauka, Moscow, 1975, Vol. 16, p. 49 [*Problemy Kinetiki i Kataliza* (Problems of Kinetics and Catalysis)]
112. R Chrusciel, J Deren, J Nowotny, J Ziolkowski *Bull. Pol. Acad. Sci. Chim.*, 1968, **16** 215
113. G K Boreskov, V I Marshneva *Dokl. Akad. Nauk SSSR*, 1973, **213** 112
114. V D Sokolovskii, G K Boreskov, A A Davydov, et al. *Dokl. Akad. Nauk SSSR*, 1974, **216** 599
115. P Gravel' *Primenenie Teploprovodyashchikh Mikrokalorimetrov v Issledovaniyakh po Geterogennomu Katalizu* (Application of Thermally Conducting Microcalorimeters in Studies on Heterogeneous Catalysis), Inst. Kataliza Sib. Otd. Akad. Nauk SSSR, Novosibirsk, 1973, p. 73
116. G M Sessler *Electrets* (Translated into Russian), Izd. Mir, Moscow, 1983, p. 25 [*Problemy Prikladnoi Fiziki* (Problems in Applied Physics)]
117. N I Pospelova, I V Myasnikov *Dokl. Akad. Nauk SSSR*, **170** 1372

118. A I Krasil'shchikov, L G Antonova, F P Ivanovskii *Kinet. Katal.*, 1960, **1** 210
119. L G Antonova, A I Krasil'shchikov *Glubokii Mekhanizm Kataliticheskikh Reaktsii* (Detailed Mechanisms of Catalytic Reactions), Izd. Nauka, Moscow, 1968, Vol. 12, p. 122 [Problemy Kinetiki i Kataliza (Problems in Kinetics and Catalysis)]
120. A I Krasil'shchikov, L G Antonova *Dokl. Akad. Nauk SSSR*, 1953, **91** 291
121. L M Dmitrienko, S S Laginov, R F Sivyakova *Kinet. Katal.*, 1960, **1** 379
122. E G Rochov *J. Inorg. Nucl. Chem.*, 1967, **29** 65
123. V-J Lee *Science*, 1966, **152** 514
124. R D Williams, S K Sikdar *J. Catal.*, 1975, **38** 147
125. N I Gol'dman, A G Zhdan *Fizika i Tekhnika Poluprovodnikov*, 1976, **10** 1839
126. Kh M Minachev, Yu S Khodakov, V S Nakhshunov *Usp. Khim.*, 1976, **45** 280 [English translation in *Russ. Chem. Rev.*, 1976(2)]
127. US P. 3 222 346
128. D Savoia, E Tagliavini, C Trombini, A Umani-Ronchi *J. Organomet. Chem.*, 1981, **204**(3) 281
129. A Ozaki, K Aika *Problems of Nitrogen Fixation* (Translated into Russian), Izd. Mir, Moscow, 1982, p. 213
130. R D Conzalez, H Miura *J. Catal.*, 1982, 77(2) 338

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Catalytic decomposition of organic and organoelemental peroxides in the presence of electron donors and electron acceptors

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ABSTRACT. The main characteristics (the kinetics and mechanism) of the radical decomposition of organic and organoelemental peroxides in the presence of active electron-donor and electron-acceptor components in alkanes and polymerising media are discussed. The decisive role of the formation of complexes of peroxides with active catalytic components and olefins in these processes is shown. The formation of triple complexes of monomer–Lewis acid–olefin plays an important part in the initiation of radical polymerisation. Examples of the practical application of the initiating systems peroxide–electron donor and peroxide–electron acceptor are given.
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I. Introduction

During the last 15–20 years research into radical polymerisation has undergone a real transformation; new ideas and possibilities have appeared, adding fresh impetus to this well-known process.[1–4]

One of the current and future trends is radical-complex polymerisation using chemical activation agents that participate in radical polymerisation.[4–11] Radical-complex polymerisation in essence consists of the directed change in reactivity of monomers and growing radicals that participate in chain propagation by using complexing agents (Lewis acids, proton acids), which results in catalytic acceleration (or selective inhibition) of this stage of the radical chain process.

In 1957 it was found[5] that the rate and degree of radical polymerisation of acrylonitrile (AN) increased in the presence of small quantities of LiCl. The increase in rate of the reaction was attributed to the interaction of the nitrile group in the AN monomer and radical with LiCl. It was recorded in subsequent studies[6–12] that there was an increase in the rate of radical homo- and co-polymerisation of the vinyl monomers methyl methacrylate (MMA) and AN in the presence of inorganic salts (LiCl, $MgCl_2$, $ZnCl_2$, $AlCl_3$, $AlBr_3$, $SnCl_4$) that are capable of forming coordinate complexes with functional groups (C=O and C≡N) in the reacting monomers and radicals.

Another trend of research is to improve the polymerisation processes by means of the chemical action of effective initiators on the fundamental initiation stage.[1,2] This idea consists of the possibility of controlling the reactivity of the initiator through its specific interaction with active donor or acceptor components which accelerate the radical decomposition of the initiator and cause it to be effective over a required range of temperature. Olefins, amines, phosphates, phosphites, sulphides, and other compounds have been used as electron donors while Lewis acids, PCl_3, and SO_2Cl_2 have been used as electron acceptors. The formation of complexes between peroxides and electron donors or electron acceptors leads to a change in the electronic configuration of the peroxide and hence its capacity to generate radicals.[13–16]

II. Effect of electron donors on the decomposition of peroxides and initiation of radical polymerisation

Binary donor–acceptor systems which have an organic peroxide as one of the components have attracted the attention of research workers for a long time because of the possibility of using them as effective initiators of radical polymerisation.[17–22] A necessary condition for such a system to function is its ability to generate radicals within the required range of temperature at a rate desirable for the process. A sufficient condition is high activity of the radicals formed, capable of initiating a radical process. It has been shown by various methods[13–16,19,20] that at the primary stage a complex is formed with charge transfer between the components of the donor–acceptor system.

A general mechanism for the radical initiation of polymerisation of different monomers by the system organic peroxide–amine (A) with low degrees of conversion[18] may be given by the following scheme:

$$P \rightleftarrows [R^{\cdot}\,R^{\cdot}] \rightarrow 2R^{\cdot},$$

$$P + A \rightleftarrows [P...A] - \begin{cases} \longrightarrow [R^{\cdot}...A] + R^{\cdot} \\ \longrightarrow \text{heterolysis} \end{cases}$$

$$[R^{\cdot}...A] - \begin{cases} \longrightarrow R^{\cdot} + A \\ \xrightarrow{M} RMA^{\cdot} \\ \xrightarrow{H} RH + A^{\cdot} \end{cases}$$

$$R^{\cdot} + M \rightarrow RM^{\cdot},$$

M – monomer

The formation of complexes between amines and peroxides was demonstrated by UV, IR and NMR spectroscopy in the same study.[18] From a quantitative study of the effect of acids and bases on the kinetics of the decomposition reactions of peroxide in the presence of amines in different media it was proposed that a complex

of amine–peroxide–solvent was formed. Amines (aminoacids) have a considerable effect on the kinetics of radical polymerisation of vinyl monomers, namely, on the rate of initiation and the ratio of chain growth constant to chain termination constant ($k_g/k_t^{1/2}$). When aromatic amines interact with organic peroxides the primary reaction in the initiation system peroxide–amine is formation of a complex between the components.[20–22] The complexing agent activates the peroxide molecule and assists the generation of radicals at a high rate within the required range of temperature. A primary complex was detected in benzoyl peroxide–aromatic amine systems at 243–253 K. The formation of benzoate free radicals was established by means of EPR using a spin trap (phenyl t-butyl nitrone).

The presence of a heteroelement in organoelemental peroxides of composition $R_{n-1}EOOR'$ makes them have a greater tendency to coordinate compared with organic peroxides. Their conversion routes in an inert solvent or polymer systems are much more complex than for organic peroxides. Reactions (1)–(7) are possible conversion routes for organoelemental peroxides in radical polymerisation processes:

$$R_{n-1}EOOR' \rightarrow R_{n-1}EO^{\cdot} + {}^{\cdot}OR', \quad (1)$$

$$R_{n-1}EOOR' \rightarrow R_{n-2}E(OR)OR', \quad (2)$$

$$R_{n-1}EOOR' \rightarrow R_{n-1}EOH + R'_{-H}O, \quad (3)$$

$$R_{n-1}EOOR' \rightarrow [R_{n-2}E{=}O] + R'OH \text{ (if one of } R = H), \quad (4)$$

$$R_{n-1}EOOR' + SH \rightarrow R'OH + [\overline{R_{n-1}EO^{\cdot}S^{\cdot}}] \quad (5)$$

$$\downarrow \qquad\qquad \downarrow$$

$$R_{n-1}EOS \qquad R_{n-1}EO^{\cdot} + S^{\cdot}$$

$$R_{n-1}EOOR' + D \rightleftarrows [R_{n-1}EOOR'.D] \rightarrow [R_{n-1}EO^{\cdot}.D] + {}^{\cdot}OR', \quad (6)$$

$$R_{n-1}EOOR' + R''E' \rightarrow R''_{n-1}E'OR' + [\overline{R_{n-1}EO^{\cdot}\ {}^{\cdot}R''}] \quad (7)$$

$$\downarrow \qquad\qquad \downarrow$$

$$R_{n-1}EOR'' \qquad R_{n-1}EO^{\cdot} + {}^{\cdot}R''$$

SH – solvent, D – donor.

Reaction (1) is the homolytic decomposition of peroxide to radicals that are responsible for initiating radical processes. An actual polymerisation or vulcanisation system is a complex multi-component mixture in which the peroxide can participate not only at the stages of initiation and chain growth but also in side reactions. For example, reactions of spontaneous non-radical conversion of peroxides[23–25] [reactions (2)–(4)] are in a number of cases fundamental for organoelemental peroxides, and the initiator then has little effect on radical polymerisation.

Reactions (5)–(7) are processes for generating radicals in bimolecular reactions with the solvent,[26] donor electrons,[13,14] or organoelemental compounds[27–30] when the latter are present in the reaction system.

During polymerisation of MMA, butyl methacrylate (BMA), or styrene, some complexing agents—electron donors—can produce a substantial change in initiating activity of organoelemental peroxides, accelerate radical polymerisation or copolymerisation, and also have an effect on the composition of the copolymer.[31–33] The activation effect on the decomposition of organoelemental peroxides in olefins is due to the formation of a donor–acceptor complex of olefin–organoelemental peroxide, which decomposes to radicals at a higher rate than does pure peroxide in an inert solvent.

$$R_{n-1}EOOR' + \rangle C{=}C\langle \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \left[\rangle C{=}C\langle \cdots R_{n-1}EOOR' \right] \xrightarrow{k_2} \left[\rangle C{=}C\langle \cdots R_{n-1}EO^{\cdot} \right] + R'O^{\cdot}$$

Organosilicon peroxides $R_{4-n}Si(OOBu\text{-}t)_n$, where n = 1–4, R = Me, CH_2 = CH, form similar complexes with acrylic monomers. Coordination occurs between the unshared electron pair of the carbonyl oxygen in the monomer an the vacant *d* orbital of silicon in the peroxide.

The formation of a complex of $Me_3SiOOBu\text{-}t$ with MMA and BMA in hexane and benzene in the temperature range 193–293 K was demonstrated by ^1H NMR spectroscopy from the change in chemical shifts of the protons of the MeO groups in MMA or the *cis*-protons of the $CH_2{=}C$ group in the monomers on changing the concentration of peroxide.[15] By measuring the chemical shifts of the protons it was possible to determine the equilibrium constants and enthalpies (ΔH) of complex formation. The displacement of the proton signals downfield is an indication that the monomers act as electron donors in the complex.

It should be noted that even t-butyl peroxide (TBP) forms a complex with MMA or BMA.[34] Measurements were made by monitoring the variation in the difference between the chemical shifts of the *cis*- and *trans*-olefinic protons in MMA (internal chemical shift ν). The concentration of TBP was varied at a fixed concentration of MMA. Addition of peroxide caused a decrease in ν in MMA by a value of Δ. The latter is dependent on the concentration of peroxide (C_n):[35]

$$\frac{1}{\Delta} = \frac{1}{K\Delta_c}\frac{1}{C_n} + \frac{1}{\Delta_c},$$

where K is the equilibrium constant for formation of complex, Δ_C is the chemical shift of complex.

It was possible to determine complexes of TBP and $Me_3SiOOBu\text{-}t$ with MMA and BMA at temperatures below 253 K.[15,34] The equilibrium constants for formation of these complexes are small, and for the MMA–TBP complex they vary from 0.22 to 0.1 over the temperature range 193–253 K while for the MMA–$Me_3SiOOBu\text{-}t$ complex the variation is 1.3 to 0.25 over the temperature range 213–253 K. The values of δH for these complexes are equal to 6.0 ± 0.3 and 23 ± 3 kJ mol^{-1} respectively. Hence organosilicon peroxides form stronger complexes with monomers than do organic peroxides, which is due to the presence in the organosilicon peroxides of an active acceptor site on the silicon atom (vacant *d* orbital).

The complexing agent activates organoelemental peroxides (the peroxide band is weakened), and the rate constant for decomposition of the peroxide bonded to the monomer in the complex is increased. For example, $Me_3SiOOBu\text{-}t$ decomposes in nonane at 373 K with a rate constant (k) equal to 2×10^{-9} s^{-1} (calculated from published data[36]), whereas in BMA the value of k increases by a factor of 1000 and has a value of 2.4×10^{-6} s^{-1}.[37] The energy of activation of the decomposition processes on changing from nonane to BMA falls from 159 to 75 kJ mol^{-1}. A similar pattern occurs for all organoelemental peroxides of the series $Me_{4-n}Si(OOBu\text{-}t)_n$ on changing from an inert solvent to a polymerisable olefin (MMA, BMA).

The formation of a donor–acceptor complex of monomer with an organoelemental peroxide is responsible for the increase in rate of decomposition of the peroxide and hence an increase in the rate of initiation of polymerisation. In one study[15] the rate of polymerisation of different vinyl monomers initiated by organosilicon peroxides is given. As the number of peroxide groups in organosilicon initiator molecule increases, the rate of polymerisation of the vinyl monomers MMA, BMA and styrene increases disproportionately to the number of peroxide groups, which is an indication of the different reactivity of the latter in the $Me_{4-n}Si(OOBu\text{-}t)_n$ molecule.

The polymerisation of vinyl monomers initiated by organosilicon peroxides is a radical process since its rate is proportional to the concentration of initiator to the power 0.5, and when the stable radical 2,2,6,6-tetramethyl-1-piperidinoxyl [$C_0 = 1-6 \times 10^{-5}$ mol litre^{-1}] is introduced into the polymer system, inhibition that is typical for a radical process occurs, the magnitude of the induction period being proportional to the concentration of the inhibitor.

Thus, organosilicon peroxides that generate radicals in an inert solvent at 423–473 K, owing to the formation of a complex with monomer, are capable of initiating radical polymerisation within the temperature range 353–373 K.

The ability of organoelemental peroxides to form complexes with olefins, as shown above, led to the assumption that they had a potential effect on the composition of copolymers during copolymerisation.[15,16] It was shown that the relative reactivities of monomers vary when copolymerisation is carried out in the presence of organosilicon peroxides. This could be accounted for by the formation of complexes of silicon peroxides not only with monomers but also with the growing radicals, while the latter effect is probably more important because of the small quantity of peroxide in the reaction system.

Table 1. Stability constants and enthalpies of formation for 1 : 1 R_3EOOR'·ligand complexes at 298 K.[32]

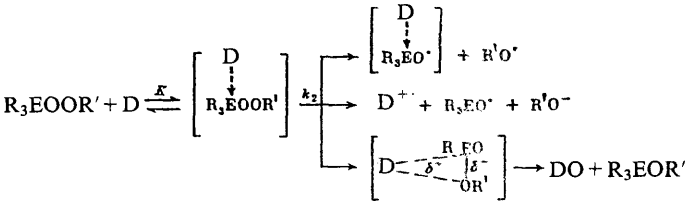
Peroxide	Ligand	$-\Delta H$, kJ mol^{-1}	K^*
$Si(OOBu\text{-}t)_4$	C_5H_5N	29.06	1.96
$Et_3(SnOOBu\text{-}t)$	C_6H_{12}	6.99	0.054
	$Ph_2C{=}CH_2$	11.40	0.055
	$PhCH{=}CH_2$	10.80	0.052
	$CH_2{=}C(Me){-}C(Me){=}CH_2$	10.55	0.034
	C_6H_5N	16.11	0.18
$Et_3SnOOCMe_2Ph$	C_5H_5N	21.5	0.88

*Solution with concentration 1 mol litre^{-1} chosen as the standard state.

It is not only the monomer itself that is capable of activating organic peroxides or organoelemental peroxides to form donor–acceptor complexes with them but other electron donors (amines, ethers, phosphates, sulphides) can also accelerate the decomposition of peroxides and increase the proportion of homolytic cleavage of the peroxide bond. In a number of studies[14,16,31–34,38–45] kinetic and activation parameters are given for the decomposition of organic peroxides and organoelemental peroxides of silicon, germanium, and tin in the presence of various donors (D). It was established by kinetic, thermochemical, and ^{1}H NMR spectroscopic methods[31,32,38–45] that the primary stage of the decomposition of peroxides in the presence of D is formation of a complex between peroxide and D [reaction (6)]. This stage was detected by means of calorimetry at 298 K [31,32] and also kinetically at the decomposition temperatures of the peroxides[38–43] and the values of K and ΔH of the peroxide–donor complexes were determined (Tables 1 and 2). The degree of charge transfer in the complexes $Si(OOBu\text{-}t)_4-C_5H_5N$ and $Et_3SnOOBu\text{-}t-C_5H_5N$ is 0.2 and 0.1 respectively.

In order to determine which of the atoms (E or O) is coordinated to D, ^{1}H NMR spectroscopy was used to study the change in chemical shifts of the protons of the Me_3C and Me_3Sn groups in the peroxide $Me_3SnOOBu\text{-}t$ in the presence of D.[45] For comparison the chemical shifts of the protons in TBP were determined in relation to the composition of the solution.[45] Gorbatov et al.[45] were able to maintain from the results obtained that coordination of D occurs on the tin heteroatom. From the nature of the change in the chemical shift in the system peroxide–chloroform (electron acceptor) it may be concluded that the latter forms a complex with both $Me_3SnOOBu\text{-}t$ and TBP, and the coordination occurs on the peroxide bond, more precisely, on the oxygen atom of the peroxide bond that has highest electron density.[46]

At the rate-limiting stage of the decomposition of the complex between peroxides and donors, either displacement of electron density along a system of σ-bonds (olefins, ethers, phosphates) or with transfer of an electron (amines, sulphides, phosphites), which assists homolysis of the peroxide, or the transfer of two electrons in a heterolytic S_N2 process (sulphides, phosphites) occurs:



If the equilibrium constant K is small, the proportion of peroxide decomposing outside the complex with rate constant k_1 may be significant:

$$R_3EOOR' \xrightarrow{k_1} R_3EO^{\cdot} + R'O^{\cdot}.$$

if [D] ≫ [organoelemental peroxide], the experimentally determined rate constant for decomposition of organoelemental peroxide (k_{exp}) is calculated from the equation:

$$k_{exp} = \frac{k_1 + k_2K[D]}{1 + K[D]},$$

where k_2 is the decomposition constant for the peroxide–donor complex. The values of k_1, k_2, K, and ΔH for certain complexes are given in Table 2.

If follows from an analysis of these results that the proportion of the peroxides bonded to the complex is small and depends on the nature of the peroxide and the basicity of the ligand. Organosilicon peroxides that have a lower capacity for complex formation mainly decompose outside the complex. Organotin monoperoxides and organosilicon polyperoxides, which have greater acceptor properties relative to D, decompose in the presence of D both in the form of a complex ($k_2 \gg k_1$) and without it.

Table 2. Values of k_1, k_2, and K for peroxide–donor complexes.

Complex	T, K	$k_1 \cdot 10^5$, s^{-1}	$k_2 \cdot 10^5$, s^{-1}	K	$-\Delta H$, kJ mol^{-1}	Refs.
$Et_3SnOOBu\text{-}t.C_6H_{10}$	433	2.8	122	0.02	—	[14]
$Et_3SnOOBu\text{-}t.Ph_2C{=}CH_2$	433	2.8	190	0.025	—	[14]
$Me_3SiOOCMe_2Ph.C_5H_5N$	453	2.5	10.3	0.64	28.0	[14]
$Me_3SiOOCMe_2Ph.Bu_2O$	463	6.6	61.6	0.13	—	[38]
$Et_3SnOOBu\text{-}t.C_5H_5N$	433	2.8	64.0	0.59	12.1	[41]
t-BuOOC(O)Ph.HTP*	383	8.1	58.9	1.14	—	[42]
$[Me(CH_2)_{10}CO]_2$.DMF**	353	13.1	50.6	0.3	—	[42]

* HTP—hexamethyltriamidophosphate;
** DMF—dimethylformamide.

III. Effect of electron acceptors on the decomposition of peroxides in alkanes and polymerising media

1. Reactions of organoelemental compounds with peroxides

The published data[28–30,47–51] on the reaction of organoelemental compounds with peroxides indicate that the systems organoelemental compound–organic peroxide and organoelemental compound–organoelemental peroxide have potential use as radical sources. The tendency to associate and form complexes is a characteristic feature of organoelemental compounds of lithium, magnesium, cadmium, etc. Therefore in reactions of organoelemental compounds of Groups I and II with peroxides the role of coordination interactions of the organoelemental reagent is displayed particularly clearly. A peroxide-base affects the organoelemental compound in several ways: it decreases the degree of association of the initial compound, increases the polarity of the C–E bond, and probably assists the transfer of an electron from the C–E bond to the peroxide bond.[52] As a result of this a radical pathway is the main one for the reaction of organoelemental compounds of Groups I and II with peroxides and a scheme for the process including coordination and association of the reactants may be represented in the following way:[28]

$$(R_nE)_x + R'OOR'' \rightleftarrows [(R_nE)_y \cdot R'OOR''] \rightleftarrows [(R_n\overset{e}{\overbrace{}}E)_y \cdot R'O\overset{e}{\overbrace{}}OR''] \rightarrow$$
$$\rightarrow \begin{bmatrix} R^{\cdot} & R_{n-1}E^{+} \\ R'O^{\cdot} & R''O^{-} \end{bmatrix} (R_nE)_{y-1} \rightarrow (\overline{R^{\cdot}\ \ OR'})\,(R_nE)_{y-1} + R''OER_{n-1}$$
$$\downarrow \qquad\qquad \downarrow$$
$$(R_nE)_{y-1} + R^{\cdot} + {}^{\cdot}OR' \qquad ROR' + (R_nE)_{y-1}\ .$$

This scheme is based on a single-electron transfer (SET) mechanism, which has been demonstrated by chemically induced polarisation of nuclei. However, the detection of radicals using this method does not provide a basis for the assumption that the whole process is radical since the effect of chemical induced polarisation of nuclei can occur even when the contribution of a radical route is small.

Not all reactions of organoelemental compounds or organoelemental peroxides can be expected to occur by a common mechanism since organoelemental compounds differ according to their degree of association in the initial state, the polarity of the E–C bond, and their ability to coordinate with electron donors. The probability that a SET mechanism will occur should increase as the ionic character of the E–C bond increases.[49]

The suggestion that the reactions of alkyl peroxides with alkyls of Group III elements are radical in character was put forward about 30 years ago.[53,54] The proof of this was subsequently obtained,[55] when it was shown that Et_3B reacts with $EtOOBEt_2$ in benzene in the absence of oxygen to form ethane, ethylene, butene, ethylbenzene, etc. It was also established that this system induces the radical polymerisation of MMA.

Quite recently when R_3Al (R = Alk, Ar) was reacted with t-$BuOOER_3$ (E = C, Si, Ge, Sn) it was possible by means of a spin trap (2-methyl-2-nitrosopropane) to detect the radicals $R^{\cdot}$ and $R_3EO^{\cdot}$,[56,57] the existence of which had previously been postulated.[58–60]

At the present time it is taken as proven that the primary reaction in the interaction of peroxides with organoelemental compounds of Groups I–III is complex formation:[61–63]

$$R_nE + R'OOR'' \rightleftarrows [R_nE \cdot R'OOR'']. \qquad (I)$$

In a number of cases these complexes have been isolated and characterised. For example, the formation of complexes between alkyllithium and organic peroxides was established kinetically.[61] The existence of the complexes n-$Bu_3B.Me_3COOCMe_3$ and n-$Bu_3B.Me_3SiOOCMe_3$ in hexane at −196 °C was demonstrated by electronic emission spectroscopy.[46,64] It was established that the alkylborane is coordinated with the oxygen atom of the Me_3CO residue.

The question then arises as to which mechanism is followed in the conversion of the complex formed and which factors are responsible for it generating radicals? How is the energy that is necessary for the homolysis of the E–C and O–O bonds, and also possibly the C–O bond, redistributed in it?

Alyasov et al.[29] considered that $Alk_3B.t\text{-}BuOOEr_3$ (E = C, Si, Be) complexes do not generate radicals in the absence of radical acceptors (solvent, monomer, halocarbon). In the absence of radical traps, radicals may possibly still be formed but they are destroyed in the solvent cage and the escape of free radicals into the main volume is negligible. Probably a radical acceptor in the reaction system is "built on" to complex (I) in such a way that in the activated state an energetically and sterically favourable structure occurs, in which all three components—peroxide, organoelemental compound, and radical acceptor stabilising the radical particles formed—are "excited". For example, it was proposed[58–60] that in the reaction of Alk_3Al with benzoyl peroxide (BP) in a polymerising medium a complex with monomer (M) is first formed—$Alk_3Al.M$ (this naturally occurs since $[M] \gg [Alk_3Al]$ and $[M] \ll [BP]$). Subsequently BP interacts with the complex formed according to the reaction

$$[Alk_3Al.M] + BP \rightleftarrows [BP.Alk_3Al.M] \rightleftarrows$$
$$Alk_2AlOC(O)Ph + Alk^{\cdot} + PhC(O)OM^{\cdot}.$$

Organoelemental compounds of Group IV (R_4E) as a rule react with peroxides at the decomposition temperatures of the latter. The peroxides constitute the source of primary radicals and tetralkyl derivatives of silicon, germanium, and tin are hydrogen donors.[47,48]

$$R_4E + R'O^{\cdot} \rightarrow R'OH + R_3ER^{\cdot}_H.$$

The subsequent fate of the radicals is determined by the nature of E. Organosilicon radicals readily dimerise, germanium-containing radicals both dimerise and undergo disproportionation, while for tin-containing radicals dimerisation is not typical. The main reaction of the latter is cleavage of their Sn–C bond:[48]

$$R_3Sn{-}CH_2\dot{C}H_2 \rightarrow R_3Sn^{\cdot} + C_2H_4.$$

Thus, organoelemental compounds of Group IV react with peroxides as a rule according to a homolytic mechanism. Firstly, homolysis of the peroxide occurs on the O—O bond, then there is a homolytic S_N2 reaction of the resulting radicals with the organoelemental compound. If the peroxide decomposes by several parallel reactions (homolysis, heterolysis, or intramolecularly), its reaction with Group IV organoelemental compounds is complicated.

It is not possible to determine unequivocally the mechanism for decomposition of a peroxide coordinated with an organoelemental compound in complex (I). It may be either a redox process involving a single-electron transfer of an S_N2 reaction of the radical generated from the peroxide with the organoelemental compound or an intramolecular reaction or a heterolytic S_N2 process. The ratio of radical to non-radical pathways is to date difficult to determine in each individual case.

For example, the formation of radicals may be due to the transfer of an electron

$$[R_nE \cdot R'OOR'] \xrightarrow{e} \begin{bmatrix} R^{\cdot} & {}^{+}ER_{n-1} \\ R'O^{\cdot} & {}^{-}OR'' \end{bmatrix} \begin{cases} \longrightarrow ROR' + R_{n-1}EOR'' \\ \longrightarrow R^{\cdot} + R'O^{\cdot} + R_{n-1}EOR'' \end{cases}$$

However, this complex can be converted via different activated states by two routes—homolytic and heterolytic:

$$[R_nE \cdot R'OOR'] \begin{cases} \longrightarrow \left[\begin{matrix} R^{-} & {}^{+}ER_{n-1} \\ R'O^{+} & {}^{-}OR'' \end{matrix}\right]^{\neq} \rightarrow ROR' + R''OER_{n-1} \\ \longrightarrow \left[\begin{matrix} R^{\cdot} & {}^{+}ER_{n-1} \\ R'O^{\cdot} & {}^{-}OR'' \end{matrix}\right]^{\neq} \rightarrow R^{\cdot} + R'O^{\cdot} + R''OER_{n-1} \end{cases}$$

Several other variants of the decomposition of the complex can be proposed (a cryptoradical process, concerted homolytic cleavage, etc.), but it is not possible at the present time to come to any definite conclusion about the mechanism of the reaction.[50]

The system organoelemental compound—peroxide generates free radicals at quite low temperatures and can serve as an effective initiator for the polymerisation of vinyl monomers.[58–60,65–72]

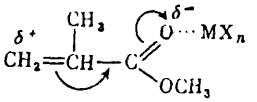
Information about the efficiency of initiation obtained by various methods provides an insight into what proportion of radicals leaves the solvent cage and is of use in radical chain polymerisation. But this method cannot be used to determine the proportion of cryptoradical processes occurring within the solvent cage.

2. Reactions of Lewis acids with peroxides

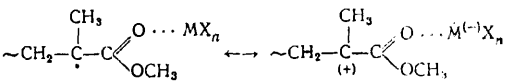
Polymerisation of acrylic monomers that is initiated by organoelemental compounds is accelerated by the addition of Lewis acids [$ZnCl_2$, $SnCl_4$, $SbCl_3$, $SbCl_5$, $TiCl_4$, R_nSiCl_{4-n} (n = 1–4), R_3SnCl, R_2SnCl_2 (R = Me, Et, n-Pr, n-Bu)] or compounds such as PCl_3 and SO_2Cl_2. Lewis acids have an effect on the fundamental stages of polymerisation and in particular on initiation and chain propagation. In the presence of Lewis acids as well as PCl_3 and SO_2Cl_2 the rate of polymerisation of acrylic monomers increases, the energy of activation of the process being reduced.[15,73–76]

Definite ideas about the mechanisms that are responsible for the change in rate and the initiation constants in radical polymerisation in the presence of the system organic(organoelemental) peroxide—Lewis acid can be put forward by studying the nature of the interaction between Lewis acids and monomers and peroxides.

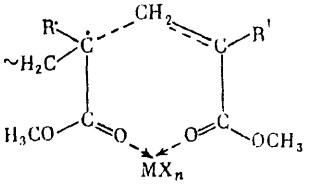
According to published results[77–80] Lewis acids (MX_n) form complexes with acrylic monomers. The composition and structure of double complexes, for example, between MMA and acids such as $AlCl_3$, $AlBr_3$, $ZnCl_2$, $AlEt_3Cl$, $SnCl_4$, were studied by IR,[79,80] UV,[78] and NMR [81,82] spectroscopy. It was shown that complexes are formed as a result of an interaction between the complexing agent and the carbonyl group of the monomer. The strength of these complexes is such that it can be determined from the magnitude of the shift of the IR absorption bands due to stretching vibrations of the carbonyl group or from the displacement of the band due to a $\pi-\pi^*$ transition in the UV region.[78] It follows from UV spectroscopic data[78] that the formation of a complex between MMA and $ZnCl_2$, for example, leads to an increase in conjugation energy in the monomer.



It was shown by EPR [80] that a complex is formed between polymethyl methacrylate (PMMA) radicals and Lewis acids, which leads to a change in properties of these radicals. Zubov et al.[80] represent the state of the radical bonded in a complex as a resonance hybrid of two structures—radical and polar:



A Lewis acid bonded in a complex with the monomer or growing radical does not act as an inert substituent but as a "complementary particle involved in the formation of an intermediate complex at the growth stage".[4]



3. Formation of triple complexes in polymerising media

In the triple system monomer—Lewis acid—organic(organoelemental) peroxide several reactions for complex formation can take place. If the monomer is MMA and the Lewis acid is $SnCl_4$, these reactions may be represented in the following manner:[34]

$$MMA + SnCl_4 \rightleftarrows [MMA - SnCl_4], \quad (8)$$

$$[MMA - SnCl_4] + MMA \rightleftarrows [MMA_2 - SnCl_4], \quad (9)$$

$$MMA + P \rightleftarrows [MMA - P], \quad (10)$$

$$P + SnCl_4 \rightleftarrows [PSnCl_4], \quad (11)$$

$$P + [MMA - SnCl_4] \rightleftarrows [P - SnCl_4 - MMA], \quad (12)$$

$$MMA + P - SnCl_4] \rightleftarrows [P - SnCl_4 - MMA]. \quad (13)$$

A molecule of organoelemental peroxide has two coordination sites—donor (O—O) and acceptor (E). According to our studies[36] complexes of different chlorides of silicon and tin having the structure R_nECl_{4-n} (E = Si, Sn, R = Alk, n = 1–4) with organoelemental peroxides have the composition 1 : 1 or 1 : 2. ^1H NMR studies on the formation of a complex between $Me_3SnOOCMe_3$ and pyridine,[45] $CHCl_3$,[83] Bu_2SnCl_2, and $SiCl_4$ [84] and the results obtained on the dependence of the change in chemical shift of the protons from the Me_3Sn and Me_3C groups on the mole fraction of the second component showed that pyridine acts as an electron donor towards the peroxide and it coordinates with the tin atom. On the other hand the tin and silicon halides, like chloroform, act as

electron acceptors and they coordinate with the peroxide bond (probably with the oxygen atom of the Me_3CO residue, which has a higher electron density).[46]

The equilibrium constants for formation of complexes between $Me_3SiOOCMe_2Ph$ and Me_3SiCl and Me_2SiCl_2 were found to be equal to 5.6 ± 0.9 and 8.3 ± 1.1 at 443 and 423 K respectively.[84]

The coordinating capacity of Lewis acids such as $SnCl_4$ or $SiCl_4$ is usually not exhausted by the addition of a single molecule of peroxide or monomer. Hence the logical conclusion is that in the presence of electron donors the process of complex formation, as depicted by equations (8), (10), and (11), can go further and result in the formation of a triple complex in which a double complex acts as an electron pair acceptor [equations (9), (12), (13)].

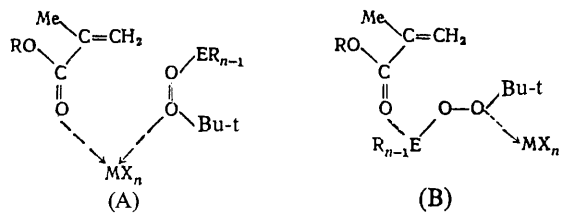
Three-component $nV\pi$-complexes that contain two monomers and a Lewis acid have been detected experimentally by IR, UV, and NMR spectroscopy.[81,82,85–88] Triple $nV\pi$-complexes of MMA–$ZnCl_2$–styrene, AN–$ZnCl_2$–styrene, methacrylonitrile-(MAN)–$ZnCl_2$–1-hexene, and MAN–$ZnCl_2$–styrene have been detected by UV spectroscopy from an analysis of the charge-transfer band in the long wavelength region of the spectrum.[85–87] Equilibrium constants and enthalpies of complex formation were calculated for some complexes. For example, the equilibrium constants for formation of an MMA–$SnCl_4$–styrene complex is equal to 0.24 and 0.67 at 298 and 233 K respectively.[86] The limiting shifts of protons in individual $nV\pi$-complexes were determined from ^{1}H NMR spectroscopic data.[82] From a quantitative analysis of the shifts and their correlation with the values calculated according to the Hückel method and the ionisation potentials of the molecules it was possible to determine the structure and possible conformations of triple complexes.

Using the known literature data on double and triple complexes that occur in the presence of Lewis acids,[4,78–88] we have developed a scheme for "including" the Lewis acid in the initiation stage of radical polymerisation involving an organoelemental peroxide.[15,34] According to this scheme double complexes are first formed. The addition of the third component to the double complex creates an energetically and sterically favourable situation for the formation of an activated complex in the initiation of radical polymerisation.

The triple systems MMA–$SnCl_4$–TBP, MMA–$SnCl_4$–$Me_3SiOOBu$-t, MMA–PCl_3–TBP, MMA–PCl_3–TBP, MMA–PCl_3–$Me_3SiOOBu$-t, and BMA–PCl_3–$Me_3SiOOBu$-t were studied using ^{1}H NMR spectroscopy in nonane in the temperature range 228–283 H by following the variation in the difference between the chemical shifts of the *cis*- and *trans*-olefinic protons of MMA or BMA (internal chemical shift ν).[34,89] The magnitude of ν depends on the structure of the monomer molecule and the distribution of electron density in it and is therefore sensitive to complex formation. Other factors (the presence of an inert solvent, temperature, concentration) have only a slight effect on it. The study of triple complexes was preceded by a study of double ones: olefin–peroxide, peroxide–Lewis acid, olefin–Lewis acid (Table 3).[34,89]

The internal chemical shift of MMA or BMA increases when $SnCl_4$ or PCl_3 is added. When the third component—an organic or organoelemental peroxide—is introduced, ν decreases. The observed chemical shift in the triple system is an average of the shifts from all the resonance forms. The values of the chemical shifts of the free monomer (MMA or BMA) and that bonded in a complex as well as the equilibrium constants for formation of double complexes served as the initial data for the calculation of the parameters of triple complexes. As a result, the formation constants of the triple complexes were obtained (Table 3).

On the basis of the strength of donor–acceptor bonds in double complexes, the most likely structure of the triple complex is that of (A), in which the relatively strong bond of monomer with Lewis acid is preserved.



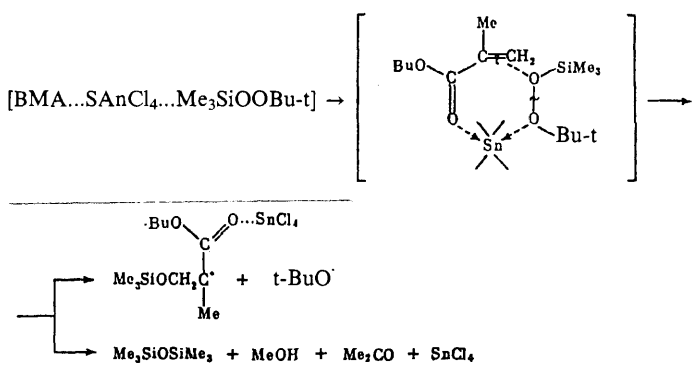
On the other hand, since we found that the formation of a complex between peroxide and monomer was possible,[34,89] structure B, in which the donor properties of the peroxide are strengthened by the supply of electron density from the monomer, cannot be completely ruled out. This type of complex (B) is probable for the system MMA(BMA)–peroxide–PCl_3.

Table 3. Parameters of complex formation in double and triple systems at 253 K.

System	K*	$-\Delta H$, kJ mol^{-1}	Refs.
MMA–PCl_3	0.17±0.02	7.5±0.5	[89]
$Me_3SiOOBu$-t–PCl_3	7±3	26±9	[89]
$Me_3SiOOBu$-t–MMA	0.23±0.02	23±4	[89]
TBP–MMA	0.1±0.04	6.0±0.3	[34]
MMA–$SnCl_4$	15±2	—	[90]
MMA_2–$SnCl_4$	3±0.3	—	[90]
MMA–PCl_3–$Me_3SiOOBu$-t	34 3	29±4	[89]
MMA–$SnCl_4$–TBP	2.7—8.7	8±4	[34]

*Solution with concentration 1 mol litre^{-1} chosen as the standard state.

We believe that in a triple complex the peroxide is activated and decomposes by both a homolytic and a heterolytic mechanism at a higher rate. For example, in the triple system BMA–$SnCl_4$–$Me_3SiOOBu$-t the scheme for "including" the peroxide and $SnCl_4$ in the initiation of polymerisation of BMA may be represented in the following manner:



When the concentration of Lewis acid is increased, the rate of the parallel reaction of non-radical decomposition of the peroxide also rises. This can be assessed from the quantitative yield of $Me_3SiOSiMe_3$ that is obtained twenty four hours after mixing stoichiometric quantities of $Me_3SiOOBu$-t and $SnCl_4$ in nonane at 298 K.[15] This apparently causes the decrease in the rate of polymerisation of BMA at relatively high concentrations of $SnCl_4$.

Thus these reactions relate to the slowest and most energy-consuming stage of radical polymerisation—the initiation stage. The main role of electron donors and acceptors as catalytic components is to form complexes with the initiator, which results in activation of the latter.

IV. Use of organoelemental peroxides for the initiation of radical polymerisation and vulcanisation

The increased production of polymeric materials and the improvement of their quality are due to the development of new, highly effective initiating compositions that can affect the physico-mechanical and performance characteristics of polymeric materials. The compositions organoelemental(organic) peroxide–electron donor or organoelemental(organic) peroxide–electron acceptor are promising initiating systems. The use of organoelemental peroxides for the initiation of polymerisation or vulcanisation as well as for promoting adhesion in the system polymer–substrate has been covered in sufficient detail in two reviews.[91,92] Here we shall only dwell on certain aspects of the use of organoelemental peroxides that have recently undergone development.

MCl_n–t-BuOOH systems, where M = Al, Sn, Ge, In, P, have a high initiating capacity. MMA, styrene, vinyl chloride, and other monomers are polymerised in their presence over a wide range of temperature at high rates and with high degrees of conversion.[93–103] Polymeric materials that are obtained using Lewis acid–peroxide systems have improved physicomechanical properties, are readily processed to sheet products and fibres, can be vulcanised, and in a number of cases have a stereoregular structure.

A large amount of data has been obtained on the initiating activity of boron alkyl–organoelemental peroxide systems, which is dependent on the nature of the boronalkyl substituent, the structure of the peroxide reagent, and the monomer.[30,104–108] The initiating activity of peroxides changes according to the series:

$$Ph_4SbOOBu\text{-t} > Et_3SnOOBu\text{-t} > Et_3GeOOBu\text{-t} > > Me_3SiOOBu\text{-t} \gg TBP.$$

The high rates for generating free radicals in reactions of alkyls of elements with organoelemental peroxides are due, in our opinion, to their ability to form complexes with each other and with monomer. Energetically and sterically favourable conditions are created in a complex for decomposition of the peroxide to radicals and for reaction of the resulting radicals with the monomer.

In the initiation of polymerisation by polyfunctional peroxides such as $R_{4-n}Si(OOCMe_3)_n$, where n = 2–4, R = Me, CH_2 = CH, it is possible to obtain macroperoxysilanes.[109,110] This opens up the possibility for synthesising block copolymers of different monomers during radical polymerisation. For example, macroinitiators obtained by polymerisation of BMA and styrene up to a degree of conversion of 20% were used to initiate the secondary polymerisation of BMA and the synthesis of block copolymers.[110] The high degree of polymerisation initiated by macroperoxysilanes is characterised by the absence of the gel effect, and the addition of Lewis acids (such as $SnCl_4$) activates the decomposition of macromolecular initiators in the same way as their low-molecular analogues.

In the formation of block copolymers the initiation of polymerisation of a second monomer is possible. In particular, active polystyrene containing from 6 to 9 peroxide groups per macromolecule was used as a macroinitiator for the polymerisation of BMA.[110] Samples of polystyrene with peroxide groups in the macromolecule were prepared as a 10% solution in BMA. The block copolymer obtained (97–98%) was separated from the homopolymer by selective extraction and analysed by IR spectroscopy. It transpired that the block copolymer was enriched with BMA units. The main feature of this method for obtaining block copolymers is the virtual absence of homopolymer of the monomer being polymerised.[110]

Thus, by using multifunctional peroxysilanes it is possible to obtain block copolymers without significant inclusion of homopolymer during radical polymerisation. This method can also be applied to other monomers that are capable of radical polymerisation.

It is known that the properties of polymeric composite materials can be improved by chemical modification of the surface of the filler with compounds that act simultaneously as initiator and binder. Silicon polyperoxides are such compounds. Several methods for obtaining peroxidised fillers have been reported.[111–114] We have developed a method for obtaining modified granular fillers (Aerosil, TiO_2, Al_2O_3) by treating them with organosilicon polyperoxides in a volatile organic solvent.[115]

The grafting of an initiator to the surface of a filler results in an increase in the rate of thermal decomposition of the peroxide attached to the surface compared to the decomposition of a similar compound in the liquid phase. The reason for this lies in the specific orientation of the molecule of peroxide in the surface layer and the coordination interaction of peroxide oxygen with the surface groups or atoms, resulting in a weakening of the peroxide bond. It has been shown by chemical and electron-microscope methods that grafting of silicon peroxides to the surface of Aerosil, TiO_2, or Al_2O_3 creates on the surface of the filler chemically bonded reaction sites that can initiate the polymerisation of monomers and chemically graft the polymer matrix to the filler.[116] Homolytic decomposition of the peroxide attached to the surface of the filler results in the formation of two radicals, one of which is chemically bonded to the surface and initiates the formation of the graft polymer and the other is freed into space and either undergoes further decomposition or initiates a homopolymerisation reaction.

The polymerisation of styrene on the surface of a filler modified with silicon polyperoxide can be used to obtain a composite in which up to 30% of the polymer is grafted to the surface of the filler.[15] The formation of a grafted product takes place not only when the peroxide is initially attached to the surface but also when silicon polyperoxide is introduced in a pure state into the system of filler–monomer.[115] This indicates that silicon polyperoxide dissolved in monomer can be grafted on to the surface during polymerisation and achieves a polymer graft to approximately the same extent as in the case of the initial attachment of this peroxide to the surface of the filler.

The highest rate of graft polymerisation and the maximum yield of graft polymer are attained when vinyltri(t-butylperoxy)silane is used as the modifier. Grafting to the filler occurs via the peroxide groups, while grafting to the polymer is via the peroxide and vinyl residues.[115]

A study of the properties of polystyrene samples filled with Aerosil or Al_2O_3 the surface of which was modified with organosilicon peroxides showed that the composite polystyrene had improved impact strength and good rigidity.[115]

It was recommended that organoelemental peroxides should be used to cure rubbers, primarily organosilicon rubbers.[117–120]

A promising method for modifying synthetic materials is the introduction of peroxidate groups into an oligomer chain. When the oligomeric peroxides are heated, macroradicals are generated and they recombine to form three-dimensional structures without the additional introduction of a vulcanising agent.[121]

We have synthesised previously unreported peroxyoligoorganosilazanes that can be used to cross-link organosilicon compounds.[122]

Heat-cured compounds have been widely used in various branches of the Soviet economy, but dicumyl peroxide (DCP) is mainly used as a curing initiator, and has a number of operating problems connected with its use. The process takes place in two stages, and at the second stage a toxic volatile product—acetophenone, which has an unpleasant acrid smell—is liberated. Organosilicon peroxides such as $RSi(OOBu\text{-}t)_3$, where R = Me, CH_2 = CH, are free from such disadvantages.

A comparative study of the characteristics of vulcanisation of methylvinylphenylsiloxane oligomers in the presence of DCP and $RSi(OOBu\text{-}t)_3$ organosilicon peroxides showed that curing with the silicon peroxides starts 10–20 °C below that with DCP, and the products formed by decomposition of the organosilicon peroxides are considerably less toxic than acetophenone.

Moreover, the products formed in the presence of $RSi(OOBu\text{-}t)_3$ have higher strength and elasticity. This establishes a promising future for the chemical activation of peroxides aimed at reducing the vulcanisation temperature.

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Thus, at the present time it can be taken as reliably established that electron-donor and electron-acceptor compounds (activators) catalyse the decomposition reactions of organic and organoelemental peroxides, including those that decompose to radicals during radical polymerisation of olefinic monomers. The effect of the activators is due to the specific interaction of the components making up activator–peroxide–monomer systems and the formation of mixed double and triple complexes with a fractional contribution differing according to the nature of the activator, peroxide, and monomer.

Electron donors form a complex with peroxide by interaction of *p* (or π) electrons with vacant *d* orbitals in the heteroatom of peroxide. Complex formation weakens the peroxide bond. The rate constant for decomposition of a donor–peroxide complex has a value which is several orders higher than the decomposition constant of pure peroxide in an inert medium.

In the system monomer–peroxide–Lewis acid, together with double complexes of monomer–Lewis acid, monomer–peroxide, and peroxide–Lewis acid, labile triple complexes of monomer–Lewis acid–peroxide are formed, in which both the monomer and peroxide have a coordinate bond with the metal atom at the same time.

From the results obtained it is possible to account for the behaviour of organic and organoelemental peroxides in actual polymerising systems and to predict the main pathways for conversion of initiators in them. The latter is useful for resolving specific problems in developing required initiating systems for the preparation of polymeric materials with given properties.

References

1. S S Ivanchev *Vysokomol. Soedin., Ser. A*, 1978, **20** 1923
2. S S Ivanchev *Radikal'naya Polimerizatsiya* (Radical Polymerisation), Izd. Khimiya, 1985, p. 280
3. B A Dolgoplosk, E I Tinyakov *Generirovanie Svobodnykh Radikalov* (The Generation of Free Radicals), Izd. Nauka, Moscow, 1982, p. 252
4. V A Kabanov, V P Zubov, Yu D Semchikov *Kompleksno-Radikal'naya Polimerizatsiya* (Radical Complex Polymerisation), Izd. Khimiya, Moscow, 1986, p. 254
5. C H Bamford, A D Jenkins, R Jonston *Proc. R. Soc., London, A*, 1957, **241** 364
6. V A Kargin, V A Kabanov, V P Zubov *Vysokomol. Soedin., Ser. A*, 1960, **2** 765
7. J Parriot, H Monteiro *C. R. Seances Soc. Biol. Ses Fil.*, 1960, **251** 2026
8. V A Kabanov, D A Topchiev *Vysokomol. Soedin., Ser. A*, 1971, **13** 1321
9. V P Zubov, V A Kabanov *Vysokomol. Soedin., Ser. A*, 1971, **13** 1305
10. M Hirooka, H Yabunchi, S Kowasumi, K Nakagushi *J. Polym. Sci., Polym. Chem. Ed.*, 1973, **11** 1281
11. V F Kornil'eva, M N Masterova, E S Garina, et al *Vysokomol. Soedin., Ser. A*, 1971, **13** 1380
12. M B Lachinov, Abu El Khair, V P Zubov, V A Kabanov *Vysokomol. Soedin., Ser. A*, 1973, **15** 504
13. Yu A Alexandrov, N V Yablokova, V V Gorbatov *Fundamental Research in Homogeneous Catalysis*, Univ. Coll. Station, Texas, New York, London, 1979, **3** 359
14. Yu A Alexandrov, N V Yablokova *Quart. Rev.*, 1982, **4** 1
15. L N Nistratova, N A Kopylova, Yu D Semchikov, et al. *Vysokomol. Soedin., Ser. A*, 1985, **27** 825
16. Yu D Semchikov, N A Kopylova, N V Yablokova, L N Nistratova *Eur. Polym. J.*, 1986, **22** 569
17. B A Dolgoplosk, E I Tinyakov *Okislitel'no-Vosstanovitel'nye Sistemy kak Istochniki Svobodnykh Radikalov* (Redox Systems as Sources of Free Radicals), Izd. Nauka, Moscow, 1974, p. 240
18. N M Beileryan *Abstract of Doctorate Thesis in Chemical Sciences*, Erevan State University, Erevan, 1974, p. 62
19. O A Chaltykyan, S A Akopyan, N M Beileryan, R O Chaltykyan *Dokl. Akad. Nauk Arm. SSR*, 1972, **54** 161
20. S D Stavrova, I P Chikhacheva, E P Efremova *IV Vsesoyuznaya Konferentsiya po Khimii Organicheskikh Peroksidov: Tezisy Dokladov* (Abstracts of Reports at the IVth All-Union Conference on the Chemistry of Organic Peroxides), Volgograd, 1980, pp 281, 307
21. S V Stavrova, I P Chikhaleva, M L Mukhina *Dokl. Akad. Nauk SSSR*, 1974, **218** 1118
22. M L Mukhina, I P Chikhaleva, S D Stavrova *Tr. Mosk. Inst. Tonkoi Khim. Tekhnol.*, 1975, **5** 65
23. V A Yablokov *Usp. Khim.*, 1980, **49**(9) 1711 [English translation in *Russ. Chem. Rev.*, 1980(9)]
24. V A Yablokov *Doctorate Thesis in Chemical Sciences*, Lensovet Leningrad Technological Institute, Leningrad, 1977, p. 355
25. V A Yablokov, N V Yablokova, A V Tomadze *Zh. Obshch. Khim.*, 1979, **49** 1171
26. I V Spirina, V P Sergeeva, V P Maslennikov, et al. *Zh. Obshch. Khim.*, 1980, **50** 1826
27. Yu A Aleksandrov, S A Lebedev, N V Kuznetsova, G A Razuvaev *Dokl. Akad. Nauk SSSR*, 1979, **245** 842

28. G I Vesnovskaya, Yu N Baryshnikov *Radiokal'nye Reaktsii Metalloorganicheskikh Soedinenii* (Radical Reactions of Organometallic Compounds), Izd. Gor'k. Gos. Univ., Gor'kii, 1986, p. 48
29. V N Alyasov, V P Maslennikov, Yu A Aleksandrov *Radiokal'nye Reaktsii Metalloorganicheskikh Soedinenii* (Radical Reactions of Organometallic Compounds), Izd. Gor'k. Gos. Univ., Gor'kii, 1986, p. 64
30. V A Dodonov, I N Aksenova *Radiokal'nye Reaktsii Metalloorganicheskikh Soedinenii* (Radical Reactions of Organometallic Compounds), Izd. Gor'k. Gos. Univ., Gor'kii, 1986, p. 83
31. Yu A Aleksandrov, V V Gorbatov, V G Tsvetkov, N V Yablokova *Zh. Obshch. Khim.*, 1978, **48** 933
32. Yu A Aleksandrov, V G Tsvetkov, V V Gorbatov, N V Yablokova *Zh. Obshch. Khim.*, 1978, **48** 1134
33. Yu A Aleksandrov, V V Gorbatov, N V Yablokova, V G Tsvetkov *J. Organomet. Chem.*, 1978, **157** 267
34. Yu A Kurskii, E G Kobanova, N V Yablokova, et al. *Zh. Obshch. Khim.*, 1988, **58** 1206
35. B I Ionin, B A Ershov, I A Kol'tsov *YaMR Spektroskopiya v Organicheskoi Khimii* (NMR Spectroscopy in Organic Chemistry), Izd. Khimiya, Leningrad, 1983, p. 269
36. N P Sluchevskaya, V A Yablokov, N V Yablokova, Yu A Aleksandrov *Zh. Obshch. Khim.*, 1976, **46** 1540
37. E G Kabanova, N V Yablokova, Yu A Aleksandrov, et al *Khimiya Elementoorganicheskikh Soedinenii* (The Chemistry of Organoelemental Compounds), Izd. Gor'k. Gos. Univ., Gor'kii, 1982, p. 37
38. V V Gorbatov, N V Yablokova, V P Kheiderov, Yu A Aleksandrov *Zh. Obshch. Khim.*, 1980, **50** 2482
39. V V Gorbatov, N V Yablokova, Yu A Aleksandrov, et al. *Zh. Obshch. Khim.*, 1980, **50** 2274
40. Yu A Aleksandrov, V V Gorbatov, N V Yablokova *Dokl. Akad. Nauk SSSR*, 1980, **250** 623
41. V V Gorbatov, N V Yablokova, Yu A Aleksandrov, et al. *Zh. Obshch. Khim.*, 1981, **51** 1346
42. A V Ganyushkin, V I Ivanov, Yu A Aleksandrov *Khimiya Elementoorganicheskikh Soedinenii* (The Chemistry of Organoelemental Compounds), Izd. Gor'k. Gos. Univ., Gor'kii, 1982, p. 53
43. V V Gorbatov, N V Yablokova, Yu A Aleksandrov, V I Ivanov *Zh. Obshch. Khim.*, 1983, **53** 1752
44. N V Yablokova, V V Goratov, E V Krasilova, Yu. A Aleksandrov *Zh. Obshch. Khim.*, 1986, **56** 642
45. V V Gorvatov, Yu A Kurskii, Yu A Aleksandrov, N V Yablokova *Zh. Obshch. Khim.*, 1978, **48** 365
46. V A Dodonov, O S Morozov, D F Grishin, et al. *Dokl. Akad. Nauk SSSR*, 1980, **225** 1123
47. T G Brilkina, V A Shushunov *Reaktsii Metalloorganicheskikh Soedinenii s Kislorodom i Perekisyami* (Reactions of Organometallic Compounds with Oxygen and Peroxides), Izd. Nauka, Moscow, 1966, p. 170
48. Yu A Aleksandrov *Zhidkofaznoe Avtokislenie Elementoorganicheskikh Soedinenii* (Liquid-phase Autoxidation of Organoelemental Compounds), Izd. Nauka, Moscow, 1978, p. 278
49. K U Ingold, B P Roberts *Free-Radical Substitution Reactions* (Translated into Russian), Izd. Mir, Moscow, 1971, p. 225
50. O A Reutov, I P Beletskaya, G A Artamkina, A N Kashin *Reaktsii Metalloorganicheskikh Soedinenii kak Redoks-Protsessy* (Reactions of Organometallic Compounds as Redox Processes), Izd. Nauka, Moscow, 1981, p. 279
51. V P Maslennikov, Doctorate Thesis in Chemical Sciences, Moscow State University, Moscow, 1977
52. C G Screttas, J F Eastham *J. Am. Chem. Soc.*, 1965, **87** 3276
53. C E H Bawn, D Margarisson, N H Richardson *Proc. Chem. Soc.*, 1959, 357
54. F J Welch *J. Polym. Sci.*, 1962, **61** 243
55. R L Hensen, R R Hammann *J. Phys. Chem.*, 1963, **67** 2868
56. V A Dodonov, D F Grishin, L P Stepovik, V K Cherkasov *Zh. Obshch. Khim.*, 1981, **51** 2245
57. V A Dodonov, D F Grishin, V K Cherkasov *Zh. Obshch. Khim.*, 1982, **52** 868
58. E B Milovskaya, T G Zhuravleva, L V Zamoyskaya *J. Polym. Sci. C*, 1967, (16) 899
59. V Ka Koop, E V Mikovskaya *Vysokomol. Soedin., Ser. B*, 1972, **14** 360
60. L V Zemoiskaya, S I Vinogradova, E B Milovskaya *Vysokomol. Soedin., Ser. B*, 1971, **13** 1484
61. Yu N Baryshnikov, G I Vesnovskaya, S G Krinsburg *Kinet. Katal.*, 1976, **17** 1603
62. E B Milovskaya *Usp. Khim.*, 1973, **42**(5) 881 [English translation in *Russ. Chem. Rev.*, 1973(5)]
63. V A Dodonov *Metallorganicheskie Soedineniya i Radikaly* (Organometallic Compounds and Radicals (Edited by M I Kabachnik), Izd. Nauka, Moscow, 1985, p. 40
64. G A Razuvaev, M A Lopatin, V A Dodonov *Zh. Obshch. Khim.*, 1978, **48** 2494
65. J Furukawa, T Tsuruta, S Shiotani *J. Polym. Sci.*, 1959, **40** 237
66. Japanese P. 6235
67. French P. 1 567 039; *Chem. Abs.*, 1969, **71** 12 582T
68. Swiss P. 223 034
69. E B Milovskaya, T G Zhuravleva, P I Dolgoploskaya, L I Velesova *Vysokomol. Soedin., Ser. A*, 1964, **6** 412
70. E B Milovskaya, T G Zhuravleva *Vysokomol. Soedin., Ser. A*, 1964, **6** 1035
71. E B Milovskaya, L V Zamoiskaya *Vysokomol. Soedin., Ser. A*, 1965, **7** 670
72. E B Milovskaya, T G Zhuravleva *Vysokomol. Soedin., Ser. A*, 1967, **9** 1128
73. E G Kabanova, N V Yablokova, Yu A Aleksandrov *Zh. Obshch. Khim.*, 1986, **56** 646
74. N A Kopylova, N V Yablokova, T M Piskareva, et al. *Vysokomol. Soedin., Ser. B*, 1987, **29** 506
75. N A Kopylova, N V Yablokova, I L Kozina, et al. *Vysokomol. Soedin., Ser. B*, 1986, **28** 627
76. N A Kopylova, E G Kabanova, N V Yablokova, et al. *Vysokomol Soedin., Ser. A*, 1989, **31** 301
77. L J Andrews, R M Keefer *Molecular Complexes in Organic Chemistry* (Translated into Russian), Izd. Mir, Moscow, 1967, p. 207
78. S Tasuke, S Okamura *J. Polym. Sci., B*, 1967, **5** 95
79. V B Golubev, V P Zubov, G S Naumov, et al. *Vysokomol. Soedin., Ser. A*, 1969, **11** 2689
80. V P Zubov, M B Lachinov, V V Golubev, et al. *J. Polym. Sci.*, 1968, **23** 147
81. H Hirai, M Komiyama *J. Polym. Sci., Polym. Chem. Ed.*, 1974, **12** 2701
82. M Komiyama *J. Polym. Sci. Polym. Chem. Ed.*, 1976, **14** 627

83. N V Kochnev, N V Yablokova, Yu A Kurskii, Yu A Aleksandrov *Zh. Obshch. Khim.*, 1989, **59** 384
84. N V Yablokova, E G Kabanova, V V Gorbatov, Yu A Aleksandrov *Zh. Obshch. Khim.*, 1988, **58** 380
85. T Ikegami, H Hirai *J Polym. Sci. A-1*, 1970, **8** 195
86. M Komiyama, H Hirai, *J. Polym. Sci., Polym. Chem. Ed.*, **1976, 14** 183
87. K Fujimori, G B Bulter *J. Macromol. Sci. A*, 1973, **7** 387
88. J Furukawa, Y Iseda, E Kobayashi *Polym. J.*, 1971, **2** 337
89. E G Kabanova, N V Yablokova, N V Kochnev, Yu A Aleksandrov *Zh. Obshch. Khim.*, 1989, **59** 985
90. H Hirai, M Komiyama *J. Polym. Sci., Polym. Lett. Ed.*, 1972, **10** 925
91. Yu A Aleksandrov, N V Yablokova, V A Yablokov, et al. *Khimiya Elementoorganicheskikh Soedinenii* (The Chemistry of Organoelemental Compounds), Izd. Gor'k. Gos. Univ., Gor'kii, 1979, p. 3
92. V A Yablokov, V E Mikhlin, N V Yablokova, et al. *Prakticheskoe Ispol'zovanie Kremniiorganicheskikh Perekisei. Ekspress-Informatsiya* (The Practical Application of Organosilicon Peroxides. Express Information), Izd. NIITEKhim, Moscow, 1979, No. 3, p. 1
93. USSR P. 1 087 529; *Byull. Izobr.*, 1984, (15) 88
94. USSR P. 883 066; *Byull. Izobr.*, 1981, (43) 105
95. V E Lelekov *Candidate's Thesis in Chemical Sciences, Gor'kii State University*, Gor'kii, 1985, p. 168
96. Yu A Aleksandrov, V E Lelekov, G I Makin *Zh. Obshch. Khim.*, 1987, **57** 1798
97. V A Dodonov, D F Grishin, O S Morozov, V K Cherkasov *Zh. Obshch. Khim.*, 1982, **52** 71
98. G S Kolesnikov, L S Fedorova *Izv. Akad. Nauk SSSR, Otd. Khim.*, 1958, 906
99. N L Zutty, F J Welch *J. Polym. Sci.*, 1960, **43** 445
100. T Taninaka, H Uemura *J. Polym. Sci., Polym. Chem. Ed.*, 1978, **16** 1549
101. USSR P. 272 196; *Byull. Izobr.*, 1970, (18) 78
102. R G Schulz, R Wolf *Makromol. Chem.*, 1967, **103**, 27
103. R G Schulz, R Wolf *Makromol. Chem.*, 1966, **99**, 76
104. G A Razuvaev, V A Dodonov, Yu A Ivanova *Dokl. Akad. Nauk SSSR*, 1980, **250** 119
105. V A Dodonov, L L Semenycheva, M B Gorshkova *Vysokomol. Soedin., Ser. B*, 1984, **26** 101
106. G A Razuvaev, V A Dodonov, I N Aksenova *Vysokomol. Soedin., Ser. B*, 1986, **28** 66
107. V A Dodonov, I N Aksenova *Vysokomol. Soedin., Ser. B*, 1986, **28** 422
108. E Kojima, M Yesikuni, D Isudzu, S Umeda *Nippon Kakagu Kaishi*, 1975, (12) 2221
109. T G Sveshnikova, N P Sluchevskaya, Yu D Semchikov, et al. *Vysokokomol. Soedin., Ser. B*, 1979, **21** 857
110. L N Nistratova, N A Kopylova, Yu D Semchikov, et al *Vysokomol. Soedin., Ser. B*, 1982, **24** 913
111. USSR P. 519 460; *Byull. Izobr.*, 1976, (24) 79
112. USSR P. 532 601; *Byull. Izobr.*, 1976, (39) 60
113. USSR P. 869 016; *Byull. Izobr.*, 1982, (1) 120
114. USSR P. 787 411; *Byull. Izobr.*, 1980, (46) 97
115. N V Yablokova, Yu A Aleksandrov, O M Titova *Vysokomol. Soedin., Ser. A*, 1986, **28** 1908
116. N V Yablokova, A V Ganyushkin, G B Sadikov, Yu A Aleksandrov *Vysokomol. Soedin., Ser. B*, 1985, **27** 553
117. US P. 2 970 982
118. USSR P. 156 673; *Byull. Izobr.*, 1963, (16) 51
119. BRD P. 1 930 574; *Chem. Abs.*, 1970, **72** 67082
120. US P. 3 631 161
121. USSR P. 476 292; *Byull. Izobr.*, 1975, (25) 78
122. N V Yablokova, Yu A Aleksandrov, V I Ivanov, S M Shekhter *Vysokomol. Soedin., Ser. B.*, 1988, **30** 762

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Fluorine-containing organic derivatives of polyvalent halogens

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ABSTRACT. The methods of synthesis and properties of fluorine-containing organic derivatives of polyvalent iodine, bromine, and chlorine are examined.

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I. Introduction

Organic derivatives of polyvalent iodine were first obtained by Willgerodt in 1886. The methods of synthesis and properties of compounds containing iodine in the trivalent and pentavalent states have been described in a monograph[1] and in reviews.[2–4] Subsequent reviews were devoted to separate types of polyvalent iodine compounds—iodonium salts and ylides,[5,6] diacyloxyiodoarenes.[7] Iodonium ylides and the applications of polyvalent iodine compounds in organic syntheses have been considered in greatest detail in Koser's[8] and Varvoglis's[9] reviews respectively.

There have been no reviews devoted to fluorine-containing derivatives of polyvalent iodine. Nevertheless certain types of compounds have been synthesised solely as a result of the introduction of fluorine atoms into the molecule.

The chemistry of fluorine-containing organic derivatives of polyvalent iodine is developing vigorously. They are finding increasingly extensive application as selective oxidants, alkylating and fluorinating agents, and physiologically active substances.

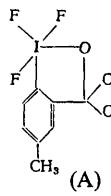
Certain fluorine-containing organic derivatives of bromine and chlorine have been synthesised in recent years.

This review deals with data on fluorine-containing organic compounds with a carbon–polyvalent-bond published up to 1987. There exist the following types of polyvalent iodine compounds of this sort.

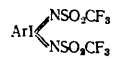
1. Compounds of trivalent iodine in which the iodine atom is linked to one carbon atom. These include iodosylperfluoroalkanes R_FIO, difluoroiodoarenes $ArIF_2$ and difluoroiodoperfluoroalkanes R_FIF_2, bis(trifluoroacetoxy)iodoarenes $ArI(OCOCF_3)_2$ and bis(trifluoroacetoxy)iodoperfluoroalkanes $R_FI(OCOCF_3)_2$, dimethoxyiodotrifluoromethane $CF_3I(OCH_3)_2$, and also μ-oxo-compounds, in which the iodine atoms are linked by an oxygen bridge, namely $ArI(OCOCF_3)-O-I(OCOCF_3)Ar$. Iminoiodoarenes, for example, $ArI=NSO_2CF_3$, belong to the same type.

2. Compounds of trivalent iodine containing an iodine atom linked to two carbon atoms. These include arylperfluoroalkyl- and aryl-αα-dihydropolyfluoroalkyliodonium salts, for example, $C_6H_5\overset{+}{I}\,C_3F_7BF_4^-$, and also iodonium ylides of the type $ArI=C(SO_2F)_2$.

3. Compounds of pentavalent iodine in which the iodine atom is linked to one carbon atom. These include iodylperfluoroalkanes R_FIO_2, difluoroiodylarenes $ArIOF_2$, and difluoroiodylperfluoroalkanes R_FIOF_2, tetrafluoroiodoarenes $ArIF_4$ and tetrafluoroiodoperfluoroalkanes R_FIF_4, tetrakis(perfluoroacyloxy)iodoarenes $ArI(OCOR_F)_4$, and bis(perfluoroacyloxy)iodylarenes $ArI(O)(OCOR)_2$. Trifluoroperiodinane (A) and bis(imino)iodoarenes (B) can also be included in this type:



(A)



(B)

4. Compounds with pentavalent iodine in which the iodine atom is linked to two carbon atoms. These include diphenyliodosyl salts, for example, $(C_6H_5)_2IF_2$ and $(C_6H_5)_2I(O)OCOCF_3$.

There are few available literature data on the fluorine-containing organic derivatives of polyvalent bromine and chlorine. The compounds R_FBRF_2, $RFBr(OCOCF_3)_2$, and R_FClF_2 have been synthesised. The available information about the synthesis of $C_6F_5Cl(F)-Cl(F)C_6F_5$ is hardly reliable.

II. Derivatives of trivalent halogen

1. Methods of synthesis

(a) Iodosyl compounds

Until recently, only aromatic iodosyl compounds ArIO were known, their stability being caused apparently by the conjugation of the positively charged iodine atom with the aromatic ring. The methods of synthesis of iodosylarenes have been described in reviews.[1–4] The most convenient of them is based on the alkaline hydrolysis of diacetoxyiodoarenes.[10]

The first representative of aliphatic iodosylperfluoro-compounds—iodosylperfluoropropane—was obtained by the hydrolysis of bis(trifluoroacetoxy)perfluoropropane in the presence of sodium bicarbonate.[11] Iodosylpentafluorobenzene was synthesised similarly:[11,12]

$$R_FI(OCOCF_3)_2 \xrightarrow{H_2,\,NaHCO_3} R_FIO, \quad R_F = C_3F_7,\ C_6F_5.$$

Contrary to the assertion[13] that iodosyl compounds are not formed when perfluoroalkyl iodides are treated with ozone, iodosyltrifluoromethane was obtained by this procedure:[14]

$$CF_3I + O_3 \xrightarrow[CCl_3F,\,-78\text{–}40\,^\circ C]{} CF_3IO + O_2.$$

The same compound is formed when difluoroiodotrifluoromethane in acetonitrile is treated with finely dispersed silica:[14]

$$2CF_3IF_2 + SiO_2 \xrightarrow[-40\text{–}0\,^\circ C]{} 2CF_3IO + SiF_4.$$

The relative stability of iodosylperfluoroalkanes is associated with the electron-accepting influence of the perfluoroalkyl group.

(b) Difluoroiodo-, difluorobromo-, and difluorochloro-compounds

The first representatives of difluoroiodo-compounds—difluoroiodoarenes—were obtained by treating iodosylarenes with 40% hydrofluoric acid.[2,4] It has also been suggested[15] that difluoroiodoarenes be obtained by the exchange of the chlorine atoms in dichloroiodoarenes with the fluorine in hydrofluoric acid in the presence of yellow mercury oxide:

$$ArICl_2 + HgO + 2HF \rightarrow ArIF_2 + H_2O + HgCl_2.$$

An important disadvantage of these methods is the presence in the reaction mixture of water, which hinders the isolation and purification of the readily hydrolysing difluoroiodoarenes. The method of synthesis of difluoroiodoarenes by treating iodosyl compounds or bis(trifluoroacetoxy)iodo-derivatives with sulphur tetrafluoride is free from this disadvantage. Apart from difluoroiodoarenes, readily removed gases—thionyl fluoride and trifluoroacetyl fluoride—are formed under these conditions:[11]

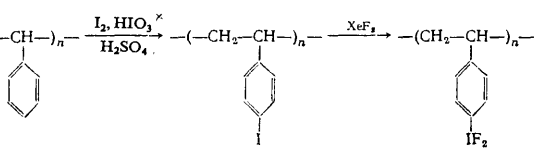
$$ArIO + SF_4 \rightarrow ArIF_2 + SOF_2,$$
$$C_6F_5I(OCOCF_3)_2 + SF_4 \rightarrow C_6F_5IF_2 + 2SOF_2 + 2CF_3COF.$$

The first representative of heterocyclic difluoroiodo-derivatives—3-difluoroiodopyridine—was also obtained by this method.[11]

Xenon difluoride can be used to synthesise difluoroiodo-compounds:[16]

$$ArI + XeF_2 \xrightarrow[20\text{–}60\,^\circ C]{} ArIF_2 + Xe.$$

Various difluoroiodoarenes[17,18] as well as polymeric difluoroiodoarene—the product of the iodination and subsequent fluorination with xenon difluoride the so called "popcorn" (cross-linked styrene–divinylbenzene copolymer)[19,20]—have been obtained with the aid of xenon difluoride:



Studies in which conditions were found for the selective fluorination of various iodoarenes by elemental fluorine have been published comparatively recently:[21,22]

$$ArI + F_2 \xrightarrow[CCl_2F,\,-100\,^\circ C]{} ArIF_2.$$

Fluorine is diluted with nitrogen in proportions of 1:20. It is then possible to avoid the fluorination of the aromatic ring even in those cases where it contains electron-donating substituents. The compound $C_6F_5IF_2$ had been obtained earlier by this procedure.[23]

The first difluoroiodoperfluoroalkane—difluoroiodotrifluoromethane—was synthesised by treating trifluoromethyl iodide with fluorine:[24]

$$CF_3I + F_2 \rightarrow CF_3IF_2$$

Subsequently various difluoroiodoperfluoroalkanes were obtained by treating the corresponding perfluoroalkyl iodides with strong fluorinating agents—elemental fluorine,[13,25,26] chlorine trifluoride, and bromine trifluoride or pentafluoride.[13] The compound $SF_5(CF_2)_2IF_2$ was also obtained with the aid of chlorine trifluoride.[27]

Difluoroiodoperfluoroalkanes[11] and difluoroiodo-αα-dihydropolyfluoroalkanes[28] are formed readily when the corresponding bis(trifluoroacetoxy)iodo-derivatives are treated with sulphur tetrafluoride.

The low-temperature fluorination of methyl iodide with elemental fluorine leads to difluoroiodotrifluoromethane.[29]

Difluoroiodoalkanes could not be obtained with the aid of elemental fluorine or strong fluorinating agents, since the C–I bond is ruptured under these conditions. Alkyl iodides cannot be oxidised to bis(trifluoroacetoxy)iodo-derivatives for the same reason. It has been found that difluoroiodomethane is formed in a quantitative yield when xenon difluoride reacts with an excess of methyl iodide:[30–32]

$$CH_3I + XeF_2 \xrightarrow[20\,^\circ C]{} CH_3IF_2 + Xe.$$

The product has been characterised only by ^1H and ^{19}F NMR spectra.

Difluoroiodoethane has been obtained from ethyl iodide using a very mild fluorinating agent—$CsSO_4F$.[33]

The formation of difluorobromoarenes in the oxidation of bromoarenes with xenon difluorides[34] and in the synthesis of diarylbromonium salts by condensing arenes with BrF_3 [35] has been detected by the ^{19}F NMR method.

The synthesis of difluorobromopentafluorobenzene by the reaction of C_6F_5Br with elemental fluorine at 128 °C was described later.[36,37] $C_6F_5BrF_2$ was isolated by preparative chromatography. However, the authors believe[38,39] that the product of the reaction of elemental fluorine with C_6F_5Br is not $C_6F_5BrF_2$. They obtained $C_6F_5BrF_2$ by substituting a fluorine atom in BrF_3 by the pentafluorophenyl residue and confirmed its formation by studying the ^{19}F NMR, IR, and mass spectra and also by means of chemical reactions:

$$C_6F_5SiF_3 + BrF_3 \rightarrow C_6F_5BrF_2 + SiF_4.$$

The formation of $C_6H_5ClF_2$ on interaction with C_6F_5Cl with elemental fluorine has been described.[40,41] It has been suggested that $C_6H_5Cl(F)-Cl(F)C_6F_5$ is formed as a side product in this reaction. A study has been devoted to the synthesis of this compound and the demonstration of its structure.[42] We believe that the existence of this compound is doubtful.

(c) Bis(trifluoroacetoxy)iodo- and bis(trifluoroacetoxy)bromo-compounds

The first representative of compounds of this kind—bis(trifluoroacetoxy)iodobenzene—was obtained by treating dichloroiodobenzene with silver trifluoroacetate or by treating iodosylbenzene with trifluoroacetic acid:[43]

$$C_6H_5ICl_2 + 2AgOCOCF_3 \rightarrow C_6H_5I(OCOCF_3)_2 + 2AgCl,$$
$$C_6H_5IO + 2CF_3COOH \rightarrow C_6H_5I(OCOCF_3)_2 + H_2O.$$

A method of synthesis of this compound from diacetoxyiodobenzene by the exchange reaction with trifluoroacetic acid at 60 °C was later proposed:[44,45]

$$C_6H_5I(OCOCH_3)_2 + 2CF_3COOH \rightarrow C_6H_5I(OCOCF_3)_2 + 2CH_3COOH.$$

Bis(trifluoroacetoxy)iodopentafluorobenzene was synthesised by oxidising iodopentafluorobenzene with nitric acid in the presence of trifluoroacetic anhydride[12] or trifluoroperacetic acid.[23]

In order to obtain bis(trifluoroacetoxy)iodoarenes containing in the benzene ring not unduly strong electron-donating and electron-accepting substituents, a method has been developed for the direct introduction of the $I(OCOCF_3)_2$ group into the aromatic ring by treatment with iodine tris(trifluoroacetate)[12,23] in trifluoroacetic acid:[46]

$$ArH + I(OCOCF_3)_3 \xrightarrow[-CF_3COOH]{} ArI(OCOCF_3)_2,$$

$$Ar = C_6H_5,\ 2,5\text{-}(CH_3)_2C_6H_3,\ 4\text{-}CH_3C_6H_4,\ 4\text{-}ClC_6H_4,\ 3\text{-}CF_3C_6H_4.$$

It was found that only the *meta*-isomer is formed from trifluoromethylbenzene, a mixture of 38% of the *ortho*-isomer and 62% of the *para*-isomer is formed from toluene, and a mixture of 6% of the *ortho*-isomer and 94% of the *para*-isomer is formed from chlorobenzene. Such composition of the isomers indicates an electrophilic mechanism of the reaction.

In the synthesis of bis(trifluoroacetoxy)iodoarenes from iodosylarenes, it is best to use trifluoroacetic anhydride instead of the acid itself. The reaction takes place with a quantitative yield:[46,47]

$$ArIO + (CF_3CO)_2O \xrightarrow[CH_2Cl_2]{-20 \text{ to } -30\,^\circ C} ArI(OCOCF_3)_2,$$

$$Ar = C_6H_5,\ 4\text{-}CH_3C_6H_4,\ 3\text{-}FC_6H_4,\ 4\text{-}FC_6H_4,\ 4\text{-}ClC_6H_4,\ 3\text{-}CF_3C_6H_4.$$

The last two methods are not applicable to the synthesis of bis(trifluoroacetoxy)iodoarenes containing strong electron-accepting substituents. In this case, the iodoarene was oxidised with fuming nitric acid in the presence of trifluoroacetic anhydride:[48]

$$XC_6H_4I + 2HNO_3 + 2(CF_3CO)_2O \rightarrow XC_6H_4I(OCOCF_3)_2 + 2NO_2 + 2CF_3COOH,$$

$$X = 3\text{-}CF_3,\ 3\text{-}NO_2,\ 4\text{-}NO_2.$$

The reaction takes place quantitatively.

The first representative of trivalent bromine carboxylates—bis(trifluoroacetoxy)bromopentafluorobenzene—was synthesised by the reaction of difluorobromopentafluorobenzene with trifluoroacetic anhydride at 0 °C in Freon 11.[39]

Until recently, saturated aliphatic di(acyloxy)iodo-compounds were unknown. The attempts to oxidise iodoalkanes to iodosyl compounds or their derivatives were unsuccessful, since this involves the dissociation of the C–I bond.

The first compounds of this type—bis(trifluoroacetoxy)iodoperfluoroalkanes and bis(trifluoroacetoxy)iodo-αα-dihydropolyfluoroalkanes—were obtained by oxidising perfluoro- and αα-dihydropolyfluoro-alkyl iodides with trifluoroperacetic acid in chloroform or trifluoroacetic acid:[11,28,49]

$$R_FI \xrightarrow[CF_3COOH]{CF_3CO_3H} R_FI(OCOCF_3)_2.$$

The reaction is general in character. The only exception is iodotrifluoromethane, which could not be oxidised by trifluoroperacetic acid. A mixture of another oxidant (nitric acid) with trifluoroacetic anhydride decomposes CF_3I, which results in the formation of iodine tris(fluoroacetate) in a quantitative yield.

Bis(trifluoroacetoxy)iodotrifluoromethane was synthesised by substituting the fluorine atoms by trifluoroacetoxy-groups in the reaction of difluoroiodotrifluoromethane with an excess of trifluoroacetic anhydride at −40 °C.[50] $CF_3IF(OCOCF_3)$ is formed as an intermediate:

$$CF_3IF_2 \xrightarrow[-CF_3COF]{(CF_3CO)_2O} CF_3IF(OCOCF_3) \xrightarrow[-CF_3COF]{(CF_3CO)_2O} CF_3I(OCOCF_3)_2.$$

Bis(trifluoroacetoxy)iodotrifluoromethane can be obtained also by treating iodosyltrifluoromethane with an excess of trifluoroacetic anhydride:[50]

$$CF_3IO + (CF_3CO)_2O \xrightarrow[-30\,^\circ C]{} CF_3I(OCOCF_3)_2.$$

(d) Fluorine-containing trivalent iodine ylides and iminoiodoarenes

Iminoiodoarenes were first obtained by the reaction of diacetoxyiodoarenes with toluene-*p*-sulphonamide in methanol in the presence of KOH.[51] Under the same conditions, trifluoroacetyliminoiodobenzene $PhI{=}NCOCF_3$ is formed from trifluoroacetamide and $PhI(OCOCH_3)_2$.[52] Compounds containing the $I{=}NSO_2CF_3$ groups could not be obtained by this method. A method consisting in the reaction of difluoroiodoarenes with *NN*-bis(trimethylsilyl)trifluoromethanesulphonamide has been developed for the synthesis of trifluoromethanesulphonyliminoiodoarenes.[53] Benzenesulphonyliminoiodoarenes have been obtained from *NN*-bis(trimethylsilyl)-benzenesulphonamide:[47,54]

$$XC_6H_4IF_2 + RSO_2N(SiMe_3)_2 \xrightarrow[-Me_3SiF]{} XC_6H_4I{=}NSO_2R,$$

$$R = CF_3,\ X = H,\ 3\text{-}F,\ 4\text{-}F;\quad R = C_6H_5,\ X = H,\ 4\text{-}CH_3,\ 3\text{-}F,\ 4\text{-}F.$$

$C_6F_5I{=}NSO_2C_6H_5$ was obtained similarly.

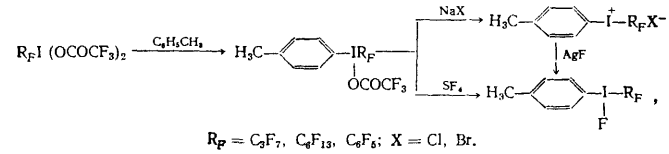
Aryliodonium di(fluorosulphonyl)methylides have been synthesised by the reaction of diacetoxyiodoarenes with methanedisulphonyl fluoride:[47,55]

$$XC_6H_4I(OCOCH_3)_2 + H_2C(SO_2F)_2 \xrightarrow[CH_2Cl_2,\ 20\,^\circ C]{} XC_6H_4I{=}C(SO_2F)_2,$$

$$X = H,\ 3\text{-}F,\ 4\text{-}F,\ 3\text{-}NO_2.$$

(e) Arylperfluoroalkyliodonium salts

These compounds were first obtained in 1971 [49] by condensing bis(trifluoroacetoxy)iodoperfluoroalkanes with benzene and toluene in trifluoroacetic acid. On treatment with sodium chloride or bromide in an aqueous acetone solution, the trifluoroacetates obtained are converted into chlorides and bromides. Arylperfluoroalkyliodonium fluorides are formed from trifluoroacetates on treatment with sulphur tetrafluoride or from chlorides by the exchange reaction with silver fluoride:



$$R_F = C_3F_7,\ C_6F_{13},\ C_6F_5;\ X = Cl,\ Br.$$

In order to increase the stability and reactivity of arylperfluoroalkyl iodonium salts, iodonium salts with the non-nucleophilic anion BF_4^- have been synthesised by the reaction of difluoroiodoperfluoroalkanes with benzene in the presence of BF_3:[56]

$$R_FIF_2 + BF_3 \xrightarrow{CH_2Cl_2,\ -60\,^\circ C} R_F\overset{+}{I}FBF_4^- \xrightarrow[-HF]{C_6H_6} C_6H_5\overset{+}{I}R_FBF_4^-,$$

$$R_F = C_3F_7,\ C_6F_{13}.$$

Arylperfluoroalkyliodonium salts with the trifluoromethanesulphonate (triflate) anion have been synthesised.[57] The condensation of bis(trifluoroacetoxy)iodoperfluoroalkanes with benzene or fluorobenzene was carried out in Freon 113 or in trifluoroacetic acid at

0 °C in the presence of trifluoromethanesulphonic, sulphuric, or fluorosulphonic acid:

$$R_FI(OCOCF_3)_2 \xrightarrow[XSO_3H]{ArH} ArI(OSO_2R)R_F,$$

$R_F = C_nF_{2n+1}$, $n = 2-10$; Ar = C_6H_5, 4-FC_6H_4; X = CF_3, OH, F.

Diiodonium salts—αω-bis(aryliodonium)perfluoroalkanes—with the BF_4^- [58] and $OSO_2CF_3^-$ [59] anions as well as aryl-1,1-dihydropolyfluoroalkyliodonium salts with the methylene group at the iodine atom and with the anions Br^-,[28] BF_4^-,[60] and $OSO_2SF_3^-$ [61] have also been obtained by these methods. Having replaced trifluoromethanesulphonic acid by the polymeric sulphonic acid Nafion-H in the synthesis of arylperfluoroalkyliodonium salts, an iodonium salt with a polymeric anion was obtained.[62] The synthesis of arylperfluoroalkyliodonium triflates has been surveyed.[63]

2. The properties of fluorine-containing organic compounds of trivalent iodine

(a) Iodosyl compounds

Iodosylarenes are yellowish or greenish solid substances with a characteristic smell. Their stability is low, they explode on fusion, and they disproportionate on standing:[4]

$$2ArIO \rightarrow ArI + ArIO_2.$$

Aromatic iodosyl compounds are insoluble in organic solvents and are sparingly soluble in water. On the basis of Mössbauer spectra[64] and comparison of IR and Raman spectra,[65] it has been suggested that the iodine atom in the iodosylbenzene crystals are coordinated in a T-fashion with oxygen atoms and are located in the same plane as the latter. It has been postulated that iodosylbenzene is not a polymer but a cyclic oligomer.[65]

Iodosylarenes behave as the anhydrides of the hypothetic dibasic acids $ArI(OH)_2$. They are amphoteric and form salts with a low stability after the addition of acids or bases:[4]

$$ArIO + H_3O^+ \rightleftarrows ArI^+OH + H_2O,$$
$$ArIO + OH^- \rightleftarrows ArIO_2H^-.$$

Iodosyltrifluoromethane is a colourless crystalline and very unstable substance. It can be stored in the dark at a low temperature. It decomposes with liberation of iodine at 20 °C and on rapid heating in a sealed capillary at 45 °C. When it is dissolved in methanol, the methoxide $CF_3I(OCH_3)_2$ is formed.[14]

Iodosylperfluoropropane is a more stable compound (decomposition temperature 70 °C). It does not change in air at 20 °C but decomposes gradually in the light.[11]

(b) Difluoroiodo- and difluorobromo-compounds.

Difluoroiodoarenes are colourless or yellowish crystalline substances readily hydrolysed by atmospheric moisture to iodosylarenes,[11] which corrode glass vessels on standing. They are soluble in methylene chloride, chloroform, and benzene. Solutions of difluoroiodotoluene in chloroform can be stored in glass vessels for 2–3 days.[4] The chemical shifts of the fluorine atoms in the IF_2 group in the ^{19}F NMR spectrum are presented in Table 1. The ^1H NMR and Raman spectra of these compounds have been published.[22]

The difluoroiodo-derivatives of pentafluorobenzene, perfluoro-n-alkanes, and αα-dihydropolyfluoroalkanes, obtained by the reaction of the corresponding bis(trifluoroacetoxy)iodo-compounds with sulphur tetrafluoride,[11,28] are low melting colourless crystalline substances or liquids, readily soluble in polar organic solvents. On heating above the melting point, they do not decompose and can be

Table 1. The chemical shifts of the fluorine atoms of iodine- and fluorine-containing substituents (δ_F, p.p.m.) relative to CCl_3F in benzene and perfluorocarbon derivatives.

C_6H_5X		R_FIF_2*		Solvent	Refs.	R_FIF_4*		Solvent	Refs.
X	δ_F**, p.p.m.	R_F	δ_{IF_2}, p.p.m.			R_F	δ_{IF_4}, p.p.m.		
$I(OCOCF_3)_2$	−75.99	CF_3	−175.7	CH_3CN	[25]	CF_3	−32.4	CCl_3F	[145]
			−172.7	CCl_3F	[141]				
$I(O)(OCOCF_3)_2$	−76.05	C_2F_5	−175.5	CH_3CN	[26]	C_2F_5	−30.2	CCl_3F	[145]
$I(OCOCF_3)_4$	−76.25	C_3F_7	−165.23***	—	[13]	C_3F_7	−23.03***	—	[13]
IF_2	−177.0	C_4F_9	−167.83***	—	[13]	$(F_3C)_2CF$	−17.3	CCl_3F	[145]
IF_4	−25.67	$F_5S(CF_2)_2$	−175.5	CH_3CN	[27]	n-C_4F_9	−29.2	CCl_3F	[145]
$I{=}C(SO_2F)_2$	−72.94	$F_2I(CF_2)_nIF_2$	—	—		$F_5S(CF_2)_2$	−33.0	CH_3CN	[27]
$I{=}NSO_2CF_3$	−76.96	$n=2$	−171.4	—	[58]	$F_5S(CF_2)_4$	−29.9	CH_3CN	[27]
$I(NSO_2CF_3)_2$	−77.11	$n=4$	−170.1	—	[58]	C_6F_5	−12.0	CH_3CN	[144]

* The spectroscopic characteristics have been published by Haas.[162]

** In CD_2Cl_2.[47]

*** Recalculated relative to CCl_3F.

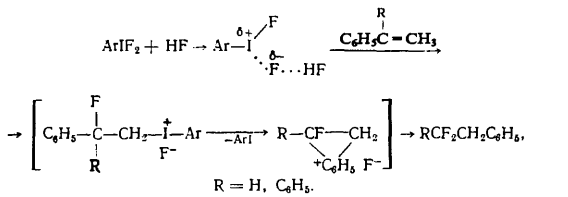
vacuum distilled. There are literature data showing that the above compounds, synthesised by other methods,[13,23,26] decompose at temperatures above 0 °C. This can probably be accounted for by the presence of impurities. The chemical shifts of the fluorine atoms of the IF_2 group in the ^{19}F NMR spectra of different difluoroiodoperfluoroalkanes are presented in Table 1 and the vibrational spectra of CF_2IF_2 have also been published.[66]

On hydrolysis of difluoroperfluoroalkanes, definite products could not be isolated. It has been suggested[13] that hydrolysis results in the formation of iodonium salts of the type $(R_F)_2\overset{+}{I}X^-$, where $X = OH^-$, IO_3^-, I^-, or F^-.

The fluorine atoms of the IF_2 group in difluoroiodotrifluoromethane can be replaced by trifluoroacetoxy-groups on treatment with an excess of trifluoroacetic anhydride,[50] while treatment with an excess of nitrogen pentoxide results in their substitution by nitrato-groups.[67] Difluoroiodotrifluoromethane forms 1:1 adducts with acetonitrile, pyridine, and quinoline. The stability of these complexes increases with increase in the electron-donating capacity of the base.[25]

Difluorobromopentafluorobenzene is a colourless crystalline substance melting at 35–36 °C and not decomposing up to 85 °C.[39]

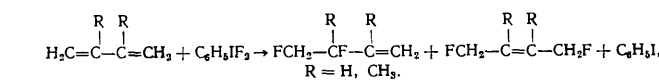
Difluoroiodoarenes and difluoroiodoalkanes are used as mild and selective fluorinating agents. The interaction of difluoroiodoarenes with 1,1-diphenylethylene,[68,69] or styrene[15] affords geminal difluoro-compounds and not 1,2-difluoro-derivatives, as was erroneously stated by Bockemüller.[68] Their formation can be explained by a rearrangement of the intermediate benzenium cation. The process is catalysed by HF:[15,18]



Rearrangements of the same type have been observed also in the fluorination with difluoroiodoarenes of 1-(3-chlorophenyl)-1-phenyl- or 1-(4-methoxyphenyl)-1-phenylethylene and also 1-phenylcyclo-pentene or 1-phenylcyclohexene.[18]

The interaction of difluoroiodoarenes with norbornene[18] results in the formation of a mixture of three products, while the reaction with norbornadiene[70] gives rise to a mixture of four products, whose proportions depend on the substituent in the benzene ring of the difluoroiodoarene.

The fluoroination of 1,3-dienes with difluoroiodobenzene[71] affords a mixture of 1,2- and 1,4-adducts in proportions of approximately 1:2:

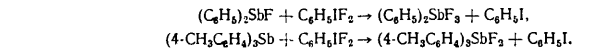


The use of aromatic difluoroiodo-derivatives as fluorinating agents was complicated by the fact that the reaction results in the formation of iodoarenes which hinder the isolation of the fluorination products. This difficulty was eliminated by employing a polymeric difluoroiodo-derivative.[19,20,72] It was found that its interaction with phenylalkenes and norbornene yields the same products as in the reaction with difluoroiodoarenes.

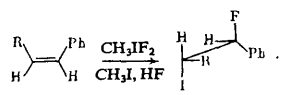
An interesting method of isolating the iodoarenes from the reaction mixture has been described.[73] 4-Difluoroiodophenylacetic acid has been proposed as a fluorinating agent. 4-Iodophenylacetic acid, formed as a result of the reaction of the fluorinating agent with substituted 1,1-diphenylethylenes, can be readily washed out with a solution of sodium carbonate.

Difluoroiodoarenes are also used to convert silylated enolic ethers into α-fluoroketones.[74]

Difluoroiodobenzene also proved to be a convenient agent for the oxidative fluorination of aromatic derivatives of trivalent antimony:[75]



As already mentioned above, difluoroiodomethane was not isolated in a pure form. However, its solutions in an excess of methyl iodide in the presence of hydrogen fluoride were made to react with phenylalkenes[76–78] and phenylalkynes.[79] It was found that this entails the addition of iodine and fluorine atoms (the elements of IF) to the double bond, which is not accompanied by a rearrangement and takes place stereoselectively in accordance with the Markovnikov rule and leads to 1-fluoro-2-iodo-derivatives:

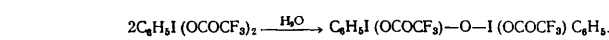


1,2- and 1,4-dihydronaphthalenes react similarly.[80] 1-Fluoro-2-iodo-1,1-diphenylethane is obtained when 1,1-diphenylethylene is treated with $C_2H_5IF_2$.[33]

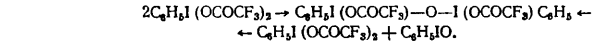
(c) Bis(trifluoroacetoxy)iodo- and bis(trifluoroacetoxy)bromo-compounds

Bis(trifluoroacetoxy)iodoarenes are colourless crystalline substances melting with decomposition at 100–150 °C, soluble in methylene chloride, chloroform, benzene, and ether, and insoluble in pentane. In solutions and during storage they decompose slowly, the decomposition being much faster on heating. Electron-donating substituents in the benzene ring reduce their stability during storage, while electron-accepting substituents increase the resistance to hydrolysis.

On hydrolysis with water, aromatic bis(trifluoroacetoxy)iodo-compounds are converted into μ-oxo-compounds:[43]



Alkaline hydrolysis yields iodosylarenes. A μ-oxo-compound is formed from bis(trifluoroacetoxy)iodobenzene on heating to 70 °C or on interaction with iodosylbenzene:[43]



μ-Oxo-compounds can be obtained by treating iodosylbenzene with a stoichiometric amount of the corresponding acid.[81] The properties, spectroscopic characteristics, and crystal structures of various μ-oxo-compounds have been examined in detail.[81]

Bis(trifluoroacetoxy)iodoarenes are reduced by sodium or potassium iodide in an acid medium to the corresponding iodo-derivatives.[46,82]

μ-Oxodiphenyldiiodosylbis(trifluoromethanesulphonate) $C_6H_5I(OSO_2CF_3)-O-I-(OSO_2CF_3)C_6H_5$, obtained by treating diacetoxyiodobenzene in chloroform with trifluoromethanesulphonic

acid[83] or by treating iodosylbenzene in methylene chloride with the anhydride of trifluoromethanesulphonic acid,[84] is a yellow substance, sparingly soluble in organic solvents, having m.p. 119–121 °C.[83]

Bis(trifluoroacetoxy)iodoperfluoroalkanes and bis(trifluoroacetoxy)iodo-αα-dihydropolyfluoroalkanes are colourless crystalline substances readily soluble in polar organic solvents. They can be stored for a long time in Teflon vessels without access of moisture. Derivatives of perfluoroalkanes are more stable than those of αα-dihydropolyfluoroalkenes.[28,49] The replacement of the aromatic groups by the more electron-accepting polyfluoro- or perfluoroalkyl group increases the tendency of bis(trifluoroacetate) to hydrolyse.[49]

In contrast to bis(trifluoroacetoxy)iodoperfluoroalkanes, bis(trifluoroacetoxy)iodo-αα-dihydropolyfluoroalkanes are converted into *meso*-oxo-compounds on treatment with water and not into iodosyl compounds.[28]

The μ-oxo-derivatives of αα-dihydropolyfluoroalkanes are colourless crystalline substances which have higher melting points and are less soluble in organic solvents than the corresponding bis(trifluoroacetoxy)iodo-derivatives. A characteristic feature of *meso*-oxo-compounds is their solubility in water (it diminishes with increase in the length of the carbon chain of the polyfluorinated group).

The hydrolysis of bis(trifluoroacetoxy)iodo-αα-dihydropolyfluoroalkanes with a 5% solution of sodium bicarbonate leads to extremely unstable iodosyl compounds, which decompose with liberation of iodine.[28]

The thermal decomposition of bis(trifluoroacetoxy)iodotrifluoromethane takes place in accordance with the scheme[50]

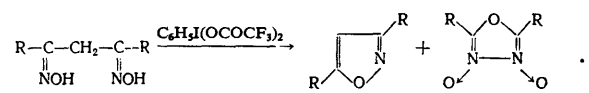
$$CF_3I(OCOCF_3)_2 \xrightarrow[-(CF_3CO)_2O]{} CF_3IO \rightarrow CF_3I + CF_3IO_2.$$

At low temperatures the reaction stops at the iodosyltrifluoromethane formation stage.

Bis(trifluoroacetoxy)bromopentafluorobenzene $C_6F_5Br(OCOCF_3)_2$ is a pale-yellow substance melting with decomposition at 54 °C. Its ^{19}F NMR, IR, and mass spectra have been published.[39] Diacetoxyiodoarenes are widely used in organic synthesis[7,9] as oxidants, acetoxylating agents, and reagents for the synthesis of iodonium salts. Bis(trifluoroacetoxy)iodoarenes are stronger oxidants and electrophiles than diacetoxyiodoarenes. The explanation is that the trifluoroacetoxy-group exhibits a greater electron-accepting inductive effect than the acetoxy-group ($\sigma_{I(OCOCH_3)} = 0.27$; $\sigma_{I(COCF_3)} = 0.65$ [85]) and a larger positive charge is concentrated on the iodine atom in bis(trifluoroacetoxy)-iodoarenes.

Bis(trifluoroacetoxy)iodoarenes have found applications in oxidation, trifluoroacetoxylation, and halogenation reactions and in the synthesis of other compounds of trivalent iodines. Bis(trifluoroacetoxy)iodobenzene is used in various dehydrogenation reactions under mild conditions. Hydrazo-compounds are converted with its aid into azo-compounds, thiophenols are converted into disulphides, hydroquinones are converted into quinones, 1,2-dioximes are converted into furoxanes, *N*-substituted hydroxylamines are converted into nitroso-compounds, and primary and secondary alcohols are converted into aldehydes and ketones.[45]

The previously unavailable furoxano[3,4-b]quinoxolines were obtained with the aid of bis(trifluoroacetoxy)iodobenzene.[9,86] 1,3-Dioximes form a mixture of isoxazoles and 1,3,4-oxadiazole 3,4-dioxides in this reaction:[7]



trans-2-Unsaturated 2,4-dioximes are oxidised to mixtures of 3a,6a-dihydroxazolo[5,4-*d*]isoxazoles and pyridazine 1,2-dioxides.[87,88]

Bis(trifluoroacetoxy)iodobenzene converts acid amides into amines (the Hofmann rearrangement) under mild conditions:[89–91]

$$R-\overset{\overset{O}{\|}}{C}-NH_2 + C_6H_5I(OCOCF_3)_2 + H_2O \rightarrow$$
$$\rightarrow R\overset{+}{N}H_3CF_3COO^- + CF_3COOH + C_6H_5I + CO_2.$$

The same reaction is used to cleave peptides with terminal COOH groups, which makes it possible to determine the aminoacid sequence[92] and also to synthesise L-2,3-diaminopropionic acid—a constituent of a polypeptide antibiotic.[93]

Arylacetylenes have been oxidised to α-diketones[94] and benzaldehydes have been oxidised to benzoic acids[95] with the aid of bis(trifluoroacetoxy)iodobenzene. It has been used in the synthesis of morphines as an agent effecting oxidative cyclisation.[96]

The oxidative cleavage of dibenzyl ethers[97] and the ring opening in oxirans (leading to hydroxyaldehydes and hydroxyketones after the hydrolysis of the trifluoroacetate[98]) and arylcyclopropanes[99–101] also belong to the class of trifluoroacetoxylation reactions.

Reactions involving the oxidative substitution of a halogen, namely iodine, in alkyl halides[102,103] lead to trifluoroacetate esters, for example:

$$n\text{-}C_7H_{15}I + C_6H_5I(OCOCF_3)_2 \rightarrow n\text{-}C_7H_{15}OCOCF_3.$$

Bis(trifluoroacetoxy)iodobenzene introduces two trifluoroacetoxy-groups into alkene molecules in a high yield, the bisesters obtained being readily hydrolysed to glycols.[9] In the interaction of bis(trifluoroacetoxy)iodobenzene with aryldiazomethanes and aryl diazoethanes, the main products are the trifluoroacetate esters $ArCH_2OCOCF_3$ or $ArCH(CH_3)OCOCF_3$.[9] The trifluoroacetoxylation reaction has been used to synthesise codeine.[104]

The phenomenon of competitive binding of superweak anions has been extended to the reactions involving the coupled addition of aryliodoso-salts to the C=C double bond in the interaction of hex-1-ene or cyclohexene with bis(trifluoroacetoxy)iodobenzene in the presence of lithium perchlorate or triflate, which leads to the formation of bistriflates or bisperchlorates of hexane-1,2-diol or cyclohexane-1,2-diol:[105,106]

$$C_4H_9CH=CH_2 + C_6H_5I(OCOCF_3)_2 + LiOZ \rightarrow C_4H_9CH(OZ)-CH_2OZ,$$
$$Z = SO_2CF_3,\ ClO_3.$$

The bistriflates and bisperchlorates of hexane-1,2-diols are also formed when hex-1-ene or cyclohexene are treated with *meso*-oxodiphenyldiiodosobis(trifluoromethanesulphonate) or the corresponding perchlorate.[83] Subsequently this reaction was extended also to butadiene.[84]

The reactions involving halogenation with a mixture of bis(trifluoroacetoxy)iodobenzene with halogens are of considerable interest. It has been shown[107] that the bis(trifluoroacetoxy)-iodobenzene/iodine system is an extremely effective agent for the iodination of aromatic compounds. Iodine has been introduced by this method into a series of alkyl- and halogeno-benzenes, various polynuclear aromatic hydrocarbons, certain heterocyclic compounds,[107,108] *o*- and *m*-carbaboranes,[109] and also arylcyclopropanes.[110]

The halogenation of various aromatic compounds by mixtures of $C_6H_5I(OCOCF_3)_2$ with the halogens and also with boron and aluminium halides has been described.[111,112] A powerful halogenating agent—trifluoroacetyl hypohalite—is apparently generated in all these reactions, for example:

$$PhI(OCOCF_3)_2 + I_2 \rightarrow PhI + 2CF_3COOI,$$
$$PhI(OCOCF_3)_2 + AlCl_3 \rightarrow PhI + CF_3COOAlCl_2 + CF_3COOCl.$$

Bis(trifluoroacetoxy)iodobenzene has also been used to synthesise other trivalent iodine compounds, for example, phenyl-2-thienyliodonium trifluoroacetate.[113] The first representative of trivalent iodine compounds containing two I–N bonds, namely diphthalimidoiodobenzene, was obtained by the reaction of bis(trifluoroacetoxy)iodobenzene with potassium phthalimide.[114] It was found that similar compounds are also formed from other cyclic imides.[115]

Nitrophenyliodonium phenoxides have been obtained by the reaction of bis(trifluoroacetoxy)iodobenzene with nitrophenols.[116]

(d) Fluorine-containing trivalent iodine ylides and iminoiodoarenes

Acyliminoiodoarenes are crystalline substances melting with decomposition at 100–130 °C. Triphenylmethanesulphonylimino- and trifluoroacetylimino-iodoarenes are readily hydrolysed by atmospheric moisture, while benzenesulphonyl- and toluene-*p*-sulphonyl-iminoiodoarenes are converted into idosylarenes only on alkaline hydrolysis. In the IR spectra of these compounds, the characteristic vibrations of the SO_2 group are displaced towards shorter wavelengths compared with the corresponding sulphonamides.[51–54]

Acyliminoiodoarenes can be used in transylidation reactions. For example, the reaction of tosyliminoiodobenzene with thioanisole, dimethyl sulphoxide, and triphenylphosphine yields the corresponding iminosulphuranes and iminophosphoranes.[51] On catalysis by iron- or manganese-porphyrins, the compounds PhI=NR (R = tosyl or $COCF_3$) react with alkenes, forming *N*-substituted aziridines.[52]

Aryliodonium di(fluorosulphonyl)methylides are colourless or slightly yellowish crystalline substances which melt with decomposition at 160–170 °C,[47,55] dissolve in polar organic solvents, and do not dissolve in pentane.

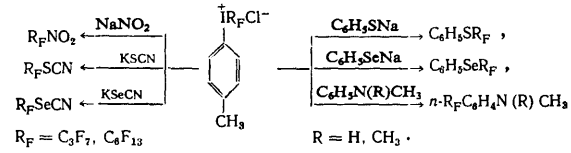
(e) Arylperfluoroalkyliodonium salts

Arylperfluoroalkyliodonium trifluoroacetates and halides are colourless crystalline substances soluble in benzene, methylene chloride, acetone, and acetonitrile. They are lower melting substances and are less stable on storage than diaryliodonium salts.[49] The low melting point can apparently be explained by the more covalent character of the bond between the iodine atom and the acid residue than in diaryliodonium salts, while their low stability is due to the intramolecular interaction of the nucleophilic anion with the onium centre.

Iodonium salts containing the BF_4^- anion are colourless crystalline substances melting with decomposition at 150–160 °C.[56] The salts containing the $OSO_2CF_3^-$ anion (the "FITS reagents")[63] melt with decomposition at lower temperatures (120–130 °C).

Arylperfluoroalkyliodonium tetrafluoroborates and triflates are stable substances which do not decompose on storage or on exposure to atmospheric moisture.

An important property of arylperfluoroalkyliodonium salts is their ability to transfer the perfluoroalkyl group to various nucleophiles. This was first demonstrated for perfluoro-n-alkyl-*p*-tolyliodonium chlorides:[117]



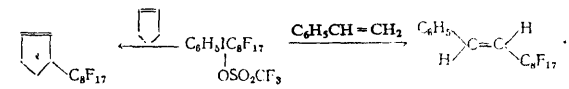
When (perfluoroalkyl)phenyliodonium tetrafluoroborates are used under the same conditions, the yields of the products of the perfluoroalkylation of sodium *p*-nitrothiophenoxide, monomethylaniline, and dimethylaniline are much higher than in the case where chlorides are used and are nearly quantitative according to GLC data.[56]

The "cationic" perfluoroalkylation reactions with the aid of FITS reagents have been extended to various carbanions,[118,119] aromatic compounds,[120] thiols,[121] phenols,[120,122] and unsaturated compounds.[123–126] The latter react with arylperfluoroalkyliodonium triflates in various ways depending on the substrate and the reaction conditions. Ethylene and other alkenes give rise to adducts in the presence of bases:[123]

$$ArI(OSO_2CF_3)-R_F + H_2C=CH_2 \xrightarrow[Na_2CO_3]{Nu^-} R_F-CH_2-CH_2-Nu,$$
$$Nu^- = HCOO^-,\ HO^-,\ CH_3O^-,\ Cl^-.$$

Alka-1,3-dienes afford exclusively 1,4-adducts.[123]

When the reaction with alkenes is carried out under other conditions, for example, in methylene chloride with added pyridine, products resulting from substitution at the vinyl or allyl carbon atom are obtained:[123]



If the reactions of iodonium triflate salts with alkenes are performed in the presence of oxygen, the perfluoroalkylation is accompanied by oxidation; perfluoroalkylated ketones are formed from alkenes, esters are formed from enol ethers, and unsaturated aldehydes and ketones are formed from dienes.[124]

The interaction of arylperfluoroalkyliodonium triflates with the trimethylsilyl ethers of enols affords high yields of α-perfluoroalkylketones, for example:

$$CH_3C(OSiMe_3)=CH_2 \xrightarrow{PhIC_6F_{17}OSO_2CF_3} \underset{88\%}{CH_3COCH_2C_6F_{17}}.$$

Depending on the reaction conditions, products resulting from substitution, addition, or oxidation are formed in the reactions with various alkynes.[126]

The alkylating effect of iodonium salts in which the perfluoroalkyl group is separated from the iodine atom by the methylene group, namely aryl-1,1-dihydropolyfluoroalkyliodonium tetrafluoroborates[60] and triflates,[61] has been investigated[60,127–129] and it has been shown that these salts are stronger alkylating agents than their perfluoroalkyl analogues, apparently as a consequence of the facilitation of the heterolysis of the $I-CH_2R_F$ bond compared with $I-CF_2R_F$.

The differences between the reactivities of iodonium salts with perfluoroalkyl and 1,1-dihydropolyfluoroalkyl groups are manifested in their interaction with nitrogen-containing compounds. Whereas

arylperfluoroalkyliodonium salts do not alkylate pyridine, aryl-1,1-dihydropolyfluoroalkyliodonium salts alkylate tertiary amines, including pyridine and other heterocyclic nitrogen-containing bases[60,127] with formation of quaternary salts. Aniline, *N*-ethylaniline, and β-phenylethylamine are polyfluoroalkylated only at the nitrogen atom,[60,127] while in the case of *NN*-dimethylaniline, a mixture of a quaternary salt and the product of polyfluoroalkylation in the *para*-position in the aromatic ring is obtained.[60]

The dialkylation of aniline has been achieved in a high yield with the aid of phenyl-1,1-dihydrotrifluoroethyliodonium triflate in the presence of a sterically hindered substituted pyridine:[127]

$$C_6H_5NH_2 \xrightarrow{C_6H_5\overset{+}{I}CH_2CF_3\overline{O}SO_2CF_3,\ 20\,^\circ C} C_6H_5N(CH_2CF_3)_2.$$
94%

The reaction with the trimethylsilyl ethers of enols in the presence of KF results in the formation of β-perfluoroalkylcarbonyl compounds in a satisfactory yield:[129]

$$PhI(OSO_2CF_3)CH_2R_F + PhC(OSiMe_3)=CH_2 \xrightarrow[CH_2Cl_2,\ 20\,^\circ C]{KF} PhCOCH_2CH_2R_F + PhI.$$

Aryl-(1,1-dihydropolyfluoroalkyl)iodonium triflates undergo dehydrofluorination on treatment with bases, forming aryl-(1-*H*-perfluoroalk-1-enyl)iodonium triflates:[128]

$$PhI(OSO_2CF_3)CH_2CF_2R_F \xrightarrow{NaH} PhI(OSO_2CF_3)CH=CFR_F \qquad R = CF_3,\ C_2F_5,\ C_6F_{13}.$$

On treatment with *O*-nucleophiles, a fluorine atom at the double bond is substituted, while on treatment with *S*-nucleophiles these compounds react as polyfluoroalkenylating agents:[128]

$$PhI(OSO_2CF_3)CH=CFCF_3 \xrightarrow{PhO^-} PhI(OPh)CH=CFCF_3 \xrightarrow{ArS^-} CF_3CF=CHSAr + CF_3C(SAr)=CHSAr$$
$$Ar = p\text{-}(CH_3)_3CC_6H_4.$$

The tetrafluoroborates of αω-bis(aryliodonium)perfluoroalkanes $C_6H_5\overset{+}{I}(CF_2CF_2)_n\overset{+}{I}C_6H_5.2BF_4^-$ (n = 2, 3) exhibit a high anti-cholinesterase activity.[130]

III. Derivatives of pentavalent halogens

1. Methods of synthesis

The starting materials for the synthesis of fluorine-containing aromatic derivatives of pentavalent iodine are iodylarenes. The methods of their synthesis and their properties are therefore briefly described below. Among the perfluoroalkyl derivatives of pentavalent iodine, tetrafluoroiodoperfluoroalkanes are most readily available.

(a) Iodyl compounds

Iodylarenes were obtained almost 100 years ago.[131] The following are the most convenient methods of their synthesis; the disproportionation of iodosylarenes with steam distillation of the iodoarenes formed,[132] the oxidation of dichloroiodoarenes with sodium hypochlorite,[133] and the oxidation of iodoarenes with 40% peracetic acid.[134] Iodylpentafluorobenzene has been obtained by the disproportionation of iodosylpentafluorobenzene.[135]

A modification of the iodosylarene disproportionation method for the preparation of iodylarenes containing strong electron-accepting substituents in the benzene ring has been proposed. It consists in the steam distillation of bis(trifluoroacetoxy)iodoarenes which are more readily available in this instance. This results in the hydrolysis and disproportionation of the iodosylarenes formed.[48]

$$2XC_6H_4I(OCOCF_3)_2 \xrightarrow{H_2O} 2XC_6H_4IO \rightarrow XC_6H_4IO_2 + XC_6H_4I,$$
X=3-CF_3, 3-NO_2, 4-NO_2.

Iodylarenes, including those with electron-accepting ring substituents, are formed in 45–50% yield when iodoarenes are oxidised with potassium bromate in sulphuric acid.[136] The method is attractive because of its simplicity and safety.

The first representative of aliphatic iodyl compounds, namely iodyltrifluoromethane, has been obtained as a result of the prolonged reaction of CF_3IF_4 with finely dispersed silica in CCl_3F at 0 °C.[14]

(b) Difluoroiodyl compounds

Difluoroiodylarenes have been obtained by dissolving iodylarenes in hot 40% hydrofluoric acid:[3,137]

$$XC_6H_4IO_2 + 2HF \rightarrow XC_6H_4IOF_2 + H_2O,$$
X=H, 2-CH_3, 3-CH_3, 4-CH_3, 4-Br.

$C_6F_5IOF_2$ has been synthesised similarly.[135]

Among aliphatic difluoroiodyl compounds, only difluoroiodyltrifluoromethane CF_3IOF_2 is known. It is formed when difluoroiodotrifluoromethane is ozonised or when tetrafluoroiodotrifluoromethane reacts with finely dispersed silica.[14]

(c) Tetrafluoroiodo- and tetrafluorobromo-compounds

Tetrafluoroiodoarenes are obtained in a quantitative yield by heating iodylarenes with sulphur tetrafluoride.[138,139] Difluoroiodylarenes react similarly, their use being safer, since they are less explosive than iodylarenes:[140]

$$XC_6H_4IO_2 \xrightarrow{SF_4} XC_6H_4IF_4 \xleftarrow{SF_4} XC_6H_4IOF_2,$$
X=H, 4-CH_3, 3-F, 4-F.

The above methods are applicable only to the synthesis of the tetrafluoroiodoarenes which contain weak electron-donating or weak electron-accepting substituents in the benzene ring. The attempts to obtain tetrafluoroiodoarenes with strong electron-donating or strong electron-accepting substituents by this method have been unsuccessful.[140]

Tetrafluoroiodopentafluorobenzene has been obtained by treating iodopentafluorobenzene with chlorine trifluoride.[141,142] *p*-$F_4IC_6F_4IF_4$ is formed similarly from *p*-diiodotetrafluorobenzene.[142] $C_6F_5IF_4$ has also been synthesised by treating difluoroiodopentafluorobenzene with xenon difluoride.[16] This compound can be obtained by the reaction of IF_5 with the stoichiometric amount of $Si(C_6F_5)_4$:[143,144]

$$4IF_5 + Si(C_6F_5)_4 + 2Py \xrightarrow[CH_3CN]{80^\circ C} 4C_6F_5IF_4 + SiF_4 \cdot 2Py.$$

IF_5 reacts much more readily with aryltrifluorosilanes:[144]

$$ArSiF_3 + IF_5 \xrightarrow[CH_3CN]{35^\circ C,\ Py} ArIF_4 + SiF_4 \cdot 2Py,$$
Ar=C_6H_5, 4-$CH_3C_6H_4$, 4-FC_6H_4, C_6F_5.

The reaction involving pentafluorophenyltrifluorosilane takes place at 20 °C in the absence of pyridine.

According to Obaleye and [illegible] tetrafluorobromopentafluorobenzene has been obtained [illegible] reaction of pentafluorobromobenzene with elementa[illegible]ine at 128 °C.

Ttrafluoroiodoperfluoroalkanes are obtained by the reaction of iodoperfluoroalkanes with elemental fluorine,[13,26] chlorine trifluoride,[27,141,145] and bromine trifluoride or pentafluoride at low temperatures in inert solvents. CF_3IF_4,[141,145] $C_2F_5IF_4$, $C_4F_9IF_4$, $C_{10}F_{21}IF_4$,[13] as well as derivatives of 1,2-diiodotetrafluoroethane $F_4ICF_2CF_2IF_4$ [26] and tetrafluoroiodoperfluoroalkylsulphur pentafluoride $F_5S(CF_2)_nIF_4$ (n = 2, 4) [27] have now been described.

The first representatives of perfluoroalkyl derivatives of pentavalent bromine, namely tetrafluorobromoperfluoro-n-propane[146] and tetrafluorobromoperfluoro-n-hexane[147] have been obtained by fluorinating the corresponding perfluoroalkyl bromides with elemental fluorine at 0 °C.

(d) Tetrakis(perfluoroacyloxy)iodo-compounds

Tetrakis(trifluoroacetoxy)iodoarenes have been obtained in quantitative yields by treating iodylarenes with trifluoroacetic anhydride:[48]

$$XC_6H_4IO_2 + 2(CF_3CO)_2O \xrightarrow{[CF_3COOH]} XC_6H_4I(OCOCF_3)_4,$$
$$X=H,\ 4\text{-}CH_3,\ 4\text{-}Cl,\ 3\text{-}F,\ 4\text{-}F,\ 3\text{-}CF_3,\ 3\text{-}NO_2,\ 4\text{-}NO_2.$$

Tetrakis(perfluorobutyryloxy)iodoarenes have been obtained similarly by reaction with perfluorobutyric anhydride.[48] The reaction of iodylarenes with the anhydride of a weaker acid (acetic) affords diacetoxyiodylarenes.[48]

The reactions are carried out at 20 °C using a large excess of the anhydride, which is then regenerated. Electron-donating substituents accelerate the reaction, while electron-accepting substituents retard it somewhat. The addition of small amounts of the corresponding acid catalyses the process.

Tetrafluoroiodobenzene reacts similarly to iodylbenzene:[48]

$$C_6H_5IF_4 + (R_FCO)_2O \rightarrow C_6H_5I(OCOR_F)_4 + R_FCOF,$$
$$R_F=CF_3,\ C_3F_7.$$

(e) Diacyloxyiodyl compounds

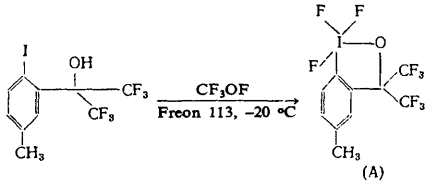
Bis(trifluoroacetoxy)iodylarenes have been obtained in quantitative yields by treating iodylarenes with trifluoroacetic acid:[148]

$$XC_6H_4IO_2 + CF_3COOH \rightarrow XC_6H_4I(OCOCF_3)_2 + H_2O,$$
$$\text{(O above I)}$$
$$X=H,\ 4\text{-}CH_3,\ 3\text{-}F,\ 4\text{-}F,\ 3\text{-}CF_3,\ 4\text{-}NO_2.$$

Diacetoxy- and bis(perfluorobutyryloxy)-iodylarenes have been synthesised similarly using an excess of acetic and perfluorobutyric acids. Small amounts of the anhydride of the corresponding acid are added to bind the water in reversible reactions. The stronger the acid, the faster the dissolution of the iodylarenes.

(f) Trifluoroperiodinanes

Trifluoroperiodinane (A) is a compound containing a pentavalent iodine atom in the ring linked to alkoxy- and aryl ligands. It has been obtained by oxidising with trifluoromethyl hypofluorite an iodoarene containing in the *ortho*-position relative to the iodine atom a tertiary carbinol residue:[149,150]



(A)

The *gem*-analogue of trifluoroperiodinane (A) has been synthesised by a procedure similar to that used for compound (A) itself.[150]

(g) Diiminoiodoarenes

Bis(sulphonylimino)iodoarenes have been obtained by the reaction of tetrafluoroiodoarenes with *NN*-bis(trimethylsilyl)derivatives of trifluoromethanesulphonamide[53] and benzene sulphonamide:[47,54]

$$XC_6H_4IF_4 + 2RSO_2N(SiMe_3)_2 \xrightarrow{\text{ether, 20 °C}} XC_6H_4I(NSO_2R)_2 + 4Me_3SiF,$$
$$R=CF_3,\ X=H,\ 3\text{-}F,\ 4\text{-}F;\ R=C_6H_5,\ X=H,\ 4\text{-}CH_3,\ 3\text{-}F,\ 4\text{-}F.$$

Instead of tetrafluoroiodoarenes, it is possible to use also tetrakis(trifluoroacetoxy)iodoarenes for the synthesis of bis(benzenesulphonylimino)iodoarenes.[54]

(h) Diaryliodosyl salts

Diphenyliodosyl hydroxide has been obtained by the self-condensation of iodylbenzene in the presence of alkali. It forms compounds with carbonic and acetic acids. They have been described as hydrogen-bonded cyclic complexes.[151]

A series of diaryliodosyl salts were subsequently obtained in accordance with the following scheme:[152]

$$ArIO_2 \xrightarrow{HO^-} Ar_2I(O)OH \xrightarrow{RCOOH} Ar_2I(O)OCOR \xrightarrow{X^-} Ar_2\overset{+}{I}(O)\ X^-,$$
$$R=CH_3,\ CF_3;\ X^-=F^-,\ Cl^-,\ Br^-,\ IO_3^-.$$

The interaction of diaryliodosyl trifluoroacetates with sulphur tetrafluoride at low temperatures leads to diaryldifluoroiodosyl trifluoroacetates.[153] On heating to 60 °C, the trifluoroacetate anion is also substituted by a fluoride ion and diphenyldifluoroiodosyl fluoride is formed:[153]

$$(XC_6H_4)_2\overset{+}{I}{=}O \xrightarrow[-10\text{–}0\,^\circ C]{SF_4} (XC_6H_4)_2\overset{+}{I}F_2\ \overline{O}COCF_3 \xrightarrow[60\,^\circ C]{SF_4} (XC_6H_4)_2\overset{+}{I}F_2\ F^-,$$
$$X=H,\ 4\text{-}F.$$

2. The properties of fluorine-containing organic compounds of pentavalent iodine

(a) Iodyl compounds

Iodylarenes are colourless crystalline substances, which explode on heating above 200 °C or on impact with liberation of iodine. They are insoluble in the majority of organic solvents and are sparingly soluble in sulpholane, dimethyl sulphoxides, and water. They are usually crystallised from water.

The structure of the solid iodylarenes has been investigated by X-ray diffraction and nuclear quadrupole resonance using *p*-chloroiodylbenzene as an example.[154] It has been shown that the iodylarene molecule is non-planar and asymmetric in the crystalline state and the IO_2 group is perpendicular to the plane of the aromatic ring. The I—O bond lengths (1.60 and 1.65 Å) are smaller than the sum of the covalent radii of oxygen and iodine (2.00 Å), which indicates a partial double bond character.[4] The effective charge on the iodine atom has been estimated from the NQR spectra. It is close to +1.7 |e|.[54] The data presented make it possible to attribute to iodylarenes the following structure:



which is similar to the structure of nitrobenzene except that the nitro-group is located in the plane of the aromatic ring.

This hypothesis has been confirmed by data obtained by comparing the IR and Raman spectra of iodylbenzene.[65] The I–O stretching vibrations in iodylbenzene occur at higher frequencies than in iodobenzene, so that the I–O distance in iodylbenzene is shorter. The Mössbauer spectra of $C_6H_5IO_2$ have been described.[64] According to the literature,[64] the O–I–O angle in the iodylbenzene molecule is close to 95 °C.

The chemical properties of iodylarenes have been little investigated. They are known to exhibit amphoteric behaviour—they react with strong acids, forming salts, and dissolve in alkalies with formation of unstable anions, which decompose on acidification.[4] Conductiometric determination of the pK_a of iodylbenzene yielded 10.4.[151]

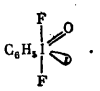
The interaction of iodylarenes with the anhydrides of carboxylic perfluoroacids and with carboxylic acids, leading to the formation of tetrakis(perfluoroacyloxy)iodoarenes[48] and diacyloxyiodylarenes,[148] proceeds via a stage involving the formation of a salt of the type $ArI^{+}(O)OH\overline{O}COR$.

The study of the chemical properties of iodylarenes is hindered by their insolubility in the usual organic solvents. The preparation of 4-t-butyliodylbenzene, soluble in hot benzene, chlorobenzene, and nitrobenzene and the study of the oxidation by this compound of alkenes, acetylenes, phenanthrene, anthracene, and tetralin have been described. The corresponding carbonyl compounds are obtained in 50–75% yield and the 4-t-butyliodobenzene dissolved can be regenerated.

Iodyltrifluoromethane is a colourless crystalline substance, stable in air, which decomposes at 50 °C with liberation of iodine. CF_3IO_2 is insoluble in CCl_3F and acetonitrile but is readily soluble in methanol, probably as a result of the formation of methoxides of the type $CF_3I(O)(OCH_3)_2$ or $CF_3I(OCH_3)_4$.[14] The IR and ^{19}F NMR spectra of iodyltrifluoromethane have been published.[14]

(b) Difluoroiodyl compounds

Difluoroiodylarenes are colourless crystalline substances, which are hydrolysed by atmospheric moisture with formation of iodylarene and hydrogen fluorides. Like iodylarenes, they are sparingly soluble in organic solvents and explode on heating above 200 °C. The following structure has been proposed for difluoroiodylbenzene on the basis of a comparison of the IR and Raman spectra:[65]



Difluoroiodyltrifluoromethane is a colourless crystalline substance which sublimes at −10 °C (0.01 mmHg). It is very readily hydrolysed by atmospheric moisture and readily dissolves in CCl_3F and acetonitrile.[14] Difluoroiodyltrifluoromethane reacts with alcohols, acids, and acid anhydrides, the fluorine atoms being substituted. All these reactions are reversible, for example:[156]

$$CF_3IOF_2 + ROH \rightleftarrows CF_3IOF(OR) + HF,$$
$$CF_3IOF(OR) + ROH \rightleftarrows CF_3IO(OR)_2 + HF.$$

When an attempt is made to isolate such compounds, they decompose. The reactions could therefore be investigated by NMR.[156]

Difluoroiodyltrifluoromethane reacts with Lewis acids (BF_3, AsF_5, and SbF_5). This probably entails the initial formation of a complex which then decomposes, being converted into tetrafluoromethane and the compounds $IO[BF_4]$, $IO[AsF_6]$, $IO[SbF_6]$, or $IO[Sb_2F_{11}]$.[157]

(c) Tetrafluoroiodo- and tetrafluorobromo-compounds

Tetrafluoroiodoarenes are colourless crystalline substances which melt without decomposition at 80–100 °C and are readily soluble in ether, benzene, and methylene chloride and less so in hexane. They are hydrolysed by atmospheric moisture to iodylarenes, they corrode glass vessels, and on heating or prolonged storage they react with quartz. On storage in platinum or Teflon vessels in the absence of moisture, they are stable.[138,140]

The ^{19}F NMR spectra of tetrafluoroiodobenzene contain one signal—an asymmetric singlet. The fluorine atoms of tetrafluoroiodobenzene are equivalent and its molecule apparently has the form of a tetragonal pyramid with fluorine atoms at the base, the iodine atom in the centre, and the phenyl residue at the apex.[138]

Tetrafluoroiodobenzene is thermally stable; it hardly changes on heating to 250 °C and decomposes at an appreciable rate only at about 300 °C.[140] On photolysis of tetrafluoroiodobenzene, atomic fluorine is evolved, which has been demonstrated by photolysing $C_6H_5IF_4$ in deuteriated benzene with subsequent mass-spectrometric analysis of the reaction products.[158]

Tetrafluoroiodobenzene is less reactive than iodine pentafluoride. In contrast to the latter, it dissolves in benzene without appreciable interaction. On dissolution in primary alcohols, a vigorous reaction takes place, leading to aldehydes (as a result of charring, the yields are 20%), iodobenzene, and hydrogen fluoride. Tetrafluoroiodobenzene dissolves in t-butyl alcohol in the cold without interaction, whilst at 30–35 °C it interacts with formation of t-butyl fluorides. Acids and their lithium salts are converted into acid anhydrides and fluorides respectively on heating with tetrafluoroiodobenzene.[140] Tetrafluoroiodobenzene fluorinates triphenylphosphine to trifluorotriphenylphosphorane, being reduced at the same time to difluoroiodo- or iodo-benzene depending on the reactant ratio employed:[138]

$$C_6H_5IF_4 + 2(C_6H_5)_3P \rightarrow C_6H_5I + 2(C_6H_5)_3PF_2.$$

Tetrafluorobromopentafluorobenzene is a colourless liquid which fumes in air. It oxidises 0.1 M KI solution and does not decolorise 0.1 M $KMnO_4$ solution.[36]

Tetrafluoroiodoperfluoroalkanes are colourless crystalline substances which are hydrolysed by atmospheric moisture and decompose at 20–60 °C. They are soluble in CCl_3F, IF_5, dioxane, and acetonitrile. The stability of the compounds R_FIF_4 increases with increase in the length of the carbon chain in the perfluoroalkyl group.[145]

On hydrolysis of tetrafluoroiodoperfluoroalkanes with water[13] or KOH in ethanol,[145] iodylperfluoroalkanes are not formed. The author suggests[13] that the iodonium salts $(R_F)_2\overset{+}{I}X^-$ are formed, but these have not been isolated in a pure form.

CF_3IF_4 decomposes in accordance with the following scheme:[145]

$$CF_3I + IF_5 \xleftarrow{[IF]} CF_3IF_4 \rightarrow CF_4 + IF_3 \rightarrow IF + IF_5$$
$$\downarrow$$
$$I_2 + IF_5$$

In the reaction with methoxytrimethylsilane, the fluorine atoms are substituted in succession by methoxy-groups:[145]

$$CF_3IF_4 + (CH_3)_3SiOMe \rightarrow CF_3IF_3(OMe) + (CH_3)_3SiF.$$

Similar substitution products are obtained also in the interaction with alcohols, acids, and anhydrides:[156]

$$CF_3IF_4 + n\,ROH \rightleftarrows CF_3IF_{4-n}(OR)_n + n\,HF.$$

Tetrafluorobromoperfluoropropane[146] and tetrafluorobromoperfluoroheptane[147] are colourless liquids. They are capable of oxidising four equivalents of KI, for example:

$$n\text{-}C_7F_{15}BrF_4 + 4KI \rightarrow n\text{-}C_7F_{15}Br + 2I_2 + 4KF.$$

(d) Tetrakis(perfluoroacyloxy)iodo-compounds

Tetrakis(perfluoroacyloxy)iodoarenes are colourless crystalline substances melting with decomposition. They are readily hydrolysed by atmospheric moisture and are unstable during storage. Electron-donating substituents in the benzene ring diminish the stability of these compounds during storage, while electron-accepting substituents diminish their resistance to hydrolysis. Tetrakis(perfluoroacyloxy)-iodoarenes are readily soluble in organic solvents but their stability in solutions is low.[48]

The IR spectrum of tetrakis(trifluoroacetoxy)iodobenzene differs from the IR spectrum of iodylbenzene by the presence of an intense band at 500 cm^{-1} and two bands at 735 and 783 cm^{-1} instead of four bands at 700–800 cm^{-1} in the spectrum of iodylbenzene. The ^{19}F NMR spectrum of $C_6H_5I(OCOCF_3)_4$ has a single signal—a symmetrical singlet. This compound apparently has a structure similar to that of tetrafluoroiodobenzene.[48]

Tetrakis(trifluoroacetoxy)iodobenzene is a fairly powerful oxidant; it oxidises *m*-nitrobenzyl alcohol to the corresponding aldehyde in 3 h at 20 °C in 80% yield,[159] while bis(trifluoroacetoxy)iodobenzene oxidises benzyl alcohol to benzaldehyde in 4 h at 80 °C in 50% yield.[45]

(e) Diacyloxyiodylarenes

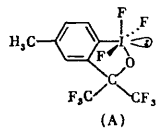
Diacyloxyiodylarenes are colourless crystalline substances melting with decomposition at higher temperatures than the corresponding tetrakis(perfluoroacyloxy)iodoarenes. They dissolve less readily in organic solvents and are more stable during storage and in hydrolysis. The IR spectra of the compounds $ArI(OCOR)_2$ are similar to the IR spectrum of $C_6H_5IOF_2$.[148]

Diacetoxyiodylbenzene has been used as an oxygen donor in the hydroxylation of steroids catalysed by cytochrome P-450.[160]

(f) Trifluoroperiodinanes

Trifluoroperiodinanes are colourless crystalline substances melting with decomposition. Trifluoroperiodinanes (A) (decomposition temperature 191–193 °C) can remain for a time in air without appreciable hydrolysis. The addition of water to this compound at 25 °C does not lead to reaction for several days. When trifluoroperiodinane is treated with an aqueous KOH solution, an iodyl derivative is probably obtained.[150] The *gem*-dimethyl analogue of trifluoroperiodinane (decomposition temperature 123–124 °C) hydrolyses faster than compound (A). In the presence of atmospheric moisture, the hydrolysis takes place over 4 h at 25 °C. The hydrolysis products have not been identified.[150] The *gem*-dimethyl analogue is also less stable during storage. It decomposes in 7 days at 25 °C and in 2–3 weeks at –20 °C.

Judging from the ^{19}F NMR spectra of perfluoroiodinanes, the fluorine atoms of the IF_3 group in these compounds are non-equivalent. An octahedral structure has been proposed for compound (A) (the sixth ligand is an electron pair):[150]



(A)

The doublet in the ^{19}F NMR spectrum of compound (A) at $\delta = -13.20$ ($J = 116$ Hz) is due to two equivalent fluorine atoms, while the triplet at $\delta = -41.57$ ($J = 116$ Hz) is due to a single fluorine atom. Other investigators[145] arrived at a similar conclusion concerning the structure of the compound $CF_3IF_3(OCH_3)$. The ^{19}F NMR spectrum of its IF_3 group consists of a doublet at $\delta = -7.0$ ($J = 113$ Hz) and a triplet at $\delta = -46.5$ ($J = 113$ Hz).

Trifluoroperiodinane decomposes slowly in acetonitrile and the solution corrodes glass in the presence of atmospheric moisture. On treatment of compound (A) with three or more equivalents of chlorotrimethylsilane, chloroiodinane, fluorotrimethylsilane, and chlorine are formed. When trifluoroperiodinane is irradiated with UV light in the presence of toluene or anisole at 50 °C, it remains unchanged.[150]

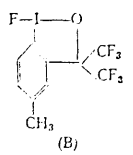
Trifluoroperiodinane reacts rapidly with phenylmagnesium bromide in accordance with the scheme

$$(A) + C_6H_5MgBr \xrightarrow{\text{ether}} \underset{90\%}{C_6H_5F}.$$

The interaction of trifluoroperiodinane with primary and secondary amines containing an α-hydrogen atom and subsequent hydrolysis afford a satisfactory yield of the corresponding carbonyl compounds.[150] In the reaction with t-butylamine, azoisobutane is formed. Trifluoroperiodinane does not react with tertiary amines.[150]

The interaction of trifluoroperiodinane with primary and secondary alcohols gives rise to aldehydes and ketones respectively.[150]

In all cases, trifluoroperiodinane is reduced as a result of the reaction to fluoroiodinane (B):



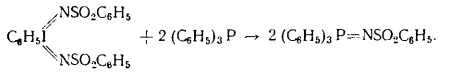
(B)

In contrast to trifluoroperiodinane, its *gem*-dimethyl analogue does not oxidise benzyl- and isopropyl-amines to the corresponding carbonyl compounds, but the reactions with alcohols proceeds with satisfactory yields.[150]

(g) Diiminoiodoarenes

Bis(trifluoromethanesulphonylimino)- [53] and bis(benzene-sulphonylimino)-iodoarenes[54] are colourless or slightly yellowish crystalline substances, melting with decomposition at 100–130 °C, and are sparingly soluble in organic solvents. They are readily hydrolysed by atmospheric moisture to iodoarenes. The absorption due to the characteristic vibrations of the O_2 group are displaced in the IR spectra of these compounds towards lower frequencies compared with trifluoromethanesulphonamide and benzenesulphonamide.[53,54]

The diimino-derivatives of pentavalent iodine can be used in transylidation reactions. For example, the reaction of bis(benzenesulphonylimino)iodobenzene with triphenylphosphine afforded a high yield of *N*-benzenesulphonyltriphenylphosphine imine:[54]

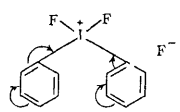


(h) Diaryliodosyl salts

Dioaryliodosyl bromides, chlorides, fluorides, and trifluoroacetates[52] are involatile and infusible crystalline substances which decompose explosively at 160–200 °C. They are readily converted into the corresponding iodonium salts on treatment with iodine, sodium bisulphite, and hydrogen peroxide.[152]

The diaryliodosyl difluoride salts are colourless crystalline substances soluble in methylene chloride, nitromethane, and acetonitrile and insoluble in ether, benzene, and hydrocarbons. In a moist atmosphere, they readily hydrolyse to diaryliodosyl salts.

The ^{19}F NMR spectra of diphenyliodosyl difluorides consist of two signals: $\delta[(C_6H_5)_2\overset{+}{I}F_2] = 22.62$ p.p.m. and $\delta(CF_3COO^-) = -13.13$ p.p.m. for the trifluoroacetate in CH_2Cl_2; $\delta[(C_6H_5)_2\overset{+}{I}F_2] = -24.5$ p.p.m. and $\delta(F^-) = 89.25$ p.p.m. (relative to trifluoromethylbenzene) for the fluoride in nitromethane.[153] As mentioned above,[138] in tetrafluoroiodobenzene all the fluorine atoms are equivalent. The replacement of one fluorine atom in tetrafluoroiodobenzene by the phenyl group led to a compound with non-equivalent fluorine atoms. The presence of two phenyl groups in the diphenyliodosyl trifluoride molecule apparently facilitates the polarisation of the I–F bond and stabilises the ionic structure $(C_6H_5)_2\overset{+}{I}F_2F^-$:[153]

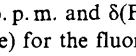
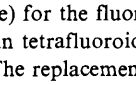


IV. The electronic nature of substituents containing polyvalent iodine

The electronic nature of substituents containing an iodine atom in the trivalent and pentavalent states has been studied systematically.[47] The investigation of the ^{19}F NMR spectra of *meta*- and *para*-fluorobenzenes demonstrated a change in the character of the electronic influence of the substituent on the benzene ring in the series iodine–iodosyl group–iodyl group and on substitution of the oxygen atoms of the iodosyl and iodyl groups by fluorine and chlorine atoms and by acetoxy-, trifluoroacetoxy-, benzenesulphonylimino-, trifluoromethanesulphonylimino-, and bis(fluorosulphonyl)methylide groups. The chemical shifts of the fluorine atoms in the iodine-containing substituent (δ_F, p.p.m.) relative to CCl_3F are presented in Table 1.

The chemical shifts of the fluorine atoms in the *meta*- and *para*-derivatives of fluorobenzene relative to fluorobenzene have been measured in methylene chloride. Taft's $\delta-\sigma$ correlation equations have been used to calculate the inductive constants σ_I and the conjugation constants σ_R of the substituent.[161] The σ constants of substituents containing polyvalent iodine are listed in Table 2. The table shows that substituents containing polyvalent iodine interact with the aromatic ring mainly via the inductive mechanisms. The high values of the constants σ_I are probably caused by the high polarity of the bonds between the iodine atom and fluorine, chlorine, oxygen, and nitrogen atoms.

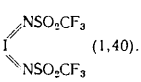
Table 2. The chemical shifts δ of the fluorine atoms in the *meta*- and *para*-derivatives of fluorobenzene relative to fluorobenzene and the σ constants of the iodine-containing substituents.[47]

Substituent	δ_m	δ_p	σ_I	σ_R	σ_m	σ_p
I	2.60	−1.25	0.45	−0.13	0.38	0.32
I=O	3.40	5.10	0.56	0.06	0.59	0.62
$I(OCOCH_3)_2$	5.45	7.13	0.85	0.06	0.88	0.91
IF_2	6.29	5.12	0.97	−0.04	0.95	0.93
$I(OCOCF_3)_2$	6.48	7.98	1.0	0.05	1.03	1.05
$I{=}NSO_2C_6H_5$	6.76	7.54	1.04	0.03	1.05	1.07
ICl_2	7.72	8.46	1.17	0.03	1.18	1.20
$I{=}NSO_2CF_3$	8.18	11.46	1.24	0.11	1.30	1.35
$I{=}C(SO_2F)_2$	8.30	9.14	1.25	0.03	1.26	1.28
$\overset{+}{I}C_6H_5BF_4^-$	8.88	9.85	1.34	0.03	1.35	1.37
IO_2	4.10	7.09	0.66	0.10	0.71	0.76
$I(OCOCF_3)_2$ ‖ O	6.55	8.42	1.01	0.06	1.04	1.07
IF_4	6.87	10.86	1.05	0.14	1.12	1.19
$I(OCOCF_3)_4$	7.46	8.43	1.14	0.03	1.15	1.17
	7.50	8.40	1.14	0.03	1.15	1.17
	8.44	12.33	1.27	0.13	1.33	1.40

The replacement of the oxygen atom in the I=O group by fluorine and chlorine atoms and by trifluoroacetoxy- or benzenesulphonylimino-groups increases appreciably the σ_I constants, while in the case of the trifluoromethanesulphonylimino- or bis(fluorosulphonyl)methylide groups the increase is by a factor greater than two.

It is of interest that the ICl_2 group is more electron-accepting than IF_2, which can be explained by the greater contribution of the polar structure $\overset{+}{I}X^-$ (X = halogen) in the dichloroiodo-derivatives compared with the difluoroiodo-derivatives.

The accumulation of fluorine atoms and the $OCOCF_3$ groups at the iodine atom [the IF_4 and $I(OCOCF_3)_4$ substituents] increases somewhat the inductive effect. In compounds with a pentavalent tricoordinate iodine atom, the difference between the σ_I constants of the trivalent and pentavalent iodine analogues diminishes with increase in the electron-accepting capacity of the second group introduced at the iodine atom (the transition from $NSO_2C_6H_5$ to NSO_2CF_3). The I–N bond in $ArI{=}NSO_2CF_3$ is apparently polarised so much that the introduction of a second NSO_2CF_3 group increases the positive charge on the iodine atom to only a slight extent. This is confirmed by the finding that, on complete charge separation in diaryliodonium tetrafluoroborates, the σ_p constant of the substituent $\overset{+}{I}C_6H_5BF_4$ (1.37) is very close to the σ_p constants of the groups $I{=}NSO_2CF_3$ (1.35) and


(1,40).

It is notable that the inductive effect of the ylide groups having the I–N and I–C bonds [I=NSO_2CF_3 and I=$C(SO_2F)_2$] is very large and almost the same (σ_I = 1.24 and 1.25 respectively), which indicates a high degree of polarisation in the ylide bond in both types of compound.

The effects of the conjugation of the iodine-containing groups are insignificant. All the iodine-containing substituents investigated, except IF_2, are characterised by small positive conjugation constants.

References

1. C Willgerodt *Die Organischen Verbindungen mit Mehrwertigem Iod* (Edited by F Enke), Stuttgart, 1914, 346 pp
2. R B Sandin *Chem. Rev.*, 1943 **32** 249
3. F M Beringer, E M Gindler *Iodine Abstr. Rev.*, 1956, **3**(3) 1
4. D F Banks *Chem. Rev.*, 1966, **66** 243
5. O Neilands *Uch. Zap. Rizhsk. Politekh. Inst.*, 1965, **16** 131
6. G A Olah *Halonium Ions*, Wiley, New York–London–Sydney–Toronto, 1975, 196 pp
7. A Varvoglis *Chem. Soc. Rev.*, 1981, **10** 377
8. G F Koser *The Chemistry of Functional Groups* (Edited by S Patai, Z Rappoport), Wiley, Chichester, 1983. Supplement D, Part 1, p. 721
9. A Varvoglis *Synthesis*, 1984, 709
10. H Saltzman, J C Sharefkin *Organic Synthesis* (Edited by B C McKusick), Wiley, New York–London–Sydney, 1963, Vol. 43, p. 60
11. V V Lyalin, V V Orda, L A Alekseeva, L M Yagupol'skii *Zh. Org. Khim.*, 1970, **6** 329
12. M Schneisser, K Dahmen, P Sartory *Chem. Ber.*, 1967, **100** 1633
13. C S Rondestvedt *J. Am. Chem. Soc.*, 1969, **91** 3054
14. D Naumann, L Deneken, E Renk *J. Fluor. Chem.*, 1975, **5** 509
15. W Carpenter *J. Org. Chem.*, 1966, **31** 2688
16. I I Maletina, V V Orda, N N Aleinikov, et al. *Zh. Org. Khim.*, 1976, **12** 1371
17. M Zupan, A Pollak *J. Fluor. Chem.*, 1976, **7** 445
18. A Gregorcic, M Zupan *Bull. Chem. Soc. Jpn.*, 1977, **50** 517
19. M Zupan, A Pollak *Chem. Commun.*, 1975, 715
20. M Zupan *Collect. Czech. Chem. Commun.*, 1977, **42** 266
21. I Ruppert *J. Fluor. Chem.*, 1980, **15** 173
22. D Naumann, G Rüther *J. Fluor. Chem.*, 1980, **15** 213
23. M Schmeisser, K Dahmen, P Sartori *Chem. Ber.*, 1970, **103** 307
24. M Schmeisser, E Scharf *Angew. Chem.*, 1959, **71** 524
25. J Baumanns, L Deneken, D Naumann, M Schmeisser *J. Fluor. Chem.*, 1973/74, **3** 323
26. D Naumann, L Deneken *J. Fluor., Chem.*, 1975, **5** 443
27. G Oates, J M Winfield *J Fluor. Chem.*, 1974, **4** 235
28. V V Lyalin, V V Orda, L A Alekseeva, L M Yagupol'skii *Zh. Org. Khim.*, 1972, **8** 1019
29. D Naumann, H Feist *J. Fluor., Chem.*, 1980, **15** 541
30. J A Gibson, A F Janzen *Chem. Commun.*, 1973, 739
31. J A Gibson, R K Marat, A F Janzen *Can. J. Chem.*, 1975, **53** 3044
32. A M Forster, A J Downs *Polyhedron*, 1985, **4** 1625
33. S Stavber, M Zupan *Chem. Commun.*, 1983, 563
34. A N Nesmeyanov, I N Lisichkina, A S Kulikov, et al *Dokl. Akad. Nauk SSSR*, 1978, **243** 1463
35. A N Nesmeyanov, A N Vanchikov, I N Lisichikina, et al. *Dokl. Akad. Nauk SSSR*, 1980, **254** 652
36. J A Obaleye, L S Sams *Inorg. Nucl. Chem. Lett.*, 1980, **16** 343
37. J A Obaleye, L C Sams *J. Inorg. Nucl. Chem.*, 1981, **43** 2259
38. H J Frohn, M Giesen *J. Fluor. Chem.*, 1983, **23** 484
39. H J Frohn, M Giesen *J. Fluor. Chem.*, 1984, **24** 9
40. J A Obaleye, L C Sams *J Fluor. Chem.*, 1980, **16** 508
41. J A Obaleye, L C Sams *J. Fluor. Chem.*, 1981, **18** 31
42. J A Obaleye, L C Sams *J. Fluor. Chem.*, 1984, **24** 413
43. N W Alcock, T C Waddington *J. Chem. Soc.*, 1963, 4103
44. E B Merkushev, A N Novikov, S F Makarchenko, et al. *Zh. Org. Khim.*, 1975, **11** 1259
45. S Spyroudis, A Varvoglis *Synthesis*, 1975, 445
46. I I Maletina, V V Orda, L M Yagupol'skii *Zh. Org. Khim.*, 1974, **10** 294
47. A A Mironova, I I Maletina, S V Iksanova, et al. *Zh. Org. Khim.*, 1989, **25** 306
48. L M Yagupol'skii, I I Maletina, N V Kandratenko, V V Orda *Synthesis*, 1977, 574
49. V V Lyalin, V V Orda, L A Alekseeva, L M Yagupol'skii *Zh. Org. Khim.*, 1971, **7** 1473
50. D Naumann, J Baumanns *J. Fluor. Chem.*, 1976, **8** 177
51. Y Yamada, T Yamamoto, M Okawava *Chem. Lett.*, 1975, 361
52. D Mansuy, J-P Mahy, A Dureault, et al. *Chem. Commun.*, 1984, 1161
53. L M Yagupol'skii, V I Popov, N V Pavlenko, et al. *Zh. Org. Khim.*, 1986, **22** 2169
54. I I Maletina, A A Mironova, V V Orda, L M Yagupol'skii *Synthesis*, 1983, 456
55. I I Malteina, A A Mironova, T I Savina, Yu L Yagupol'skii *Zh. Org. Khim.*, 1979, **15** 2416
56. L M Yagupol'skii, A A Mironova, I I Maletina, V V Orda *Zh. Org. Khim.*, 1980, **16** 232
57. T Umemoto, Y Kuriu, H Shuyama, et al. *J. Fluor. Chem.*, 1982, **20** 695
58. A A Mironova, I I Maletina, V V Orda, L M Yagupol'skii *Zh. Org. Khim.*, 1983, **19** 1213
59. T Umemoto, T Nakamura *Chem. Lett.*, 1984, 983
60. A A Mironova, I I Maletina, I V Soloshonok, et al . *Zh. Org. Khim.*, 1988, **24** 593
61. T Umemoto, Y Goton *J. Fluor. Chem.*, 1985, **28** 235
62. T Umemoto *Tetrahedron Lett.*, 1984, **25** 81
63. T Umemoto, Y Kuriu, H Shuyama, et al. *J. Fluor. Chem.*, 1986, **31** 37
64. B S Ehrlich, M Kaplan *J. Chem. Phys.*, 1971, **54** 612
65. H Siebert, M Handrich *Z. Anorg. Allg. Chem.*, 1976, **426** 173
66. E Lehmann, D Naumann, W Stopshinski *Spectrochim. Acta, Part A*, 1975, **31** 1905
67. D Naumann, H H Heinsen, E Lehmann *J. Fluor. Chem.*, 1976, **8** 243
68. W Bockemüller *Chem. Ber.*, 1931, **64** 522
69. J Bornstein, M R Borden, F Nunes, H Tarlin *J. Am. Chem. Soc.*, 1963, **85** 1609
70. A Gregorcic, M Zupan *J. Chem. Soc., Perkin Trans. I*, 1977, 1446
71. D F Shellhamer, R J Conner, R E Richardson, V L Heasley *J. Org. Chem.*, 1984, **49** 5015
72. B Sket, M Supan, P Supet *Tetrahedron*, 1984, **40** 1603
73. T B Patrick, J J Scheibel, W E Hall, J H Lee *J. Org. Chem.*, 1980, **45** 4492
74. T Tsushima, K Kawada, T Tsuji *Tetrahedron Lett.*, 1982, **23** 1165

75. V I Popov, N V Kondratenko *Zh. Obshch. Khim.*, 1976, **46** 2597
76. M Zupan, A Pollak *Tetrahedron Lett.*, 1975, 3525
77. M Zupan, A Pollak *J. Chem. Soc., Perkin Trans. I*, 1976, 1745
78. M Zupan, A Pollak *J. Org. Chem.*, 1976, **41** 2179
79. M Zupan *Synthesis*, 1976, 473
80. S Stavber, M Zupan *J. Fluor. Chem.*, 1978, **12** 307
81. J Gallos, A Varvoglis, N W Alcock *J. Chem. Soc., Perkin Trans. I*, 1985, 757
82. N Fukuyama, H Nishino, K Kurosawa *Bull. Chem. Soc. Jpn.*, 1987, **60** 4363
83. N S Zefirov, V V Zhdankin, Yu V Dan'kov, A F Koz'min *Zh. Org. Khim.*, 1984, **20** 446
84. R T Hembre, C P Scott, J R Norton *J. Org. Chem.*, 1987, **52** 3650
85. W A Sheppard, R W Taft *J. Am. Chem. Soc.*, 1972, **94** 1919
86. J K Gallos, D N Nicolaides *Synthesis*, 1981, 638
87. S Spyroudis, A Varvoglis *Synthesis* 1976, 837
88. A Ohsawa, H Arai, H Igeta, et al. *J. Org. Chem.*, 1979, **44** 3524
89. A S Radhakrishna, M E Parham, R M Riggs, G M London *J. Org. Chem.*, 1979, **44** 1746
90. G M London, A S Radhakrishna, M R Almond, et al., *J. Org. Chem.*, 1984, **49** 4272
91. R N Boutin, G M London *J. Org. Chem.*, 1984, **49** 4277
92. G M London, M E Parham *Tetrahedron Lett.*, 1978, 437
93. M Waki, Y Kitajima, N Izumiya *Synthesis*, 1981, 266
94. E B Merkushev, L G Karpitskaya, G I Novosel'tseva *Dokl. Akad. Nauk SSSR*, 1979, **245** 607
95. E B Merkushev, L G Karpitskaya *Zh. Org. Khim.*, 1983, **19** 887
96. C Szantay, G Blasko, M Barczai-Beke *Tetrahedron Lett.*, 1980, **21** 3509
97. S Spyroudis, A Varvoglis *Chem. Commun.*, 1979, 615
98. S Spyroudis, A Varvoglis *J. Org. Chem.*, 1981, **46** 5231
99. Yu S Shabarov, E V Pisanova, L G Saginova *Zh. Org. Khim.*, 1981, **17** 1338
100. R A Gazzaeva, Yu S Shabarov, L G Saginova *Zh. Org. Khim.*, 1984, **20** 220
101. L G Saginova, O B Bondarenko, R A Gazzaeva, Yu S Shabarov *Zh. Org. Khim.*, 1985, **21** 526
102. J Gallos, A Varvoglis *J. Chem. Soc., Perkin Trans. I*, 1983, 1999
103. N S Zefirov, V V Zhdankin, A S Koz'min *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 1682
104. J D White, G Caravatti, T B Kline, E Edstrom *Tetrahedron*, 1983, **39** 2393
105. N S Zefirov, V V Zhdankin, Yu V Dan'kov, et al. *Zh. Org. Khim.*, 1984, **20** 444
106. N S Zefirov, V V Zhdankin, Yu V Dan'kov, et al. *Tetrahedron Lett.*, 1986, **27** 3971
107. E B Merkushev, N D Simakhina, G M Koveshnikova *Synthesis*, 1980, 486
108. E B Merkushev, N D Yudina *Zh. Org. Khim.*, 1981, **17** 2598
109. E B Merkushev, N D Simakina, M G Grigor'ev *Izv. Akad. Nauk SSSR, Ser . Khim.*, 1980, 2649
110. L G Saginova, O B Bondarenko, Yu S Shabarov, R S Gazzaeva *Zh. Org. Khim.*, 1984, **20** 2124
111. J Gallos, A Varvoglis *J. Chem. Res. (S)*, 1982, 150
112. J Gallos, A Varvoglis *J. Chem. Res. (M)*, 1982, 1649
113. F M Beringer, H E Bachofner, R A Falk, M Leff *J. Am. Chem. Soc.*, 1958, **80** 4279
114. L Hadjiarapoglou, S Spyroudis, A Varvoglis *Synthesis*, 1983, 207
115. M Papadopoulou, A Varvoglis *J. Chem. Res. (S)*, 1983, 66
116. S Spyroudis, A Varvoglis *J. Chem. Soc., Perkin Trans. I*, 1984, 135
117. L M Yagupolskii, I I Maletina, N V Kondratenko, V V Orda *Synthesis*, 1978
118. T Umemoto, Y Kuriu *Tetrahedron Lett.*, 1981, **22** 5197
119. T Umemoto, Y Goton *Bull. Chem. Soc. Jpn.*, 1986, **59** 439
120. T Umemoto, Y Kuriu, H Shuyama *Chem. Lett.*, 1981, 1663
121. T Umemoto, Y Kuriu *Chem. Lett.*, 1982, 65
122. T Umemoto, O Miyano *Bull. Chem. Soc. Jpn.*, 1984, **57** 3361
123. T Umemoto, Y Kuriu, Sh Nakayama *Tetrahedron Lett.*, 1982, **23** 1169
124. T Umemoto, Y Kuriu, Sh Nakayama *Tetrahedron Lett.*, 1982, **23** 4101
125. T Umemoto, Y Kuriu, Sh Nakayama, O Miyano *Tetrahedron Lett.*, 1982, **23** 1471
126. T Umemoto, Y Kuriu, O Miyano *Tetrahedron Lett.*, 1982, **23** 3579
127. T Umemoto, Y Goton *J. Fluor. Chem.*, 1986, **31** 231
128. T Umemoto, Y Goton *Bull. Chem. Soc. Jpn.*, 1987, **60** 3307
129. T Umemoto, Y Goton *Bull. Chem. Soc. Jpn.*, 1987, **60** 3823
130. A P Brestkin, A F Danilov, E S Dmitrieva, et al. *Dokl. Akad. Nauk SSSR*, 1984, **275** 1425
131. C Willgerodt *Ber. Bunsenges. Phys. Chem.*, 1892, **25** 3494
132. H J Lucas, E R Kennedy *Organic Syntheses* (Translated into Russian) (Edited by B A Kazanskii), Inostr. Lit., Moscow, 1952, Vol. 3, p. 261
133. M W Formo, J R Johnson *Organic Syntheses* (Translated into Russian) (Edited by B A Kazanskii), Inostr. Lit., Moscow, 1952, Vol. 3, p. 262
134. J G Sharefkin, H Saltzman *Organic Syntheses* (Edited by B C McKusick), Wiley, New York–London–Sydney, 1963, Vol. 43, p. 65
135. V V Bardin, G G Furin, V G Yakobson *Zh. Org. Khim.*, 1980, **16**
136. A Banerjee, G Ch Banerjee, S Bhattacharya, et al. *J. Indian Chem. Soc.*, 1981, **58** 605
137. R F Weinland, W Stille *Ber. Bunsenges. Phys. Chem.*, 1901, **34** 2631
138. L M Yagupol'skii, V V Lyalin, V V Orda, L A Alekseeva *Zh. Org. Khim.*, 1968, **38** 2813
139. V V Lyalin, G P Syrova, V V Orda, et al. *Zh. Org. Khim.*, 1970, **6** 1420
140. V V Lyalin, Candidate's Thesis in Chemical Sciences, Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev, 112 pp
141. O R Chambers, G Oates, J M Winfield *Chem. Commun.*, 1972, 839
142. J A Berry, G Oates, J M Winfield *J. Chem. Soc., Dalton Trans.*, 1974, 509
143. H J Frohn, M Maurer, W Pahlmann *J. Fluor. Chem.*, 1980, **16** 591
144. H J Frohn *Chem.-Ztg.*, 1984, **108** 146
145. G Oates, J M Winfield *J. Chem. Soc., Dalton Trans.*, 1974, 119
146. M H Habibi, L C Sams *J. Fluor. Chem.*, 1981, **18** 277
147. M H Habibi, L C Sams *J. Fluor. Chem.*, 1982, **21** 287

148. I I Maletina, N V Kondratenko, V V Orda, L M Yagupol'skii *Zh. Org. Khim.*, 1978, **14** 873
149. R L Amey, J C Martin *J. Am. Chem. Soc.*, 1978, **100** 300
150. R L Amey, J C Martin *J. Am. Chem. Soc.*, 1979, **101** 5294
151. I Masson, E Race, F E Pouder *J. Chem. Soc.*, 1935, 1669
152. F M Beringer, P Bodlaender *J. Org. Chem.*, 1968, **33** 2981
153. V V Lyalin, V V Orda, L A Alekseeva, L N Yagupol'skii *Zh. Org. Khim.*, 1972, **8** 210
154. A N Nesmeyanov, G K Semin, V V Saatsadov, et al. *Dokl. Akad. Nauk SSSR*, 1977, **237** 395
155. S Ranganathan, D Ranganathan, S K Singh *Tetrahedron Lett.*, 1985, **26**
156. D Naumann, W Habel *J. Fluor. Chem.*, 1980, **16** 509
157. D Naumann, W Habel *Z. Anorg. Allg. Chem.*, 1981, **482** 139
158. M Ya Turkina, V V Orda, I P Gragerov *Dokl. Akad. Nauk SSSR*, 1974, **216**
159. I I Maletina, Candidate's Thesis in Chemical Sciences, Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev, 1978, 115 pp
160. J A Gustafsson, L Rondahl, J Bergman *Biochemistry* 1979, **18** 865
161. R W Taft, E Price, I I Fox, et al. *J. Am. Chem. Soc.*, 1963, **85** 3146
162. A Haas *Gmelin Handbook of Inorganic Chemistry*, System No. 5, Supp. Vol. 3, Springer-Verlag, Berlin–Heidelberg, 1987, p. 257

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The thermal gas-phase synthesis of heterocyclic compounds with one or several silicon atoms in the ring

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ABSTRACT. The results of studies on the synthesis of organosilicon heterocyclic compounds under the influence of high temperatures in a flow system at atmospheric pressure and in a high vacuum are surveyed. The preparative possibilities of the gas-phase thermal method for the synthesis of new or previously difficult to obtain mono-, bi-, and poly-cyclic compounds with one or several silicon atoms in the ring are examined. The principal aspects of the thermal heterocyclisation processes are described.

Attention is concentrated on the synthesis of heterocycles with functional group substituents at the silicon atom as well as high-temperature reactions with participation of unstable intermediates: silylenes, sila-alkenes, and siladienes.

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I. Introduction

The chemistry of heterocyclic compounds of silicon constitutes at the present time an independent branch of organosilicon chemistry. The number of publications devoted to the method of synthesis and the study of the structure and properties of organosilicon heterocyclic compounds has been steadily increasing. The interest in these compounds is associated both with their practical applications (biological activity, thermal stability, etc.) and with theoretical aspects due to the appearance of new properties in the compounds after the introduction of a silicon atom into the carbon ring and their different behaviour in chemical reactions compared with acyclic organosilicon compounds.

One of the simplest and most effective methods of synthesis of many classes of organosilicon heterocyclic systems, previously impossible to obtain, is the gas-phase thermal method, which consists in the interaction of various silicon-containing and organic compounds at temperatures in the range 300–700 °C in a flow system (the reactor consists of a hollow quartz or metallic tube). It is simple as regards apparatus and in most cases is distinguished by a high selectivity.

The present review is devoted to the discussion of the synthetic possibilities of this method and includes studies published up to the middle of 1987.

Extensive experimental data have now accumulated, which makes it possible to discover the principal fundamental aspects of the high-temperature synthesis of silicon heterocycles. These are primarily the intramolecular thermal cyclisation of organosilicon compounds containing structural fragments necessary for cyclisation in the presence of thermally labile bonds as well as bonds exhibiting an increased reactivity as a consequence of steric interaction with bulky substituents in the α-position in naphthalene and in the *o*-position in benzene or biphenyl. Another aspect vigorously developing recently has been the thermal synthesis of silicon heterocycles with participation of unstable species and compounds: silylenes, sila-alkenes, and siladienes. The sources from which these highly reactive intermediates can be generated in the gas phase as well as acceptors—systems capable of trapping them with formation of thermally stable compounds—have been found. The use of hexachlorodisilane and higher perchloropolysilanes as sources of dichlorosilylene have made it possible to extend greatly the preparative possibilities of the pyrolytic cyclisation method. The high reactivity of the thermally generated dichlorosilylene and the appreciable selectivity of its interaction with specific chemical bonds have made it possible to synthesise specifically various classes of heterocycles with one or several silicon atoms in the ring, whose preparation by other methods was difficult or impossible.

Interesting communications concerning the thermal method for the generation of unstable silicon intermediates in extremely short time intervals (vacuum flash pyrolysis) have appeared comparatively recently. The latest review of these studies was published in 1985.[1] The detection of these species and the study of their properties are mainly of theoretical interest. Nevertheless, despite the increased complexity of the apparatus required for their synthesis, in many cases, the high-temperature reactions of these intermediates can be considered also on the preparative scale—for the synthesis of silicon-containing heterocyclic systems.

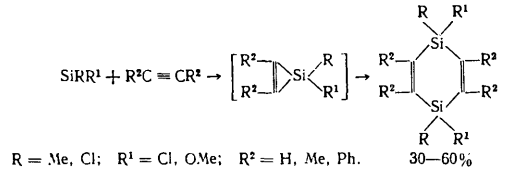
II. Monocyclic compounds

1. Synthesis with participation of silylenes

(a) The addition of silylenes to multiple bonds

The interactions of silylenes with unsaturated compounds must be regarded as some of their most characteristic reactions. Such reactions are of great preparative interest for the synthesis of silicon-containing heterocyclic systems. The most active silylene "trapping agents" are alkynes and conjugated dienes. The most convenient and fairly general method of synthesis of silylenes is the thermolysis of various disilanes. Thus the gas-phase reaction of

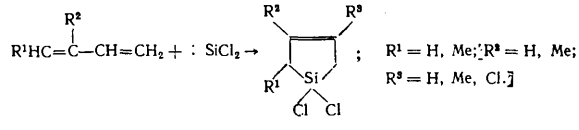
tetrachlorodimethyl-, tetramethoxydimethyl-, and hexachlorodisilanes with acetylene and its derivatives is widely used for the synthesis of disilacyclohexa-2,5-dienes with functional group substituents at the silicon atom:[2–8]



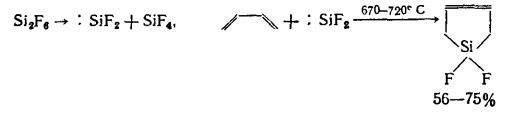
R = Me, Cl; R^1 = Cl, OMe; R^2 = H, Me, Ph. 30—60%

A report of the synthesis of 1,1,4,4-tetramethoxy-1,4-disilacyclohexa-2,5-diene in the copyrolysis of hexamethoxydisilane with acetylene (temperature 370 °C, yield of heterocycle 56%) appeared in 1985.[9] An excellent source from which dimethoxysilylene can be generated, namely hexamethoxydisilane, was proposed in that study. Evidently, the primary step in the thermal interaction is the addition of the corresponding silylene to the triple bond of the alkyne with formation of a silacyclopropene derivative and its subsequent reaction.[2,3,8,10,11]

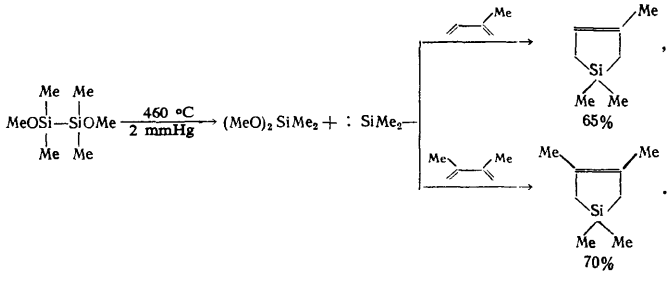
The thermal generation of $:SiCl_2$ from hexachlorodisilane has led to effective ways of synthesising the simplest unsaturated organosilicon heterocycles—derivatives of silacyclopent-3-ene—from conjugated dienes:[2,3,7,8,12–14]



The yields of the heterocycles are almost quantitative (90–95%). A report has recently appeared[15] of the synthesis of 1,1-difluoro-1-silacyclopent-3-ene by the gas-phase pyrolysis of hexafluorodisilane in an excess of buta-1,3-diene:



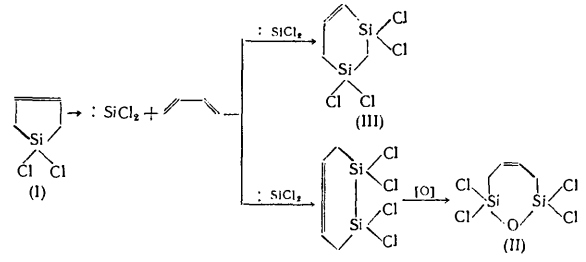
By carrying out the process in a flow system with a reactant contact time of 0.01–0.2 s, it has been possible to capture the highly reactive monomeric $:SiF_2$. The reactions involving the addition of dimethylsilylene, generated thermally from 1,2-dimethoxytetramethyldisilane, to acyclic 1,3-dienes both at atmospheric pressure[10,16] and *in vacuo*[17] also take place readily in the gas phase, for example:



The authors[17] suggest the concerted 1,2-addition of dimethylsilylene to substituted buta-1,3-dienes with subsequent opening of the vinylsilacyclopropane ring.

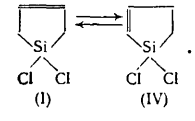
On the other hand, the evidence obtained[2,8,18–20] for the retrodiene thermal decomposition of 1,1-dichloro-1-silacyclopent-3-ene justifies the assumption that the gas-phase interaction of $:SiCl_2$ with buta-1,3-dienes formally corresponds to the Diels–Alder reaction and therefore proceeds via the concerted 1,4-cycloaddition mechanisms.

The ability of 1,1-dichloro-1-silacyclopenta-3-ene (I) to generate $:SiCl_2$ has been used for the preparative high-temperature synthesis of new heterocycles with two silicon atoms in the ring: 1,1,3,3-tetrachloro-1,3-disila-2-oxacyclohept-5-ene (II) and 1,1,3,3-tetrachloro-1,3-disilacyclohex-4-ene (III):[2,8,21]



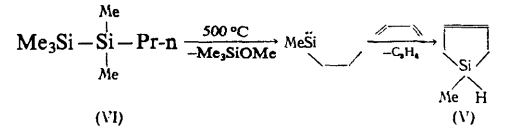
In the pyrolysis of the heterocycle (I) (680 °C), the yields of compounds (II) and (III) and 25 and 45% respectively. When the temperature is reduced, the yields of these compounds diminish and amount to only 7 and 3% at 500 °C. The heterocycle with the Si—Si bond is evidently unstable and is converted into compound (II) under the conditions of the pyrolysis.

A detailed study of the thermal reactions of the heterocycle (I) showed that it is also capable of isomerising to 1,1-dichloro-1-silacyclopent-2-ene (IV) and that this reaction is reversible:[12,22,23]



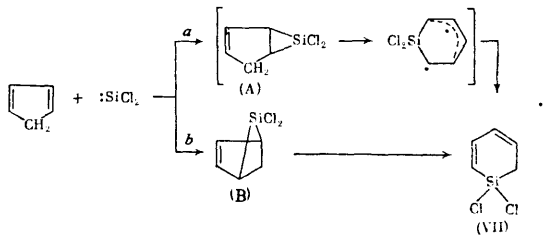
A method has been proposed for the synthesis of compound (IV) by passing its more readily available isomer (I) repeatedly (5–6 times) through a quartz flow reactor at 540 °C.[22]

The generation of dimethylsilylene by the vacuum flash pyrolysis (750 °C, 1 mmHg) of 1,1-dimethyl-1-silacyclopent-3-ene has been reported.[24,25] The isomeric 1-silacyclopent-2-ene is also formed under these conditions. The same workers proposed a new source of $:SiMe_2$ in pyrolytic cyclisation reactions—dimethyl(*cis*-prop-1-enyl)-vinylsilane.[25] The synthesis of the 1-silacyclopent-3-ene hydride derivative (V) via methylpropylsilylene, generated from the disilane (VI), merits special attention:[26]



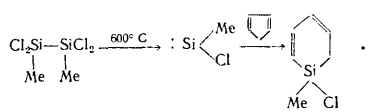
A new aspect of the chemistry of silylenes is the study of their reactions involving addition to cyclic conjugated systems with formation of previously inaccessible monocyclic silicon compounds. Such a reaction was carried out in the thermal interaction of hexachlorodisilane with cyclopentadiene.[2,3,7,13,14,27] The copyrolysis of hexachlorodisilane with cyclopentadiene or its dimer at 500 °C led

to the formation of 1,1-dichloro-1-silacyclohexa-2,4-diene as the main product (yield up to 50%):

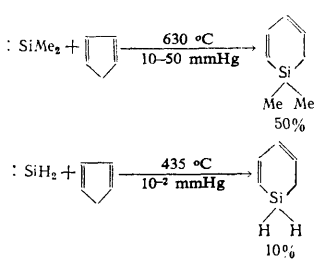


It is notable that the preparation of this compound by other methods is difficult, since these are multistage syntheses leading to low yields of compound (VII) with an admixture of isomers which are difficult to separate.[28] It is possible to put forward two alternative schemes for the expansion of the ring in the five-membered cyclic diene: by adding to it dichlorosilylene in the 1,2-positions (pathway *a*) or in the 1,4-positions (pathway *b*). The first version provides for the formation of the silacyclopropane intermediate (A), which then rearranges to the final reaction product via a biradical. A similar biradical mechanism has been proposed for the thermal rearrangement of the hydrocarbon analogue[29] and also in the study of the gas-phase interaction of dimethylsilylene with cyclopentadiene.[30] However, one cannot rule out also the possibility of the 1,4-cycloaddition of $:SiCl_2$ to cyclopentadiene, which has a fixed cisoid conformation. A fairly pronounced strain in the four-membered ring of the intermediate bicyclic compound (B) is created, as a result of which it can rearrange to the final product—1,1-dichlorosilacyclohexa-2,4-diene. The possibility of the thermal generation of dichlorosilylene in the pyrolysis of compound (VII), demonstrated by the method of "chemical trapping agents",[31] and also the mass-spectrometric study of the pathways leading to the decomposition of this compound[32] confirm to some extent the pathway *b*.

The method described in a number of studies[2,3,7,13,14,27] has been frequently reproduced.[30,33] The preparative possibilities of the method proposed have been greatly expanded by employing both a series of different sources of silylenes as well as certain other organic cyclic compounds with a diene group. 1-Chloro-1-methyl-1-silacyclohexa-2,4-diene has been synthesised in this way:

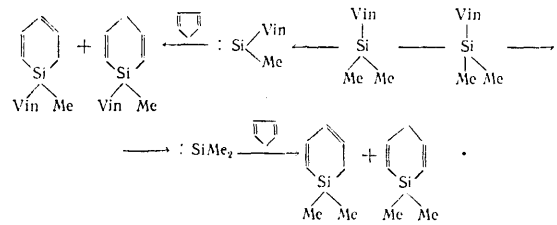


A similar reaction has also been carried out *in vacuo* (650 °C, 10^{-2} mmHg).[35] The interaction of dimethylsilylene and the unsubstituted silylene, generated from the corresponding disilanes, with cyclopentadiene led to the formation of silacyclohexadienes with methyl or hydride substituents at the silicon atom:[30]

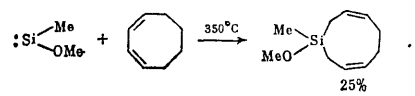


In all cases, except the last, the formation of small amounts of the corresponding derivatives of silacyclohexa-2,5-diene has been noted.

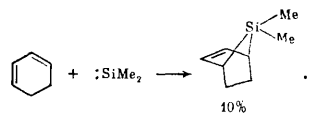
The copyrolysis of 1,1,2,2-tetramethyl-1,2-divinyldisilane $(Me_2VinSi)_2$ with cyclopentadiene has been investigated[35] (650 °C, 10^{-2} mmHg). Four cyclic compounds in approximately equal amounts were detected in the reaction products; non-selective decomposition of the organic disilane via two schemes has been proposed:



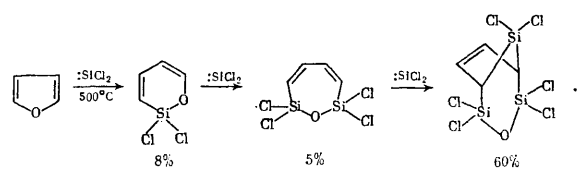
Methoxymethylsilylene adds to cycloocta-1,3-diene with formation of a non-conjugated cyclic diene:[36]



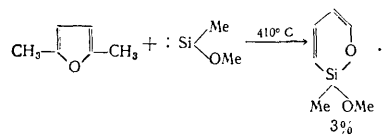
On the other hand, the expansion of the ring of the organic diene is not observed in the interaction of dimethylsilylene with cyclohexa-1,3-diene; only a bicyclic compound is formed in a low yield:[30]



The interaction of dichlorosilylene with furan takes place in a more complex manner. An oxygen-containing analogue of silacyclohexa-2,4-diene, namely 1,1-dichloro-2-oxa-1-silacyclohexa-3,5-diene, was isolated from the reaction mixture in a very low yield.[2,3,7,13,14] The principal product of this reaction is a bicyclic compound with three dichlorosilylene fragments:

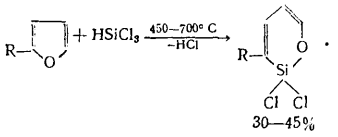


The pyrolytic interaction of methoxymethylsilylene with 2,5-dimethylfuran also does not lead to the specific formation of the six-membered diene system with the Si—O fragment. The yield of the heterocycle does not exceed 3%:[37]



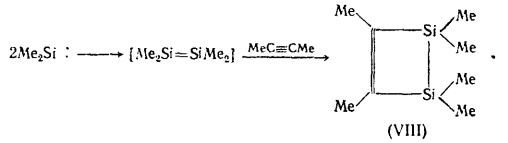
Heterocycles of a similar type are formed in much higher yields in the pyrolytic interaction of furan and its α-substituted derivatives with trichlorosilane. The method proposed makes it possible to obtain derivatives of 2-oxa-1-silacyclohexa-3,5-diene with functional

group substituents at the silicon atom from readily available reactants:[8,38–40]

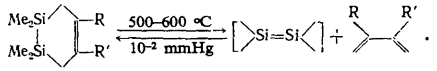


(b) Disilenes. The isomerisation of disilenes to silylsilylenes

In a study of the gas-phase reaction of dimethylsilylene, generated from dimethoxy-tetramethyldisilane, with dimethylacetylene in 1973, a new heterocyclic compound was isolated—permethyldisilacyclobutene (VIII):[41]

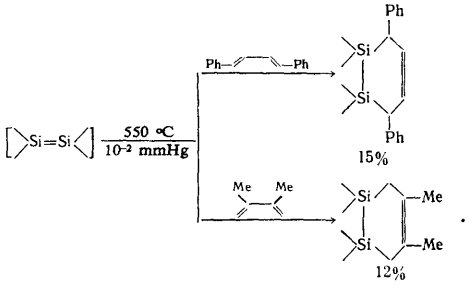


Several schemes for the formation of compound (VIII) have been proposed; one of them involves a stage in which :$SiMe_2$ dimerises to disilene—an unstable intermediate with π-bonded silicon atoms.[10,11] Reaction involving the [6 → 4 + 2]cyclo-elimination of tetramethyldisilene in the extensive gas-phase vacuum pyrolysis of 1,2-disilacyclohex-4-ene has been proposed recently:[42]

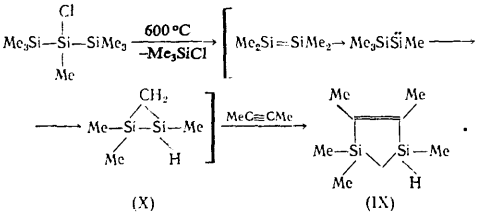


R, R′ = H, Me.

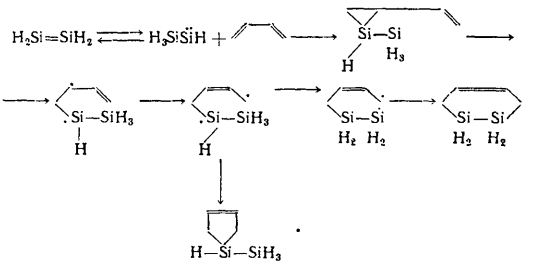
The pyrolysis of this compound in the presence of "trapping agents" made it possible to extend the set of heterocycles with the structure indicated above:



A novel method of synthesis of unsaturated heterocyclic systems with one or two silicon atoms in the ring involving disilenes has been described.[10,11,43,44] The proposed schemes for the preparation of these heterocycles reflect a specific property of disilenes—their ability to isomerise to silylsilylenes during pyrolysis. Thus 1,1,2,3,4-pentamethyl-1,3-disilacyclopentene (IX) has been synthesied by the cothermolysis of various sources of tetramethyldisilene, namely 7,7,8,8-tetramethyl-1-phenyl-2,3-benzo-7,8-disilabicyclo[2.2.2]octa-2,5-diene[10,11] and 2-chloroheptamethyltrisilane,[43] in the presence of dimethylacetylene in 25–28% yield. The authors regard the heterocycle (IX) as the formal product of the insertion of an alkyne in the Si–Si bond of the intermediate disilacyclopropane (X). The isomerisation of tetramethyldisilene to methyl(trimethylsilyl)silylene is postulated under these conditions:[43]

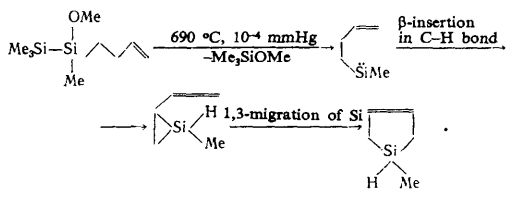


Heterocyclic compounds with endocyclic and exocyclic Si–Si bonds have been obtained in proportions of 1 : 1 by the thermal interaction of butadiene with trisilane, which is apparently capable of generating during pyrolysis not only :SiH_2 but also the product of its recombination with subsequent isomerisation to silylsilylene:[44]



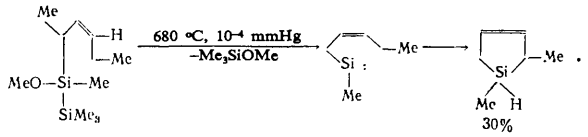
(c) Intramolecular reactions of silylenes

A new apsect of the high-temperature chemistry of organic silylenes, associated with the study of their intramolecular reactions, has begun to develop in the last few years. A method has been proposed for the intramolecular trapping of silylenes, the idea of which consists in the fact that the role of the chemical trapping agent is assumed by the very source from which the silylene is generated. In order to limit the contribution of intermolecular reactions and secondary processes in the generation of such silylenes, they are investigated in a high vacuum. Some of the reactions of this kind can be regarded as methods of synthesis of unsaturated silicon-containing heterocyclic structures. Thus it has been established[45] that 3-butenylmethylsilylene, thermally generated from 1-(3-butenyl)-1-methoxytetramethyldisilane, cyclises to 1-methyl-1-silacyclopent-3-ene in 56% yield:

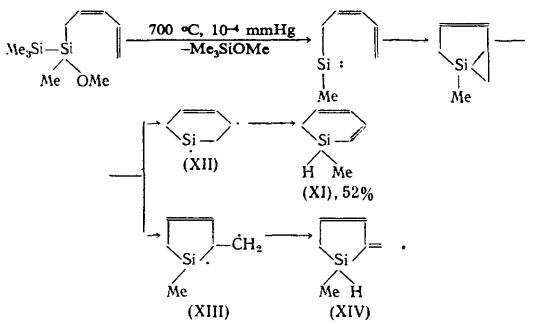


The same heterocycle has been obtained in a satisfactory yield also from another source of 3-butenylmethylsilylene—butenyldichloromethylsilane in its interaction with alkali metal atoms (K/Na) in the gas phase (flow system, temperature 300–340 °C, pressure

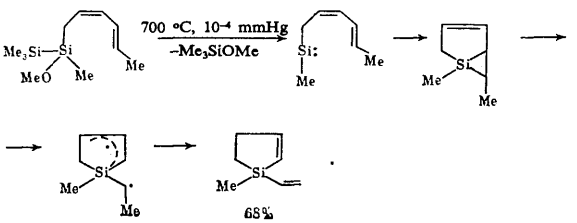
10^{-1} mmHg, K/Na = 7/1).[46] The intramolecular reaction of another alkenylsilane, namely methyl-4-(2-pentenyl)silylene, leads to the formation of 1,2-dimethyl-1-silacyclopent-3-ene:[45]



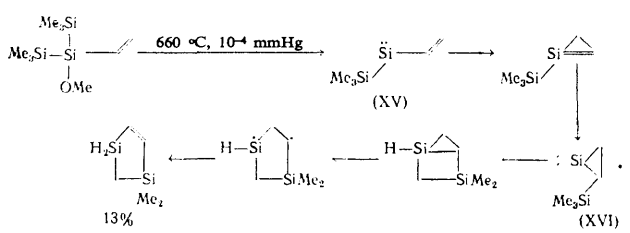
A six-membered heterocycle with a diene group—1-methyl-1-silacyclohexa-2,4-diene (XI)—is the main product of the intramolecular reactions of methyl-5-(penta-1,3-dienyl)silylene.[45] The latter undergoes intramolecular π-addition to the terminal double bond with the subsequent formation of the biradicals (XII) and (XIII), whose further reactions lead to the final products (XI) and (XIV). 2-Methylene-1-methylsilacyclopentene (XIV) has been isolated in 13% yield:



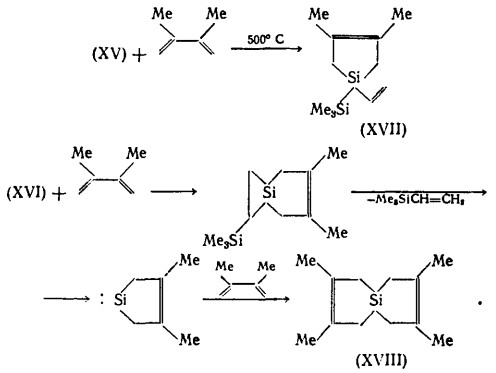
The pyrolysis of the methyl-substituted hexadienyldisilane can be regarded as a thermal method of synthesis of 1-methyl-1-vinyl-1-silacyclopent-2-ene:[45]



A very interesting vinylsilylene intramolecular rearrangement has been observed in the vacuum pyrolysis of 2-methoxy-2-vinylhexamethyltrisilane.[47] The hypothesis of the possible existence of silacyclopropanylidene as an intermediate was proposed for the first time and a scheme for the preparation of 1,1-dimethyl-1,3-disilacyclopent-4-ene with its participation was put forward:

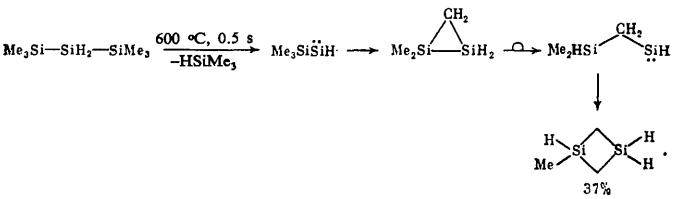


The existence of the intermediates (XV) and (XVI) has been confirmed by the reaction of the initial trisilane with dimethylbutadiene, whereupon also the new heterocyclic systems (XVII) and (XVIII) were obtained:



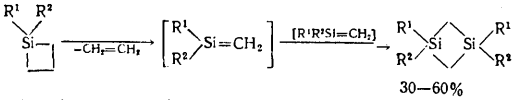
With increase in the excess of dimethylbutadiene, the yield of the spiro-product (XVIII) also increases. It amounts to 20 and 44% for the diene:trisilane ratios of 3:1 and 8:1 respectively. The yield of the heterocycle (XVII) does not exceed 8% in both cases.

An interesting new intramolecular thermal rearrangement of α-silylsilylenes, discovered recently[48] in the pyrolysis of 1,1,1,3,3,3-hexamethyltrisilane, can be regarded as a method of synthesis of 1-methyl-1,3-disilacyclobutane:



2. Synthesis with participation of silaalkenes

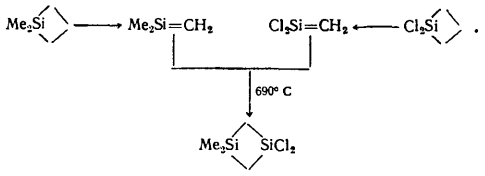
Systematic study of the processes involved in the pyrolysis of monosilacyclobutanes with various substituents at the silicon atom has led to the discovery of an interesting highly selective thermal [4 → 2 + 2]cycloelimination reaction, which proceeds with formation of disilacyclobutanes.[49–51] A unimolecular mechanism of the decomposition of the initial cyclic sila-compounds to ethylene and an unstable intermediate with an unsaturated bond at the silicon atom—silaalkene (silene)—was established. Stabilisation of the silaalkene by cyclodimerisation leads to the formation of disilacyclobutanes:[51–53]



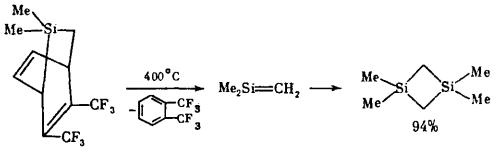
$R^1 = R^2$ = Me, Cl; R^1 = Me, R^2 = Cl; R^1 = Me, R^2 = CH=CH$_2$.

The reaction takes place in an inert gas atmosphere or at reduced pressure in flow reactors (a hollow tube or a tube filled with a heat exchanger) or in static reactors (quartz bulb). In the general case, the pyrolysis of monosilacyclobutanes is a relatively simple and convenient method of synthesis of 1,3-disilacyclobutanes, especially those whose synthesis by other methods is difficult. In the chemistry of organosilicon compounds, this method has been frequently used for preparative purposes, for example, for the synthesis of tetrachloro-1,3-disilacyclobutanes[50,51] and also its

derivatives with mixed substituents at the silicon atom,[54] which are difficult to obtain:

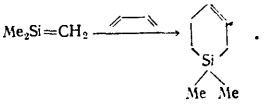


Another highly selective method for the synthesis of tetramethyl-1,3-disilacyclobutane, in which dimethylsilene is generated by the pyrolysis of 7,7-dimethyl-2,3-bis(trifluoromethyl)-7-silabicyclo-[2.2.2]octa-2,5-diene, has been proposed:[55]

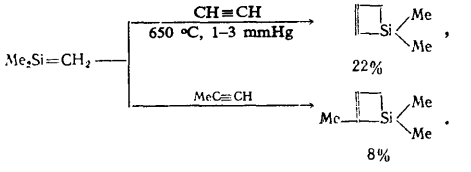


A high yield of the target product was obtained only on thermolysis of the initial compound in a stream of cyclohexane. In the absence of the carrier gas, the yield of the heterocycle was only 4%.

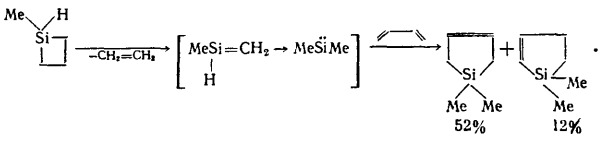
The application of the chemical trapping agent method made it possible to use the properties of silaalkenes as excellent dienophiles for the synthesis of silicon-containing unsaturated heterocycles. The pyrolysis of dimethylsilacyclobutane in the presence of a threefold excess of butadiene afforded 1,1-dimethyl-1-silacyclohex-3-ene in 65% yield. Under these reaction conditions, the formation of tetramethyldisilacyclobutane was fully suppressed:[51]



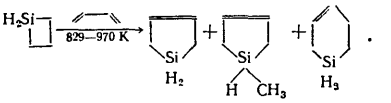
When the same source was used to generate the dimethylsilaalkene, the derivatives of silacyclobutene were isolated in the reaction with alkynes:[56]



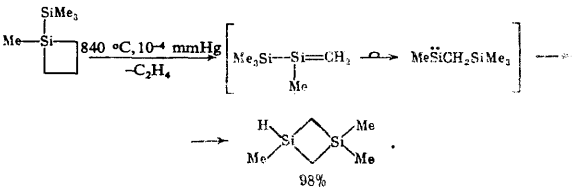
Yet another reaction of silaalkenes, namely their thermally induced isomerisation to silylenes, proved extremely useful as regards synthesis. Thus a study of the copyrolysis of 1-methyl-1-silacyclobutane with butadiene established that the main reaction product is 1,1-dimethylsilacyclopentene (a mixture of isomers), which enabled the authors to propose a scheme for their formation via the isomerisation of intermediates:[57,58]



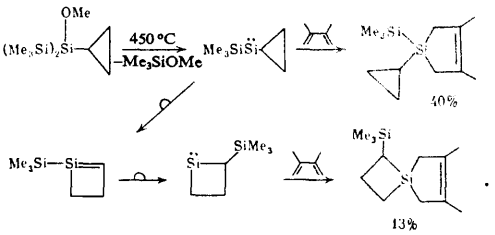
In a study of the pyrolysis of silacyclobutane in the presence of a chemical "trapping agent" for the intermediates in a high vacuum flow system, three heterocyclic compounds were identified—the products of the reactions of silylene, methylsilylene, and silaalkene with butadiene:[59]



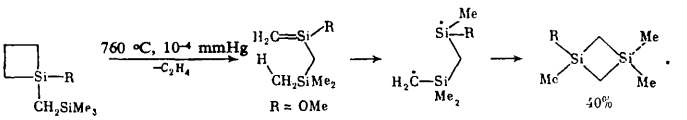
The quantitative formation of 1,1,3-trimethyl-1,3-disilacyclobutane from 1-methyl-1-(trimethylsilyl)-1-silacyclobutane under the conditions of vacuum pulse pyrolysis can also be treated as a process proceeding via the silene–silylene rearrangement:[60]



It is striking that the copyrolysis of 2-cyclopropyl-2-methoxyhexamethyltrisilane in the presence of a sixfold excess of 2,3-dimethylbutadiene led to the main reaction product (a substituted silacyclopentene) via the usual "silylene" scheme. On the other hand, the authors attribute the formation of the spiro-product to a complex silylene–silene–silylene rearrangement illustrated schematically below:[61]



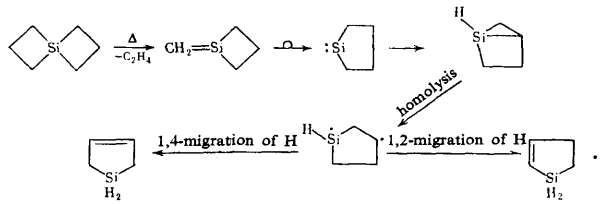
Yet another new rearrangement of silene has been recently proposed[62] in relation to the thermal reactions of certain silyl derivatives of silacyclobutane.[62] Methyl-substituted 1,3-disilacyclobutanes with the methoxy-group at the silicon atom have been obtained on the basis of this rearrangement:



The process is concluded by the ejection of ethylene from the initial compound with formation of an intermediate silene, the subsequent 1,5-shift of a hydrogen atom in it, and subsequent recombination of the 1,4-radical.

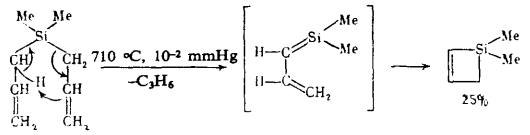
The thermal decomposition *in vacuo* of silaspiro[3,3]heptane is also of theoretical interest.[62,63] The principal products of this reaction are 1-silacyclopentenes. It may be that the primary stage of the process is the formation of a silacyclic silene with its

subsequent rearrangement to a silylene, whose further reactions are presented in the scheme below:

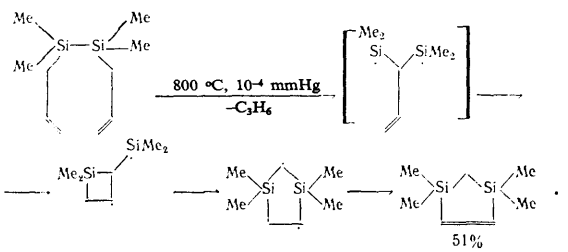


3. Synthesis with participation of siladienes

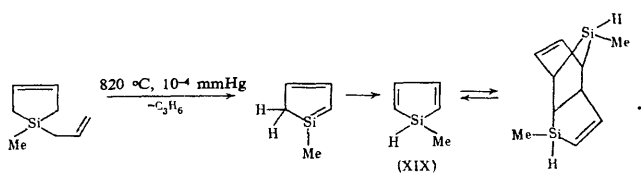
A simple single-stage method of synthesis of 1,1-dimethyl-1-silacyclobutene under the conditions of the vacuum pyrolysis of diallyldimethylsilane was proposed in 1978.[64] The authors put forward a novel scheme for the formation of the heterocycle involving the generation of an unstable compound with an unsaturated bond involving the silicon atom and a diene group (1-silabuta-1,3-diene) in the retroene elimination of propene from the initial compound with subsequent cyclisation of the intermediate:



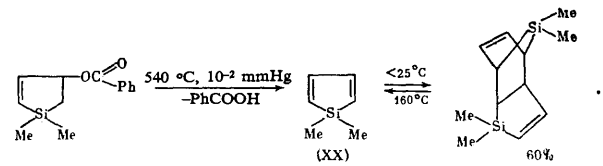
Later a similar scheme was widely used[65–69] in novel syntheses of silicon-containing heterocycles, including monocyclic compounds.[65–67] Thus the pyrolysis of 1,2-diallyl-1,1,2,2-tetramethyl-1,2-disilane yielded 1,1,3,3-tetramethyl-1,3-disilacyclopentene:[65]



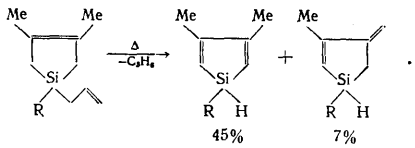
A pathway leading to the synthesis of methyl-1-silacyclopenta-2,4-diene (XIX) in the vacuum pyrolysis of 1-allyl-1-methyl-1-silacyclopent-3-ene has been put forward:[66,67]



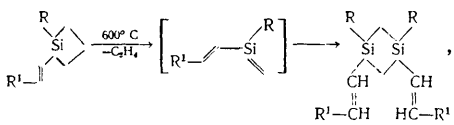
The heterocycle (XIX) was not isolated in a pure form, but its dimer was obtained in 74% yield. The thermolysis of the dimer at 150 °C leads to the formation of compound (XIX), which produces an adduct with maleic anhydride. 1,1-Dimethyl-1-silacyclopentadiene (XX) was synthesised by the vacuum pyrolysis of 4-benzoyloxy-1,1-dimethyl-1-silacyclopent-2-ene:[70]



In the absence of a trapping agent, compound (XX) dimerises at room temperature but can be regenerated on thermolysis of the dimer. In 1986 a group of French investigators[71] succeeded in obtaining the first stable *C*-methyl-substituted 1-silacyclopentadiene containing a Si–H bond:

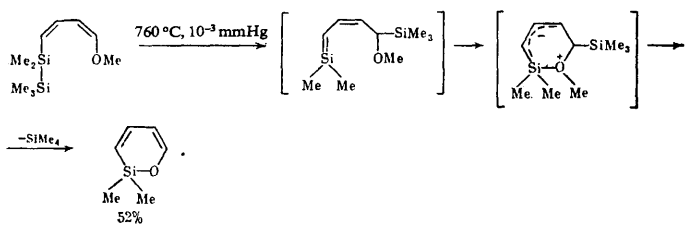


Examples of the thermal transformations of certain silacyclobutanes vinyl-substituted at the silicon atom, proceeding via a hetero-1,3-diene with formation of divinyldisilacyclobutanes, are also known:[72]

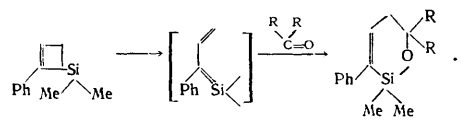


R = Me, R¹ = H; R = Me, R¹ = Ph; R = R¹ = Me; R = Ph, R¹ = H.

The thermal synthesis of certain oxygen-containing silicon heterocycles with participation of siladienes also proved to be possible. An interesting version of the synthesis of 2,2-dimethyl-1-oxa-2-silacyclohexadiene has been described.[73] The scheme for the vacuum pyrolysis of the pentamethyldisilane derivative of buta-1,3-diene includes the generation of a sildadiene intermediate with subsequent elimination of tetramethylsilane:



The copyrolysis of 1,1-dimethyl-2-phenyl-1-silacyclobut-2-ene with acetone or formaldehyde in the gas phase also leads to the formation of heterocycles with the Si–O fragment.[74] The authors suggest the intermediate formation of the siladiene intermediate (XXI):

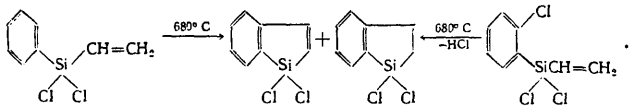


R = Me, 38%; R = H, 35%.

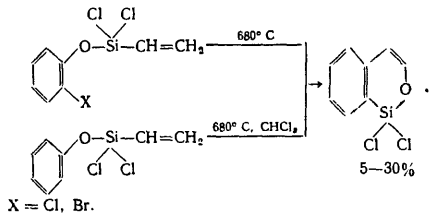
III. Bicyclic compounds

1. Bicyclic compounds with one silicon atom in the ring

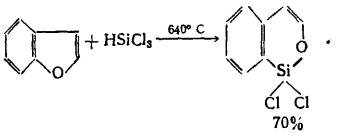
The thermal method proved to be extremely fruitful in the synthesis of bicyclic heterocyclic systems with silicon atoms in the ring. 1,1-Dichloro-1-silaindene was synthesised in a low yield for the first time, simultaneously with 1,1-dichloro-1-silaindan, by the intramolecular thermal cyclisation of dichlorophenylvinylsilane:[8,14,75]



The formation of heterocycles can be explained by the successive occurrence of two stages: the intramolecular thermal alkylation of the initial compound to a saturated heterocycle—1,1-dichloro-1-silaindan—and its subsequent thermal dehydrogenation. The intramolecular dihydrochlorination of dichloro(*o*-chlorophenyl)-vinylsilane also proceeds similarly.[8,75] The pyrolysis of dichlorophenylvinylsilane in the presence of halogenohydrocarbons (chloroform, methylene chloride, chloroethylenes, and hexachloroethane) resulted in an increase in the yield of 1,1-dichloro-1-silaindene to 30% and there was an appreciable rise in the process selectivity—the saturated analogue was not detected and in addition the temperature of the reaction zone was reduced to 520–550 °C.[8,76] The copyrolysis of dichloro(*o*-chlorophenyl)vinylsilane in the presence of another initiator, namely hexachlorodisilane, led to a similar positive result.[8] Using the same principle of pyrolytic synthesis as in the preparation of 1,1-dichloro-1-silaindene, it is possible to cyclise also a series of organosilicon compounds containing the Si–O fragment:

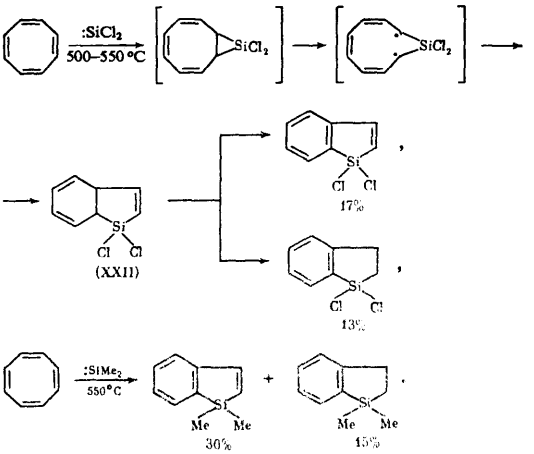


1,1-Dichloro-2-oxa-1-sila-1,2-dihydronaphthalene can be obtained also by the thermal expansion of the benzofuran ring in the presence of trichlorosilane:[8,38–40]

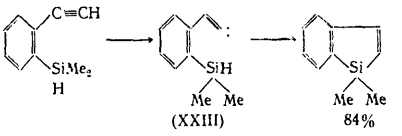


The high yield of the target compound and the ready availability of the starting material make it possible to regard this reaction as a preparative method of synthesis of oxasiladihydronaphthalene.

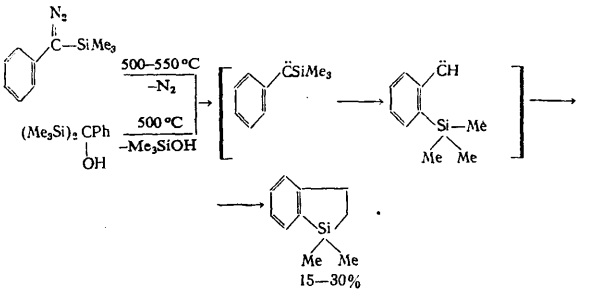
Another method of synthesis of the heterocyclic 1-silaindene and 1-silaindan structures involves the pyrolytic interaction of cyclooctatetraene with hexachlorodisilane[2,8,14,78] and 1,2-dimethoxy-1,1,2,2-tetramethyldisilane,[79] which are sources of dichloro- and dimethyl-silylenes in the gas phase. Tentatively, the 1,2-adduct isomerises to the heterocycle (XXII), which undergoes aromatisation at high temperatures:



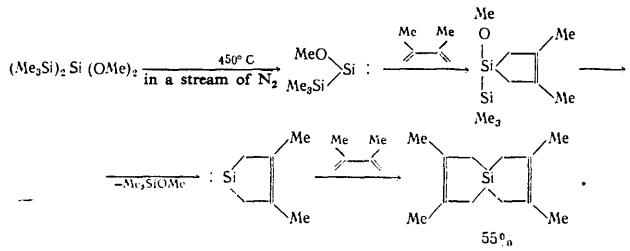
Finally, the specific properties of certain phenylsilylcarbenes, formed in the pyrolytic process from a series of phenyl-substituted organosilicon compounds, have also been used[80–83] for the synthesis of 1,1-dimethyl derivatives of silaindene and silaindan. The recently described study[80] of the vacuum pyrolysis of *o*-dimethylsilylphenylacetylene is novel in this sense. The scheme for the synthesis of 1,1-dimethyl-1-silaindene in this reaction, put forward by the authors, includes the thermally induced acetylene–vinylidene rearrangement of the initial compound to the carbene (XXIII) with the subsequent insertion of the resulting intermediate in a Si–H bond. The high yield of the heterocycle merits special attention:



Well argued evidence for the formation of 1,1-dimethyl-1-silaindan via the intramolecular reactions of phenyltrimethylsilylcarbene has been published in a series of communications.[81–83] The sources from which this α-silylcarbene was generated are phenyltrimethylsilyldiazomethane[81,82] and phenyl-1,1-bis(trimethylsilyl)methanol:[83]



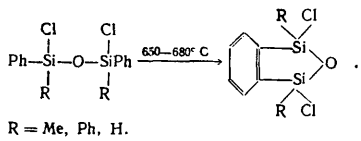
The copyrolysis of 2,2-dimethoxyhexamethyltrisilane in the presence of an excess of dimethylbuta-1,3-diene in accordance with the scheme[84]



may serve as a preparative method of synthesis of 5-silaspiro[4,4]nona-2,7-diene.[84]

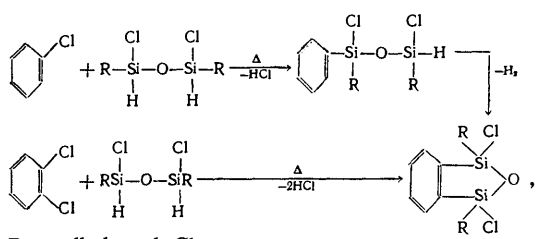
2. Bicyclic compounds with two silicon atoms in the ring

The study of the pyrolytic reactions of various 1,3-diphenyldisiloxanes substituted at a silicon atom has led to the discovery of a new intramolecular cyclisation reaction with elimination of a benzene molecule:[85–87]



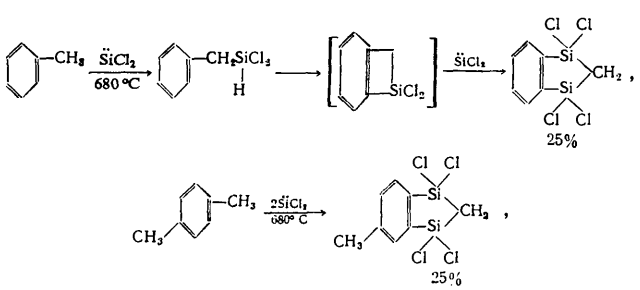
R = Me, Ph, H.

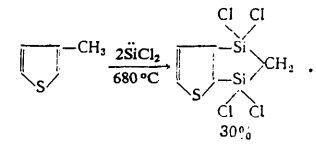
Representatives of a new class of silicon heterocycles—derivatives of 2-oxa-1,3-disilaindan—have been obtained in this reaction in 20% yield. The recovery of the initial disiloxanes amounts to 50%. Heterocycles of a similar kind are also formed via a two-stage scheme—the gas-phase cocondensation of chlorobenzene or *o*-dichlorobenzene with organodihydrodisiloxanes and the subsequent intramolecular cyclisation of the hydrodisiloxane formed:[87,88]



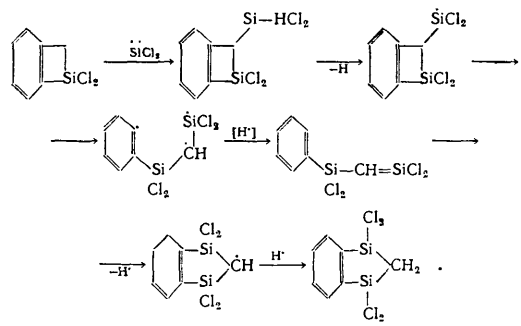
R = alkyl, aryl, Cl.

The formation of heterocyclic structures with the disilmethylene group proved possible in the thermal interaction of a series of methyl-substituted aromatic hydrocarbons with a source of dichlorosilylene such as hexachlorodisilane:[2,3,8,14,89–91]



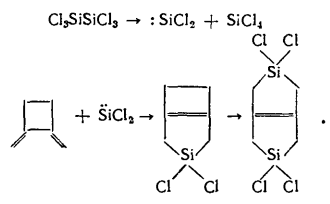


Compounds with a Si—Si bond have not been detected. It may be that conditions for the cyclisation of the primary product of the insertion of $:SiCl_2$ into benzosilacyclobutene are achieved in the first place in this reaction. The next stage represents formally the insertion of $:SiCl_2$ in the $C_{ar}-C_{alk}$ bond of the strained four-membered ring. Bearing in mind the available literature data concerning the insertion of carbenes in the benzyl carbon—hydrogen bond,[92] presumably here too the same type of insertion of the carbene analogue takes place with subsequent elimination of the silyl hydrogen atom. Subsequently, the weakened $C_{ar}-C_{alk}$ bond in the molecule of the strained silacyclobutene is ruptured and the resulting structure undergoes intramolecular addition to the double bond:



The formation of 1,1,3,3-tetrachloro-1,3-disilaindan in the reaction of benzyldichlorosilane with hexachlorodisilane under the conditions investigated has been confirmed experimentally.[91]

Yet another pathway leading to the formation of heterocyclic structures with two silicon atoms has been described.[93,94] The use of 1,2-dimethylenecyclobutane as a dichlorosilylene acceptor has made it possible to synthesise a new unsaturated heterocycle—3,3,7,7-tetrachloro-3,7-disilabicyclo[3.3.0]oct-1(5)-ene:

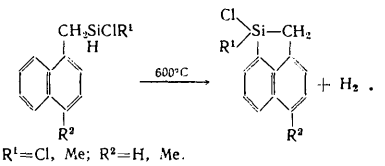


High selectivity of the reaction suggests that yet another carbenoid species is inserted immediately in the $C_{alk}-C_{alk}$ bond of the strained cyclobutene ring of the intermediate heterocycle—the primary product of the addition of $:SiCl_2$ to the conjugated system of double bonds of the initial compound.

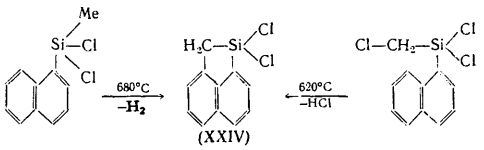
IV. Tricyclic and polycyclic silicon compounds

1. Homolytic *peri*-cyclisation reactions of naphthalene derivatives

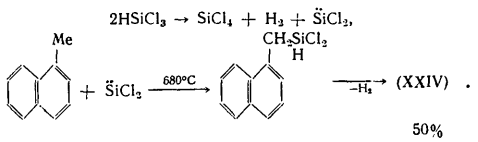
The increased reactivity of the *peri*-hydrogen atom in α-substituted naphthalenes containing the structural fragment necessary for cyclisation, which is induced by its steric interaction with the bulky substituents in the α-position, has made it possible to achieve the specific synthesis of many new classes of tricyclic and polycyclic systems with one or two silicon atoms in the ring, in which there are functional group substituents at the silicon atoms. This principle was first used to obtain a new tricyclic structure—1,1-dichloro-1-silaacenaphthene (XXIV) and its derivatives:[8,14,95-99]



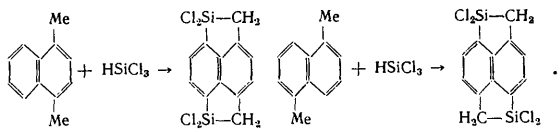
It has been established in a series of studies[8,14,97] that intramolecular cyclisation with formation of 1,1-dichloro-1-silaacenaphthene can take place not only at a Si—H bond but also at C—H and C—Cl bonds but with a lower yield of the heterocyclic compound:



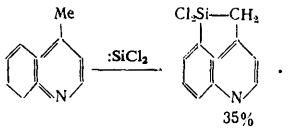
An unusual thermal cyclisation reaction was discovered in 1963 [100] when α-methylnaphthalene was allowed to interact with trichlorosilane, which also led to the synthesis of 1,1-dichloro-1-silaacenaphthene. It was established that this reaction proceeds via the insertion of $:SiCl_2$, formed in the pyrolysis of trichlorosilane,[2,101] in a C—H bond of the methyl substituent with subsequent intramolecular dehydrocyclisation of α-dichlorosilylmethylnaphthalene:[2,8,96,101]



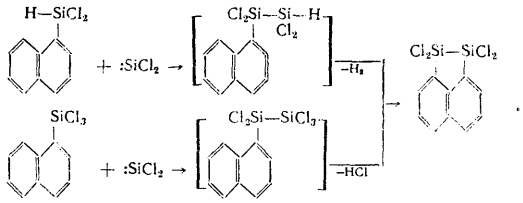
The appreciable selectivity of this interaction, the high yield of compound (XXIV), and the availability of the initial reactants stimulated the development of the method involving the high-temperature *peri*-cyclisation of naphthalene derivatives in the presence of trichlorosilane. The extension of this reaction to 1,4- and 1,5-dimethylnaphthalenes has made it possible to synthesise tetracyclic compounds with two silicon-containing bridges—the corresponding tetrachlorodisilapyracenes:[14,96,98]



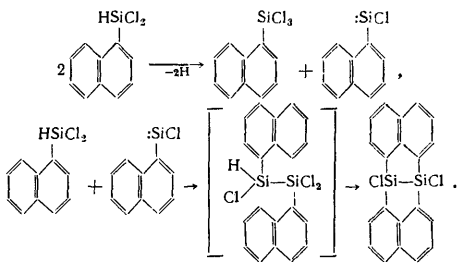
The thermal interaction of 4-methylquinoline with trichlorosilane led to the synthesis of a heterocycle containing silicon and nitrogen atoms in the cyclic system—1,1-dichloro-1-sila-5-azaacenaphthene:[102,103]



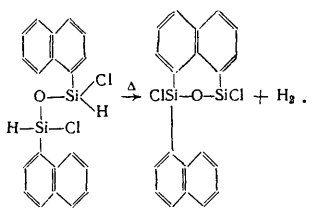
The preparation of the tricyclic 1,1,2,2-tetrachloro-1,2-disila-acenaphthene system, with an extremely stable endocyclic Si—Si bond, is synthetically extremely interesting. This compound was synthesised by the gas-phase copyrolysis of dichloro-α-naphthylsilane or trichloro-α-naphthylsilane in a mixture with trichlorosilane.[9,14,95,101] In this case, the reaction proceeds via the insertion of dichlorosilylene in a Si—H bond and even a Si—Cl bond in the corresponding chloro-α-naphthylsilanes:



The gas-phase pyrolysis of dichloro-α-naphthylsilane in the absence of trichlorosilane led to the formation of yet another heterocyclic system with an endocyclic Si—Si bond, which has no hydrocarbon analogues, namely dichlorobis(1,8-naphthylene)disilane.[2,14,104,105] The "silylene" mechanism of the formation of this heterocycle, postulating the insertion of the intermediate chloro-α-naphthylsilylene in a Si—H bond of the initial compound, is the most probable:

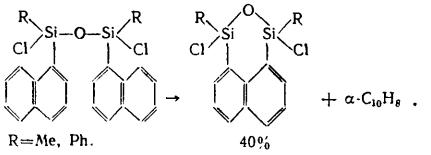


The possibility of the *peri*-cyclisation of the intermediate insertion product has been confirmed by the synthesis of 1,3-dichlorobis-(1,8-naphthylene)disiloxane by the intramolecular dehydrogenation of the corresponding symmetrical disiloxane:[2,14,87,106]

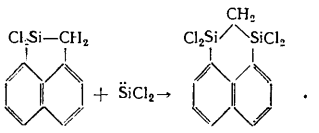


Other thermal reactions of symmetrical disiloxanes with α-naphthyl groups are also of preparative interest. The gas-phase pyrolysis of these compounds eliminates naphthalene and leads to the formation

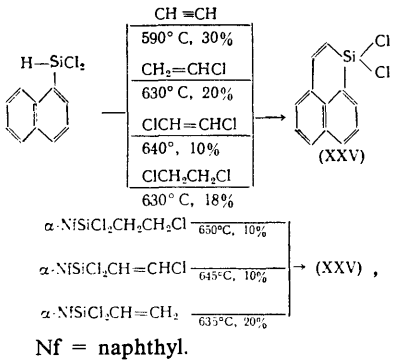
of representatives of a new class of silicon heterocycles—the organochloro-derivatives of 2-oxa-1,3-disilaphenalan:[2,14,87,107]



Similar disilaphenalan structures, where the silicon atoms are linked up to form a six-membered heterocycle via a methylene bridge, have been obtained by the thermal interaction of 1,1-dichloro-1-sila-acenaphthene with trichlorosilane. Formally, the formation of 1,1,3,3-tetrachloro-1,3-disilaphenalan can be represented as the insertion of :$SiCl_2$ in the $C_{ar}-C$ bond:[2,14,101]

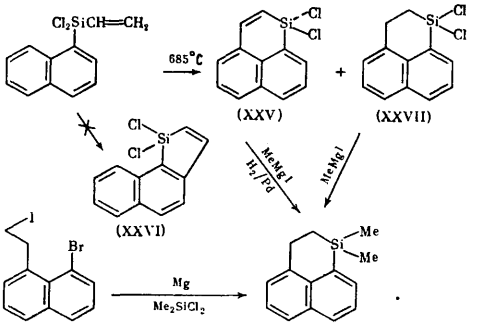


The mobility of the hydrogen atom in the *peri*-position in α-substituted naphthalenes has made it possible to achieve also a series of other thermal reactions designed to obtain a new tricyclic 1,1-dichloro-1-silaphenalene system (XXV), where the silicon atom is incorporated in an unsaturated six-membered ring.[95,108,109] The common features of these reactions are the presence in the initial reactants of, on the one hand, the dichloro-α-naphthylsilyl group and, on the other, of a two carbon atom fragment necessary for the formation of a bridge between the silicon atoms and the C(8) carbon atom of naphthalene:

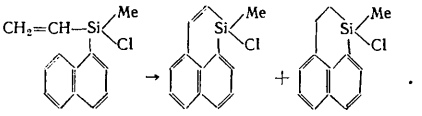


Nf = naphthyl.

A detailed study of the pyrolysis products of dichloro(α-naphthyl)-vinylsilane was undertaken somewhat later.[110] The authors doubted the validity of the postulated structure of compound (XXIV) as a *peri*-cyclisation product. On the basis of literature and their own data indicating the impossibility of obtaining a stable hydrocarbon analogue—the α-halogenophenalene—it was suggested that 1,1-dichloro-1-silaphenalene is thermally unstable and that its structural isomer—the heterocycle (XXVI)—is therefore formed in the pyrolytic reaction investigated. However, two heterocycles, (XXV) and (XXVII), were isolated in the pyrolysis of dichloro-(α-naphthyl)vinylsilane. Their structures were confirmed by the specific synthesis of 1,1-dimethylsilaphenalan:

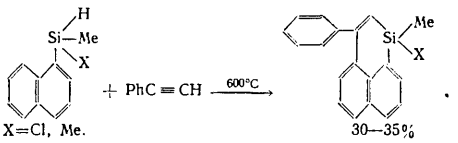


Having thus recognised that the pyrolysis of dichloro(α-naphthyl)-vinylsilane is the best method of synthesis of the heterocycle (XXV), the authors synthesised by this method also 1-chloro-1-methyl-1-silaphenalene mixed with its saturated analogue:

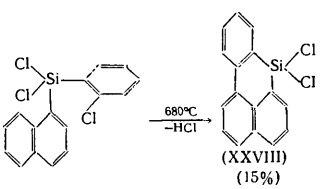


The overall yield of the heterocycles was 25%.

1-Chloro-1-methyl- and 1,1-dimethyl-1-silaphenalenes have been obtained by the thermal interaction of acetylene with chloromethyl-(α-naphthyl)silane and dimethyl(α-naphthyl)silane respectively.[111] Phenylacetylene enters into an analogous *peri*-cyclisation reaction:

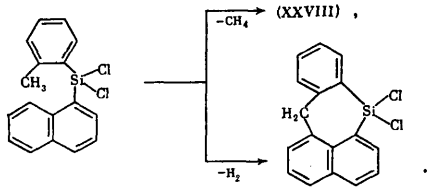


The position of the phenyl substituent in the 1-silaphenalene derivative synthesised has been confirmed by X-ray diffraction data.[111] A more selective method has been proposed[2,14,112] for the synthesis of 1,1-dichloro-1-silaphenalene—by the thermal cyclisation of dichloro(α-naphthyl)vinylsilane in the presence of process initiators (halogenohydrocarbons); the temperature of the reaction zone is then also appreciably reduced (to 520–550 °C). For example, the pyrolysis of dichloro(α-naphthyl)vinylsilane in the presence of hexachloroethane or tichloroethylene leads to the formation of the heterocycle (XXV) in a yield up to 50–60%. The method of the pyrolytic *peri*-cyclisation of naphthalene derivatives has been used successfully also for the synthesis of a new tetracyclic structure—1,1-dichloro-1-sila-2,3-benzophenalene (XXVIII).[2,14,113,114] The latter was synthesised by the intramolecular cyclisation of dichloro(*o*-chlorophenyl)(α-naphthyl)silane:



Compound (XXVIII) is formed also from another *ortho*-derivative—dichloro(α-naphthyl)(*o*-tolyl)silane. However, in this case the

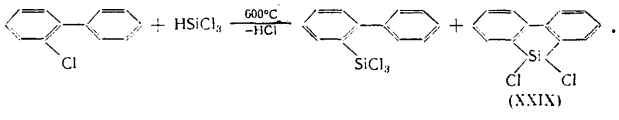
thermal reactions are not so selective and proceed via two mechanisms with ejection of H_2 or CH_4:



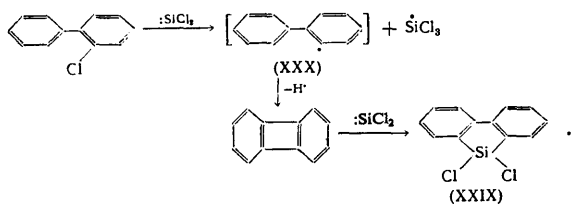
The reaction in which methane is ejected can be accounted for by the tendency to cyclise to a more stable six-membered heterocyclic structure.

2. Thermal cyclisation of *ortho*-substituted biphenyls

The successful use of the mobility of the hydrogen atom in the *peri*-position in α-naphthalene derivatives in order to build up silicon-containing rings aroused interest in the similar cyclisation of *ortho*-substituted biphenyls, which are also a classical example of the manifestation of steric interactions in the aromatic series. The mobility of the *ortho*-hydrogen atoms of *o*-silylbiphenyls has made it possible to devise novel high-temperature methods for the synthesis of new tricyclic silicon-containing structures—the analogues of fluorene and phenanthrene. It was shown[2,115,116] that the interaction of *o*-chlorobiphenyl with trichlorosilane at 600 °C results in the formation of *o*-trichlorosilylbiphenyl, while the subsequent intramolecular cyclisation at higher temperatures (680–700 °C) leads to 9,9-dichloro-9-silafluorene (XXIX) in 45% yield:

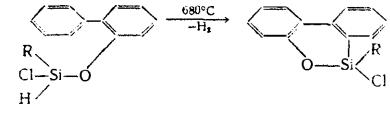


This reaction was the first example of homolytic silylation involving such a high yield with participation of the Si–Cl and C–Ar–H bonds, for which reactions of this type are uncharacteristic. Evidently, the presence of appreciable steric hindrance in the *o*-trichlorosilylbiphenyl molecule and the impossibility of overcoming it without the rupture of the bonds indicated as well as the high temperature of the reaction zone led to the cleavage of the Si–Cl and C_{ar}–H bonds. A new more effective method of synthesis of the heterocycle (XXIX), by the thermal interaction of *o*-chlorobiphenyl with hexachlorodisilane, has been proposed recently;[117] the heterocycle (XXIX) is formed under milder conditions (500–550 °C) and in a higher yield (up to 80%). The principal side product is biphenyl. It is extremely remarkable that *o*-trichlorosilylbiphenyl, which can be regarded in this reaction as the product of the insertion of $:SiCl_2$ and the C_{Ar}–Cl bond of *o*-chlorobiphenyl, is formed in an insignificant yield (up to 5%). The hypothesis of its possible instability under the reaction conditions in the presence of hexachlorodisilane was not confirmed. These factors made it possible to put forward a reaction mechanism via biphenylenes:



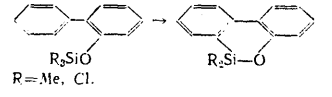
Evidently, the selective abstraction of a chlorine atom from the initial compound by dichlorosilylene leads to the appearance of the radical (XXX), capable of intramolecular cyclisation to biphenylene. On the other hand, the formation of the heterocycle (XXIX) can be regarded as a result of the insertion of $:SiCl_2$ in the strained biphenylene ring. An increase in the $:SiCl_2$ concentration in the reaction mixture increases the yield of the heterocycle, which agrees fully with the proposed reaction mechanism.

The thermal method for the synthesis of silicon-containing heterocycles by the pyrolysis of siloxybiphenyls proved to be extremely fruitful. In contrast to *o*-trichlorosilylbiphenyl, in the latter compounds the relative positions of the atoms seemingly give rise to a much smaller probability of the interaction of the Si–H bonds with the *ortho*-hydrogen atom of the biphenyl group. However, in this case intramolecular cyclisation takes place successfully—the main reaction products are new cyclic compounds with two heteroatoms containing functional group substituents at the silicon atom—derivatives of 9-oxa-10-sila-9,10-dihydrophenanthrene:[2,40,118,119]

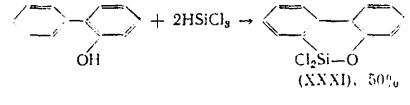


The yield of the heterocycle is ~60% for R = Cl and 30–35% for R = Me or Ph.

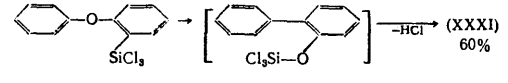
The cyclisation of *o*-siloxybiphenyls can proceed not only at a Si–H bond but also at other bonds involving the silicon atom. However, the yield of the heterocycles is then appreciably lower:[39]



The version of the pyrolytic synthesis of 10,10-dichloro-9-oxa-10-sila-9,10-dihydrophenanthrene (XXXI) from *o*-hydroxybiphenyl, which does not include the stage involving the specific synthesis of *o*-dichlorosiloxybiphenyl, is of great preparative value:[40,120]



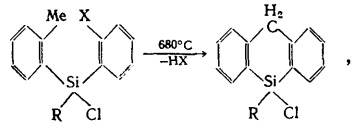
The pyrolysis of phenyl *o*-trichlorosilylbiphenyl ether also leads to the formation of the heterocycle (XXXI). In this case, the cyclisation is accompanied by a rearrangement with formation of the Si–O fragment:[40]



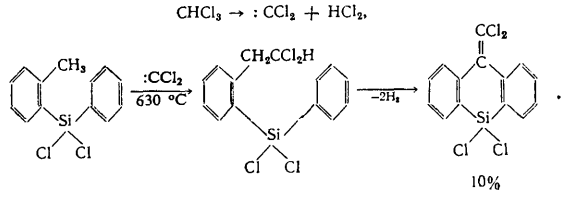
3. Thermal cyclisation of *o*-silylbenzenes

The high-temperature method for the cyclisation of various *o*-substituted benzenes, in which one of the substituents is the silyl group, has opened up extensive possibilities for the synthesis of silicon-containing tricyclic systems. Thus 9-sila-9,10-dihydroanthracenes with the chloro-substituent at the silicon atom have

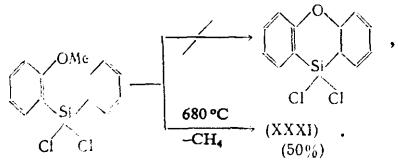
been obtained by the thermal intramolecular cyclisation of dichloro(phenyl)(*o*-tolyl)silane or dichlorobis(*o*-tolyl)silane with ejection of hydrogen or methane:[2,14,95,121,122]



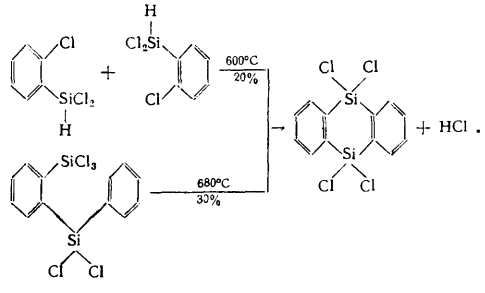
The reactions are distinguished by a high specificity and lead to heterocycles having only the 9-sila-9,10-dihydroanthracene skeleton. 9,9-Dichloro-10-dichloromethylene-9-sila-9,10-dihydroanthracene has been isolated in the cylisation of dichloro(phenyl)(*o*-tolyl)silane in the presence of chloroform or carbon tetrachloride.[2,14,123] Evidently this heterocyclic compound is formed with participation of dichlorocarbene and insertion of the latter in a $C_{alk}-H$ bonds of the initial reactant:



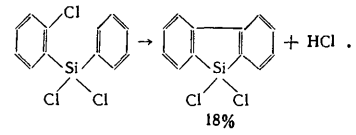
When an attempt was made to synthesise 10,10-dichloro-9-oxa-10-sila-9,10-dihydroanthracene by the pyrolysis of *o*-anisyldichloro(phenyl)silane, 10,10-dichloro-9-oxa-10-siladihydrophenanthrene was isolated instead of the expected heterocycle:[40,124]



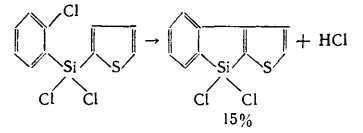
It may be that the first stage of this process is also the ejection of methane from the initial compound, but subsequently the silicon atom migrates to the oxygen atom, which is accompanied by cyclisation to the silaphenanthrene structure. The observed rearrangement with formation of the Si–O fragment is undoubtedly of theoretical interest. The heterocyclic system with two silicon atoms in the central ring—9,9,10,10-tetrachloro-9,10-disila-9,10-dihydroanthracene—was obtained by the pyrolysis of dichloro(*o*-chlorophenyl)silane.[95,124,125] The intramolecular cyclisation of dichloro(phenyl)(*o*-trichlorosilylphenyl)silane leads to the same result but with a higher yield:[2,126]



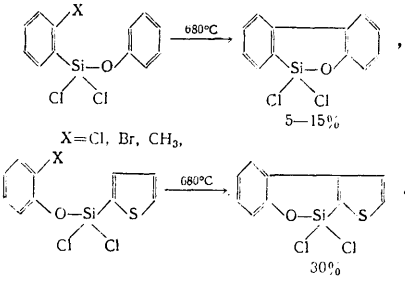
The introduction of a chlorine atom in the *o*-position in dichlorodiphenylsilane promotes the formation of another tricyclic structure—9,9-dichloro-9-silafluorene:[2,85,126]



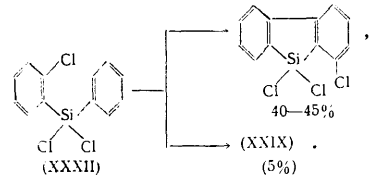
The cyclisation of another *o*-chloro-substituted derivative—dichloro(*o*-chlorophenyl)thienylsilane—takes place with ejection of hydrogen chloride:[2,85,127]



Using the same principle of the pyrolytic synthesis of silicon-containing heterocycles, it is possible to cyclise a series of organosilicon compounds in which two benzene rings are separated by the Si–O fragment instead of the silicon atom alone:[2,40]



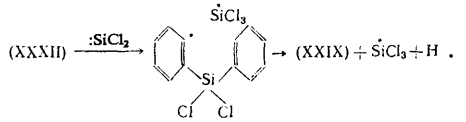
It is extremely remarkable that the copyrolysis of dichloro(*o*-chlorophenyl)phenylsilane (XXXII) with chloroform at 620 °C and with trichloroethylene at 560 °C leads to the virtually selective formation of 1,9,9-trichloro-9-silafluorene; 9,9-dichloro-9-silafluorene (XXIX), unsubstituted in the aromatic ring, was isolated from the reaction mixture in a low yield:[8,14,123]



Thus the cyclisation process takes place in this instance with a high degree of selectivity with respect to the $C_{ar}-H$ bond and not the $C_{ar}-Cl$ bond of the initial compound.

Very interesting results have been achieved in the study of the thermal interaction of a series of organosilicon *o*-chloro-compounds, for example, dichloro(*o*-chlorophenyl)phenylsilane or dichloro(*o*-chlorophenyl)thienylsilane in the presence of sources of dichlorosilylene such as hexachlorodisilane and trichlorosilane. A new gas-phase reaction, involving the formation of silicon-containing heterocycles and having no analogies in the chemistry of carbenes and other intermediates, was discovered in the course of this study. It consists in the selective abstraction of a chlorine atom from the above *o*-chloro-compounds by dichlorosilylene, which promotes the intramolecular cyclisation of these compounds, but the $:SiCl_2$

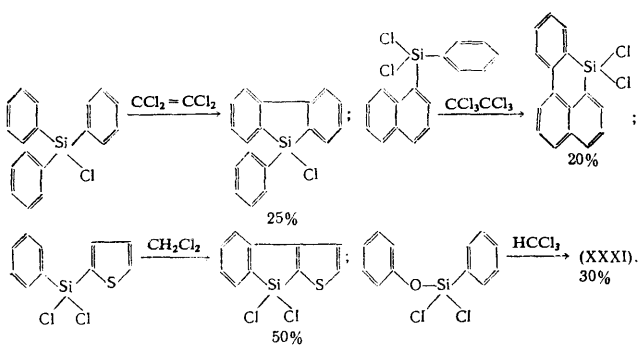
itself does not enter into the composition of the heterocycle formed.[2,14,128,129] Thus the interaction of compound (XXXII) with hexachlorodisilane at 500 °C affords 9,9-dichloro-9-silafluorene in an almost quantitative yield:



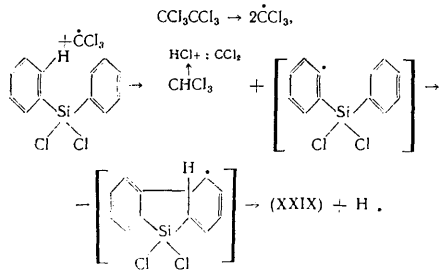
It is extremely instructive that the intermediate formation of a free radical with an unpaired electron at the *o*-carbon atom only, when the radical centre and the aromatic system are close to one another in space, leads to intramolecular cyclisation. The interaction of dichloro(*p*-chlorophenyl)phenylsilane with hexachlorodisilane under the same conditions does not lead to a cyclisation product. Dichloro(phenyl)(*p*-trichlorosilylphenyl)silane—the product of the insertion of $:SiCl_2$ in a $C_{ar}-Cl$ bond of the initial compound—was obtained in this case (yield 30%). The leading role of $:SiCl_2$ in the cyclisation process is also confirmed by the experimental data obtained in the copyrolysis of compound (XXXII) with hexachlorodisilane at the same reaction temperature but at a lower $:SiCl_2$ concentration in the reaction zone. For the reactant ratio (XXXII):HCDS = 1.0–0.5 [HCDS = hexachlorodisilane], the yield of dichlorosilafluorene falls to 40%. This factor may be associated with the fact that the trichlorosilyl radicals formed in the reaction do not participate in the cyclisation process.

4. Cyclisation of unsubstituted chloroarylsilanes

The study of the pyrolysis of unsubstituted aromatic chlorosilanes, for example, such as dichlorodiphenylsilane, dichloro(phenyl)-thienylsilane, chlorotriphenylsilane, and dichloro(α-naphthyl)-phenylsilane, at temperatures up to 700 °C showed that they do not give rise to cyclisation products. The new reaction involving the thermal cyclisation of these compounds in the presence of halogeno-derivatives of methane and ethylene as well as hexachloroethane, which we have proposed, makes it possible to obtain silicon heterocycles with fragments of aromatic systems from more readily available raw material.[8,14,123,130] For example, the pyrolysis of dichlorodiphenylsilane in the presence of $CHCl_3$, CH_2Cl_2, CH_2F_2, and CCl_4 at temperatures in the range 650–680 °C leads to the heterocycle (XXIX) in 30–40% yield. The use of di-, tri-, and tetrachloroethylenes and hexachloroethane in this reaction permits the synthesis of the same heterocycle in a yield up to 60% at a lower temperature of the reaction zone (520–580 °C).[8,14,122,130] Other aromatic organosilicon heterocycles have also been obtained similarly:



The observed thermal interaction, which evidently proceeds via a stage involving the formation of a free radical with the unpaired electron at the *ortho*-carbon atom, is most probably homolytic in character. It may be that unstable species—radicals and carbenes whose formation presupposes the thermal decomposition of the above halogenohydrocarbons—make a significant contribution to this process. The role of these intermediates apparently reduces to creating conditions for intramolecular arylation, for example, in the cyclisation of dichlorodiphenylsilane:



The preparative possibilities of the thermal cyclisation reaction discovered are far from exhausted. It can evidently serve as a basis for the synthesis of various new silicon-containing heterocyclic systems.

Thus inspection of the data presented shows that the thermal gas-phase synthesis is one of the most promising methods of synthesis of organosilicon heterocyclic compounds. The wide-scale employment of this method will undoubtedly lead to the discovery of new highly selective processes for their synthesis.

References

1. G Raabe, J Michl *Chem. Rev.*, 1985, **85** 419
2. E A Chernyshev, N G Komalenkova, S A Bashkirova *J. Organomet. Chem.*, 1984, **271** 129
3. E A Chernyshev, N G Komalenkova, S A Bashkirova *Usp. Khim.*, 1976, **45**(10) 1782 [English translation in *Russ. Chem. Rev.*, 1976(10)]
4. W H Atwell, D R Weyenberg *J. Am. Chem. Soc.*, 1968, **90** 3438
5. E G Janzen, J B Pickett, W H Atwell *J. Am. Chem. Soc.*, 1968, **90** 2719
6. W H Atwell, D R Weyenberg *Angew. Chem.*, 1969, **81** 485
7. E A Chernyshev, N G Komalenkova, S A Bashkirova, USSR P. 368271; *Byull. Izobret.*, 1973, (9) 95
8. E A Chernyshev, N G Komalenkova *Advances in Organosilicon Chemistry*, Izd. Mir, Moscow, 1985, p. 109
9. G Meier, K Schötller, H P Reisenauer *Tetrahedron Lett.*, 1985, **26** 4079
10. T J Barton, J A Kilgour *J. Am. Chem. Soc.*, 1974, **96** 7150
11. T J Barton, J A Kilgour *J. Am. Chem. Soc.*, 1976, **98** 7746
12. E A Chernyshev, N G Komalenkova, S A Bashkirova, V V Sokolov *Zh. Obshch. Khim.*, 1978, **48** 830
13. E A Chernyshev, N G Komalenkova, S A Bashkirova *Dokl. Akad. Nauk SSSR*, 1972, **205** 868
14. N G Komalenkova, S A Bashkirova, L N Shamshin, E A Chernyshev *Gazofaznye Vysokotemperaturnye Metody Sinteza Kremniiorganicheskikh Monomerov* (The Gas-Phase High-Temperature Methods for the Synthesis of Organosilicon Monomers) (Edited by D Ya Zhinkin), Izd. NIITEKhIM, Moscow, 1979, p. 59

15. S Konieczny, P P Gaspar, J Wormhoudt *J. Organomet. Chem.*, 1986, **307** 151
16. D R Weyenberg, W H Atwell *Pure Appl. Chem.*, 1969, **19** 343
17. D Lei, Hwang Rong-Juh, P P Gaspar *J. Organomet. Chem.*, 1984, **271** 1
18. E A Chernyshev, S A Bashkirova, N G Komalenkova, et al. *Dokl. Akad. Nauk SSSR*, 1984, **276** 1151
19. I V Ovchinnikov, A V Golovkin, N G Komalenkova, et al. *Zh. Obshch. Khim.*, 1987, **57** 1421
20. A K Mal'tsev, N T Kagramanov, I O Bragilevskii, et al. *IV Vsesoyuznaya Konferentsiya po Khimii Karbenov. Tezisy Dokladov* (The IVth All-Union Conference on the Chemistry of Carbenes. Abstracts of Reports), Izd. Nauka, Moscow, 1987, p. 125
21. E A Chernyshev, N G Komalenkova, S A Bashkirova, et al. *Zh. Obshch. Khim.*, 1981, **52** 2135
22. E A Chernyshev, S A Bashkirova, N G Komalenkova, et al. *Zh. Obshch. Khim.*, 1985, **55** 1650
23. E A Chernyshev, N G Komalenkova, V G Bykovchenko, et al. *Zh. Obshch. Khim.*, 1987, **57** 1270
24. D Lel, P P Gaspar *Organometallics*, 1985, **4** 1471
25. P P Gaspar, D Lel *Organometallics*, 1986, **5** 1276
26. J M T Davidson, A Fenton, S Jjadi-Maghsoodi, et al. *Organometallics*, 1984, **3** 1593
27. E A Chernyshev, N G Komalenkova, S A Bashkirova, et al. *Zh. Obshch. Khim.*, 1980, **50** 697
28. R Benkeser, R F Cunico *J. Organomet. Chem.*, 1965, **4** 284
29. R J Ellis, H M Fray *J. Chem. Soc. A*, 1966, 553
30. R-J Hwang, R T Conlin, P P Gaspar *J. Organomet. Chem.*, 1975, **94** 38
31. E A Chernyshev, N G Komalenkova, D A Zagorets, M Ya Kel'man, see Ref. 20, p. 156
32. V N Bochkarev, A N Polivanov, N G Komalenkova, et al. *Zh. Obshch. Khim.*, 1973, **43** 2702
33. G Maier, G Mihm, H P Reisenauer *Angew. Chem.*, 1980, **92** 58
34. T J Barton, D S Banasiak *J. Am. Chem. Soc.*, 1977, **99** 5199
35. N Auner, J Grobe *J. Organomet. Chem.*, 1980, **190** 129
36. M E Childs, W P Weber *Tetrahedron Lett.*, 1974, 4033
37. M E Childs, W P Weber *J. Org. Chem.*, 1976, **41** 1799
38. E A Chernyshev, T L Krasnova, V V Stepanov, M O Labartkava *Zh. Obshch. Khim.*, 1978, **48** 2798
39. E A Chernysehv, T L Krasnova, V V Stepanov, USSR P. 507 568; *Byull. Izobret.*, 1976, (11) 72
40. T L Krasnova, V V Stepanov, E A Chernyshev, see Ref. 14, p. 137
41. W H Atwell, J G Uhlman *J. Organomet. Chem.*, 1973, **52** 21
42. A Marchand, P Gerval, F Duboudin, et al., *J. Organomet. Chem.*, 1984, **267** 93
43. W P Wulff, W F Goure, T J Barton *J. Am. Chem. Soc.*, 1979, **100** 6236
44. R L Jenkins, R A Kedrowski, L E Elliott, et al. *J. Organomet. Chem.*, 1975, **86** 347
45. T J Barton, G T Burns *Organometallics*, 1983, **2** 1
46. E A Lopatnikova *Dokl. Akad. Nauk SSSR*, 1983, **268** 108
47. T J Barton, G T Burns *Tetrahedron Lett.*, 1983, **24** 159
48. B H Boo, P P Gaspar *Organometallics*, 1986, **5** 698
49. N S Nametkin, V M Vdovin, L E Gusel'nikov, V I Zav'yalov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1966, 584
50. N S Nametkin, L E Gusel'nikov, V M Vdovin, et al. *Dokl. Akad. Nauk SSSR*, 1966, **171** 630
51. L E Gusel'nikov, N S Nametkin *Chem. Rev.*, 1979, **79** 529
52. L E Gusel'nikov, N S Nametkin *Advances in Organosilicon Chemistry*, Izd. Mir, Moscow, 1985, p. 63
53. N Auner, J M T Davidson, S Jjadi-Maghsoodi, F T Lawrence *Organometallics*, 1986, **5** 431
54. N Auner, J Grobe *J. Organomet. Chem.*, 1980, **188** 151
55. T J Barton, E Kline *J. Organomet. Chem.*, 1972, **42** 21
56. R T Conlin, Y W Kvak, H B Haffaker *Organometallics*, 1983, **2** 343
57. R T Conlin, D J Wood *J. Am. Chem. Soc.*, 1981, **103** 1843
58. R T Conlin, Y W Kwak *Organometallics*, 1984, **3** 918
59. R T Conlin *J. Am. Chem. Soc.*, 1983, **105** 618
60. T J Barton, S A Burna, G T Burns *Organometallics*, 1982, **1** 210
61. S A Burns, G T Burns, T J Barton *J. Am. Chem. Soc.*, 1982, **104** 6140
62. T J Barton, G T Burns, D Gscgmeidner *Organometallics*, 1983, **2** 8
63. N S Nametkin, L E Gusel'nikov, Yu Orlov, et al. *Dokl. Akad. Nauk SSSR*, 1973, **211** 106
64. E C Block, L K Revelle *J. Am. Chem. Soc.*, 1978, **100** 1630
65. T J Barton, S A Jacobi *J. Am. Chem. Soc.*, 1980, **102** 7979
66. T J Barton, G T Burns *J. Organomet. Chem.*, 1979, **179** 17
67. T J Barton *Pure Appl. Chem.*, 1980, **52** 615
68. T J Barton, G T Burns, E V Arnold, J Clardy *Tetrahedron Lett.*, 1981, **22** 7
69. T J Barton, G T Burns *Organometallics*, 1982, **1** 1455
70. G T Burns, T J Barton *J. Organomet. Chem.*, 1981, **209** C25
71. J P Beteille, G Manuel, A Laporterie, et al. *Organometallics*, 1986, **5** 1742
72. G Bertrand, G Manuel, P Mazerolles, G Trinquier *Tetrahedron*, 1981, **37** 2875
73. T J Barton, W D Wulff *J. Am. Chem. Soc.*, 1979, **101** 2736
74. D Tzeng, R H Fong, H S Dilanjan Soysa, W P Weber *J. Organomet. Chem.*, 1981, **219** 153
75. E A Chernyshev, N G Komalenkova, L I Shamshin, USSR P. 483 398; *Byull. Izobret.*, 1975, (33) 79
76. N G Komalenkova, L N Shamshin, T M Kuz'mina, E A Chernyshev, USSR P. 734 209; *Byull. Izobret.*, 1980, (18) 155
77. E A Chernyshev, T L Krasnova, V V Stepanov, USSR P. 480 712; *Byull. Izobret.*, 1975, (30) 74
78. E A Chernyshev, N G Komalenkova, S A Bashkirova, et al. *Zh. Obshch. Khim.*, 1975, **45** 2221
79. T J Barton, M Juvet *Tetrahedron Lett.*, 1975, **45** 3893
80. T J Barton, B L Groh *Organometallics*, 1985, **4** 575
81. T J Barton, J A Kilgour, R R Gallucci, et al. *J. Am. Chem. Soc.*, 1975, **97** 657
82. W Ando, A Sekiguchi, A Rothschild, et al. *J. Am. Chem. Soc.*, 1977, **99** 6995
83. A Sekiguchi, W Ando *Tetrahedron Lett.*, 1979, **42** 4077
84. T J Barton, S A Burns, P P Gaspar, Y S Chen., *Synth. React. Inorg. Metal.-Org. Chem.*, 1983, **13** 881
85. E A Chernyshev, N G Komalenkova, L I Shamshin, see Ref. 14, p. 83
86. E A Chernyshev, N G Komalenkova, T A Klochkova, et al. USSR P. 410 018; *Byull. Izobret.*, 1974, (1) 82
87. E A Chernyshev, N G Komalenkova, T A Klochkova, et al. *Zh. Obshch. Khim.*, 1975, **45** 2229
88. E A Chernyshev, N G Komalenkova, T A Klochkova, T M Kuz'mina, USSR P. 406 835; *Byull. Izobret.*, 1973, (46) 69
89. E A Chernyshev, N G Komalenkova, S A Bashkirova, USSR P. 432 154; *Byull. Izobret.*, 1974, (22) 73

90. E A Chernyshev, N G Komalenkova, S A Bashkirova, USSR P. 437769; *Byull. Izobret.*, 1974, (28) 54
91. E A Chernyshev, N G Komalenkova, S A Bashkirova, T A Zhavoronkova *Zh. Obshch. Khim.*, 1976, **46** 1278
92. D Seyferth, H-M Shir, J Dubac, et al. *J. Organomet. Chem.*, 1973, **50** 39
93. E A Chernyshev, N G Komalenkova, M Ya Kel'man, et al. *VI Vsesoyuznaya Konferentsiya po Khimii i Primeneniyu Kremniiorganicheskikh Soedinenii. Tezisy Dokladov* (The VIth All-Union Conference on the Chemistry and Applications of Organosilicon Compounds. Abstracts of Reports), Inst. Org. Sinteza Akad. Nauk Latv. SSR, Riga, 1986, p. 228
94. E A Chernyshev, N G Komalenkova, M Ya Kel'man, et al., see Ref. 20, p. 156
95. E A Chernyshev *Khimiya i Tekhnologiya Elementoorganicheskikh Soedinenii* (The Chemistry and Technology of Organoelemental Compounds), Izd. NIITEKhIM, Moscow, 1972, No. 1, p. 49
96. E A Chernyshev, N G Tolstikova, S A Shchepinov, USSR P. 215990; *Byull. Izobret.*, 1968, (14) 29
97. E A Chernyshev, N G Tolstikova *Zh. Obshch. Khim.*, 1970, **40** 1052
98. E A Chernyshev, S A Shchepinov *Zh. Obshch. Khim.*, 1970, **40** 1744
99. E A Chernyshev, T L Krasnova, A A Bernadskii, N G Komalenkova, USSR P. 298588; *Byull. Izobret.*, 1971, (11) 86
100. E A Chernyshev, N G Tolstikova *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1963, 1146
101. E A Chernyshev, N G Komalenkova, T A Klochkova, et al. *Zh. Obshch. Khim.*, 1971, **41** 122
102. E A Chernyshev, N G Komalenkova, T A Klochkova, S A Shchepinov *Zh. Obshch. Khim.*, 1971, **41** 617
103. E A Chernyshev, N G Komalenkova, T A Klochkova, USSR P. 327207; *Byull. Izobret.*, 1972, (5) 72
104. E A Chernyshev, N G Komalenkova, T A Klochkova, T M Kuz'mina *Zh. Obshch. Khim.*, 1975, **45** 2223
105. E A Chernyshev, N G Komalenkova, T A Klochkova, T M Kuz'mina, USSR P. 374319; *Byull. Izobret.*, 1973, (15) 51
106. E A Chernyshev, N G Komalenkova, T A Klochkova, T M Kuz'mina, USSR P. 391149; *Byull. Izobret.*, 1973, (31) 74
107. E A Chernyshev, N G Komalenkova, T A Klochkova, T M Kuz'mina, USSR P. 364622; *Byull. Izobret.*, 1973, (5) 76
108. E A Chernyshev, S A Shchepinov, N G Tolstikova, USSR P. 210862; *Byull. Izobret.*, 1968, (7) 21
109. E A Chernyshev, S A Shchepinov *Zh. Obshch. Khim.*, 1970, **40** 1747
110. P Boudjouk, J S Kiely, Ratnasabapthy Soorigakunarah *J. Organomet. Chem.*, 1981, **221** 33
111. E A Chernyshev, N G Komalenkova, V A Sharapov, et al. *Zh. Obshch. Khim.*, 1987, **57** 1730
112. N G Komalenkova, L N Shamshin, T M Kuz'mina, E A Chernyshev, USSR P. 734209; *Byull. Izobret.*, 1980, (18) 155
113. E A Chernyshev, N G Komalenkova, L N Shamshin *Zh. Obshch. Khim.*, 1974, **44** 303
114. E A Chernyshev, N G Komalenkova, L N Shamshin, USSR P. 379577; *Byull. Izobret.*, 1973, (20) 74
115. E A Chernyshev, S A Shchepinov, T L Krasnova, N P Filimonova, USSR P. 217395; *Byull. Izobret.*, 1968, (16) 21
116. E A Chernyshev, S A Shchepinov, T L Krasnova *Zh. Obshch. Khim.*, 1970, **40** 1058
117. E A Chernyshev, N G Komalenkova, O V Elagina, et al. *Zh. Obshch. Khim.*, 1985, **55** 2314
118. E A Chernyshev, T L Krasnova, S A Shchepinov *Zh. Obshch. Khim.*, 1970, **40** 1735
119. E A Chernyshev, T L Krasnova, S A Shchepinov, USSR P. 214535; *Byull. Izobret.*, 1968, (12) 27
120. E A Chernyshev, T L Krasnova, T V Pokrasova, USSR P. 405353; *Byull. Izobret.*, 1975, (47) 169
121. E A Chernyshev, N G Komalenkova, A N Shamshin, N V Bochkarev *Zh. Obshch. Khim.*, 1972, **43** 1373
122. E A Chernyshev, N G Komalenkova, L N Shamshin, USSR P. 276054; *Byull. Izobret.*, 1971, (16) 236
123. E A Chernyshev, N G Komalenkova, L N Shamshin, I A Shashkov *Zh. Obshch. Khim.*, 1985, **55** 2317
124. E A Chernyshev, T L Krasnova, E F Shchipanova *Zh. Obshch. Khim.*, 1973, **44** 1652
125. E A Chernyshev, S A Shchepinov, N G Komalenkova, L N Shamshin, USSR P. 295765; *Byull. Izobret.*, 1971, (8) 65
126. E A Chernyshev, N G Komalenkova, L N Shamshin, S A Shchepinov *Zh. Obshch. Khim.*, 1971, **41** 843
127. E A Chernyshev, N G Komalenkova, L N Shamshin, USSR P. 514818; *Byull. Izobret.*, 1976, (19) 59
128. E A Chernyshev, N G Komalenkova, L N Shamshin, USSR P. 514840; *Byull. Izobret.*, 1976, (19) 54
129. E A Chernyshev, N G Komalenkova, S A Bashkirova, et al. *Zh. Obshch. Khim.*, 1985, **55** 2309
130. E A Chernyshev, N G Komalenkova, L N Shamshin, USSR P. 571486; *Byull. Izobret.*, 1977, (33) 68

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Isoprenoid petroleum hydrocarbons

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ABSTRACT. The outcome of studies on the chemistry of petroleum carried out during the last 10–15 years is examined. It is shown that petroleum is a very complex mixture of natural products, the most important place among which is occupied by $C_{10}-C_{40}$ isoprenoid hydrocarbons represented by aliphatic, alicyclic, and aromatic compounds.

The relations between the isoprenoid petroleum hydrocarbons and their possible bioorganic precursors are discussed. The possibility of using isoprenoid hydrocarbons (as biomarkers) in discovering the pathways leading to the genesis and chemical evolution of petroleums and also prospecting for petroleum deposits is demonstrated.

The bibliography includes 104 references.

Contents

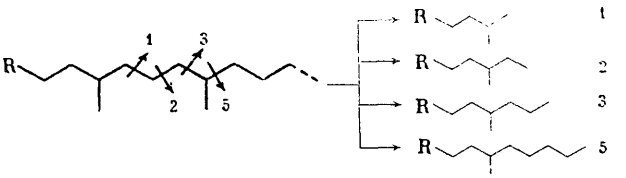
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I. Introduction

The identification of a large number of relict hydrocarbons (biomarkers)—compounds retaining the main features of the structure of the initial bioorganic molecules—in petroleums, coals, shales, and other fossil fuels is undoubtedly one of the most important advance in the organic chemistry of the second half of the XXth century. A new independent scientific discipline—organic geochemistry—arose in the middle of the 1960s. Its aim is the study (at the molecular level) of the characteristic features of the composition and structure of the organic molecules in the Earth's core, seas, and oceans. It involves the study of both "modern" compounds as well as compounds formed hundreds of millions of years ago. Much attention has also been devoted to questions concerning the chemical changes in organic molecules under geological conditions. In the course of its development, organic geochemistry has been based on the present scientific level of its precursor—the chemistry of natural products, utilising fully both the methodology and the analytical procedures of the latter. The advances in the study of organic molecules in the Earth's core and, in particular, hydrocarbons, achieved during the last 20–25 years, are very considerable. Thus more than 300 $C_{10}-C_{40}$ hydrocarbons, having a clear biological origin, have been identified in petroleums and other fossil fuels. Not only their structure but also the characteristic features of their stereochemistry, frequently changing during the transformation of bioorganic molecules under geological conditions, have been determined. The practical importance of such studies, especially in the prospecting for petroleum deposits and in problems concerning ecology and the protection of the environment has led to the biannual holding of International Congresses on Organic Geochemistry. The publishing house Pergamon Press has been publishing a special periodic journal. In a number of developed capitalist countries, there are institutes (or large departments) concerned with various problems of organic geochemistry.

The framework of the present review restricts us to the isoprenoid petroleum hydrocarbons. However, this group of compounds is the most important and the most representative. Advances in this field have been achieved by the efforts of a large group of investigators in England, France, the Federal Republic of Germany, the Soviet Union, the USA, and many other countries.

All the isoprenoid petroleum hydrocarbons can be divided into three large groups: aliphatic isoprenoids, alicyclic isoprenoids, and isoprenoids containing aromatic rings. A common property of the majority of petroleum isoprenoids is their homologous nature. This property is associated with the characteristic features of their genesis. The homologous nature of isoprenoids has one important feature. Since petroleum hydrocarbons are frequently formed via a stage involving the degradation of biopolymers, after three homologues, the next (fourth) homologue is usually (for a regular chain structure) "omitted" as a result of the branched structure of the isoprenoid chain.



The homologous nature of these hydrocarbons makes it necessary to give preference to the term isoprenoid hydrocarbons and to avoid using the term, which is in many cases more usual, terpenoid compounds.

In studies on the most complex mixtures of petroleum hydrocarbons, modern achievements in the analytical chemistry of organic compounds have played a very important role, especially methods such as gas chromatography using high performance capillary columns, combined gas chromatography–mass spectrometry (with computer treatment of data), mass fragmentography and mass chromatography, and also ^1H and ^{13}C nuclear magnetic resonance. Numerous syntheses of model hydrocarbons have undoubtedly played a special role. The majority of compounds examined below were first obtained in laboratories. An extensive scientific literature has been devoted to isoprenoid petroleum hydrocarbons. Here we shall quote references mainly to studies during the last 10–15 years especially since there are already reviews and monographs devoted to

these aspects.[1-3] The data on the mass spectra of certain isoprenoid hydrocarbons examined below may be found in the review of Golovkina et al.[4]

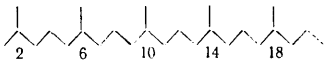
II. Aliphatic isoprenoids

Isoprenoid alkanes (isoprenanes) are compounds whose discovery in natural fossil products has promoted the establishment of modern organic geochemistry. Hydrocarbons important for petroleum such as pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,10,14-tetramethylhexadecane) have been described.[5]

Aliphatic petroleum isoprenoids have both regular and irregular carbon chains, the number of their carbon atoms ranging from 9 to 45. There is no doubt that the leading role is assumed by irregular isoprenoids having a structure of the main carbon chain with "head to tail" fragments, which is characteristic of polyisoprene.

1. Regular isoprenoids

It is possible to distinguish the following homologous series of these hydrocarbons: 2,6-dimethylalkanes (C_9-C_{13}); 2,6,10-trimethylalkanes ($C_{14}-C_{18}$); 2,6,10,14-tetramethylalkanes ($C_{19}-C_{23}$); 2,6,10,14,18-pentamethylalkanes ($C_{24}-C_{28}$), etc. For understandable reasons, hydrocarbons having the C_{12}, C_{17}, C_{22}, C_{27}, etc. compositions are absent from the homologous series.



The degradation of any C—C bond in the main chain can result in the formation of only regular isoprenoids. Fig. 1 presents chromatogram of the saturated hydrocarbons of the petroleum from the Severo-Tol'kinskoe deposit (Western Siberia). The predominance of regular $C_{14}-C_{20}$ isoprenoids, which is usual for petroleums, and the much lower concentration of similar structures having the $C_{21}-C_{25}$ composition can be clearly seen. Data on the proportions of regular isoprenoids in other petroleums in the Soviet Union can

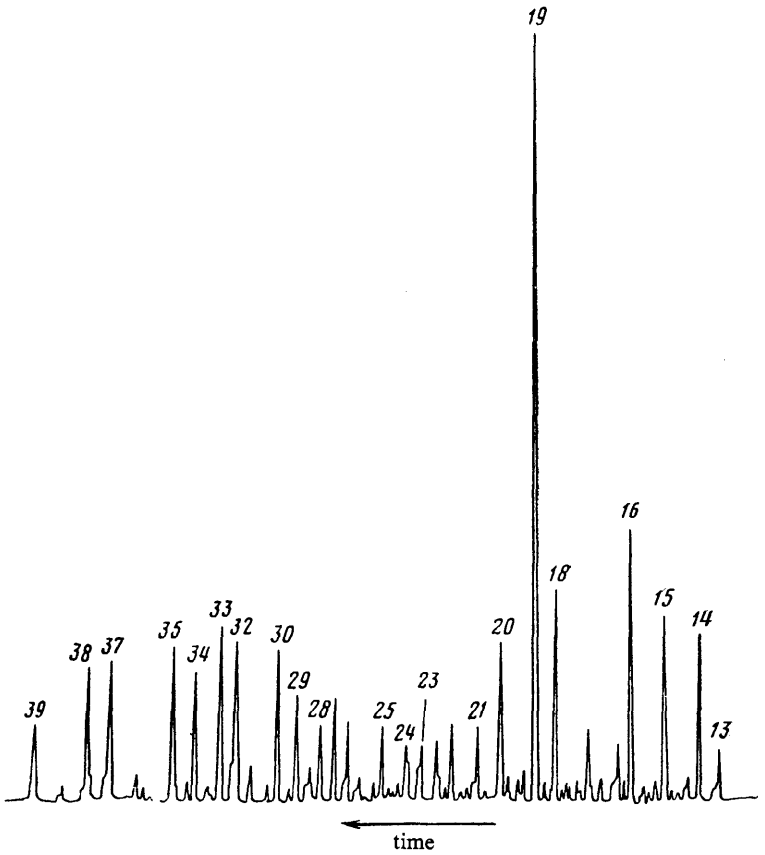
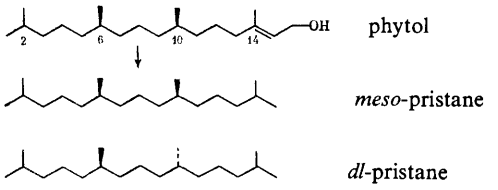


Figure 1. Chromatogram of a mixture of saturated hydrocarbons from petroleum of the Severo-Tol'kinskoe deposits; capillary column (80 m) with Apiezon; linear temperature programming (4 K min^{-1}). Analysis started at 100 °C and ended at 320 °C; the number of carbon atoms in the molecule is indicated; $C_{13}-C_{25}$, isoprenoid alkanes with a regular structure (2,6,10-trimethylalkanes, 2,6,10,14-tetramethylalkanes, etc.); $C_{28}C_{39}$, irregular isoprenoids ("head to head" fragment); 2,6,10,14,17,21,25,29-octamethylhentriacontane (C_{39}); 2,6,10,14,17,21,25,29-octamethyltriacontane (C_{38}); 2,6,10,14,17,21,25-heptamethyltriacontane (C_{37}); nonacosane (C_{35}), etc.[13]

be found in monographs.[1,6] The main source of regular isoprenoids in petroleums is phytol (C_{20}) and solanosol (C_{45}).[7,8] The stereochemistry of isoprenoid alkanes is of interest.[9–11] The relation between the stereochemistry of phytol and the pristane formed from it is considered in Scheme I, whereas *meso*-pristane [having the configuration of the C(6) and C(10) chiral centres characteristic of phytol] clearly predominates in recent fossil deposits (young, "unripe" deposits and also in brown coals), a 1 : 1 mixture of the *meso*- and *dl*-epimers is usually found in petroleums.

Scheme I

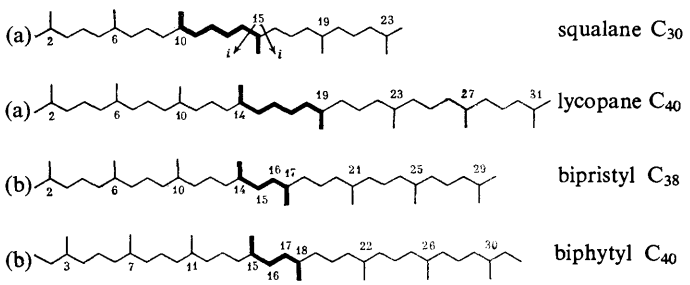


Another (minor) series of regular isoprenoid alkanes belonging to the series of 3,7-dimethyl-, 3,7,11-trimethyl-, and 3,7,11,15-tetramethylalkanes has been described.[1–8] In the original communication,[8] such structures have been called "quasi-regular".

2 Irregular isoprenoids

Two types of isoprenoid alkanes with an irregular structure of the main carbon chain have been found in petroleums: (a) those having an irregular unit of the "tail to tail" type and (b) those having an irregular unit of the "head to head" type (Scheme I).

Scheme II

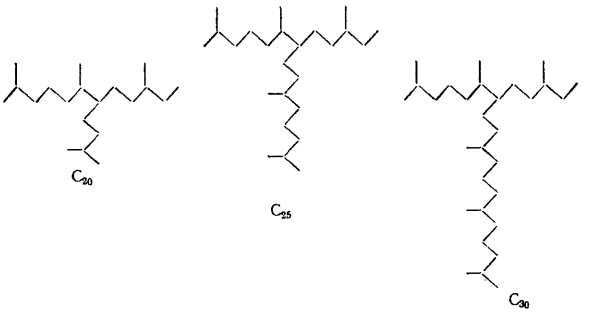


The degradation of the aliphatic chain of irregular isoprenoids can lead to the appearance of two series of homologues: (1) irregular homologues if an irregular unit is retained on degradation, for example, 2,6,10,15-tetramethylalkanes from squalane and 2,6,10,14,17-pentamethylalkanes from bipristyl; (2) the so called pseudoregular homologues[12] in those cases where the rupture of the bond involves an irregular unit. In particular, the degradation of squalane via the pathways (*i*) yields "forbidden" regular 2,6,10-trimethyltetradecane (C_{17}) and 2,6,10-trimethylhexadecane (C_{19}).

The homologous series of irregular isoprenoid $C_{28}-C_{39}$ alkanes (having a "head to head" unit) has been found in the petroleum the Severo-Tol'kinskoe deposit already mentioned[13] (Fig. 1). These hydrocarbons have been identified also in other petroleums.[14,15] The formation of these structures can be accounted for by the microbiological abstraction of hydrogen from the C(1) atom of regular isoprenoids (pristane, phytane, etc.) with subsequent coupling of the radicals (15–16 and 16–17 bonds are formed in bipristyl and biphytyl respectively).

A new series of isoprenoid alkanes, having a T-shaped structure, have been discovered in petroleums in recent years[16,18] (Scheme III).

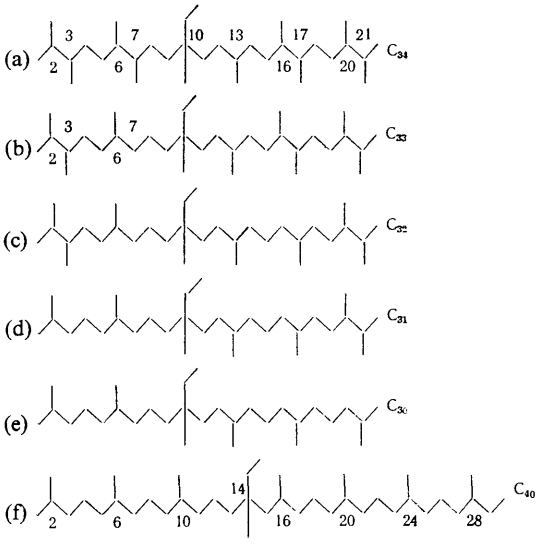
Scheme III



It is of interest that these hydrocarbons are represented only by compounds having the C_{20}, C_{25}, and C_{30} compositions, i.e. they are diterpenoids, sesterterpenoids, and triterpenoids.

There is an unusual group of petroleum isoprenoids containing a geminal methylethyl group.[19–22] Botryococcane (C_{34}) and its lower-molecular-weight homologues ($C_{33}-C_{30}$) and also isolycopane (C_{40}) merit attention here (Scheme IV).

Scheme IV



III. Cyclic isoprenoids

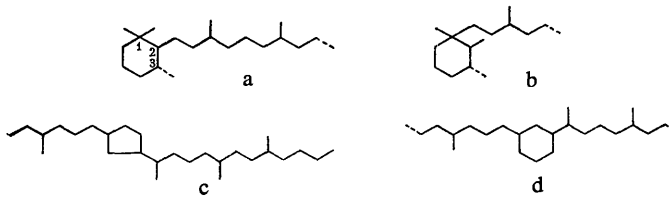
Saturated cyclic petroleum isoprenoids are characterised by different numbers of rings in the molecule (from one to six). These compounds constitute the basis of relict petroleum hydrocarbons (biomarkers).

1. Monocyclic isoprenoids

The simplest monocyclic isoprenoids are 1,2- and 1,4-methylisopropylcyclohexanes.[23] The interesting $C_{10}-C_{30}$ homologous series of isoprenoids, formed by the degradation of the aliphatic chain of β-carotane, has been described.[24,25] The first representative of these hydrocarbons, namely 1,1,3-trimethylcyclohexane, is present in appreciable amounts in almost all petroleums.[1]

Apart from the main homologues (Va), the products of their 1,2-rearrangement (Vb) have also been found.

Scheme V

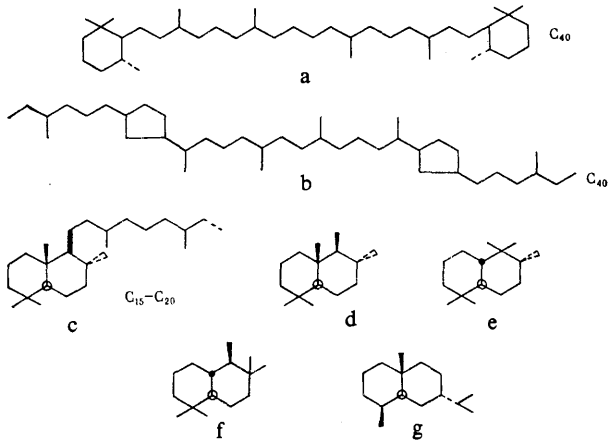


It has been stated that monocyclic isoprenoids with long isoprenoid chains of both irregular (Vc) and regular (Vd) types are present in petroleums.[9] The hydrocarbon (Vd) must be regarded as a saturated compound corresponding to the product of the dimerisation of phytadiene via the Diels–Alder reaction. The presence of lower-molecular-weight homologues of these hydrocarbons in petroleums is also probable.

2. Bicyclic isoprenoids

Among bicyclanes with isolated rings, except perhydro-β-carotane (VIa), bicyclic five-membered cyclanes with isolated rings and isoprenoid chains (VIb) have also been identified in petroleums. There is a larger group of bicyclanes with condensed rings (Scheme VI).

Scheme VI



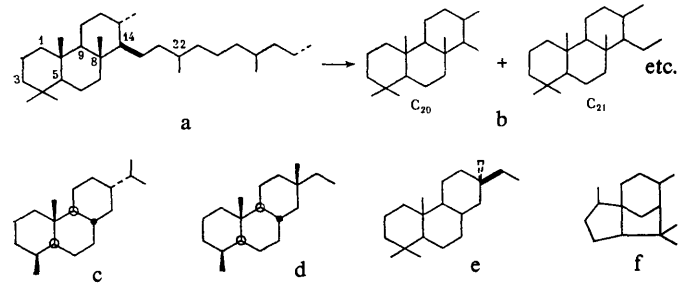
In this group of compounds, both hydrocarbons with the 8βH-drimane† (VId) skeleton and the products of their 1,2-rearrangement—the structures (VIe) and (VIf)—have been determined in hydrocarbons.[26–28] The parent of this group of compounds is probably the C_{20} hydrocarbon—labdane (VIc); the degradation of its chain results in the formation of the homologous series of tetramethylalkyldecalins. Eudesmane (cadinane) (VIg), present only in the form of the "pure" sesquiterpane, has a different structure.

3. Tricyclic isoprenoids

The most interesting representatives of the tricyclic petroleum isoprenoids are undoubtedly hydrocarbons belonging to the homologous series of pentamethylalkylperhydrophenanthrenes, which have been called hydrocarbons of the cheilanthane series. A number of these compounds having the $C_{18}-C_{40}$ composition have been discovered. The compounds have a regular isoprenoid chain which is the reason for the absence of the C_{22}, C_{27}, etc. homologues.[29–32]

The formulae of the hydrocarbons considered are listed in Scheme VII. The C_{25} and higher hydrocarbons are eluted on the chromatograms in the form of two diastereoisomers (22*S* and 22*R*) because the C_{22} atom becomes chiral.

Scheme VII



The hydrocarbons (VIIa, b) can be conveniently identified by mass fragmentography on the basis of the fragment ion with m/z = 191. Apart from cheilanthanes, tricyclic diterpenoids such as fichtelite (VIIc), norpimarane, and pimarane (VIId, e) have also been found in petroleums.[34] Nor can one rule out the possibility of the presence of the sesquiterpane cedrane (VIIf).

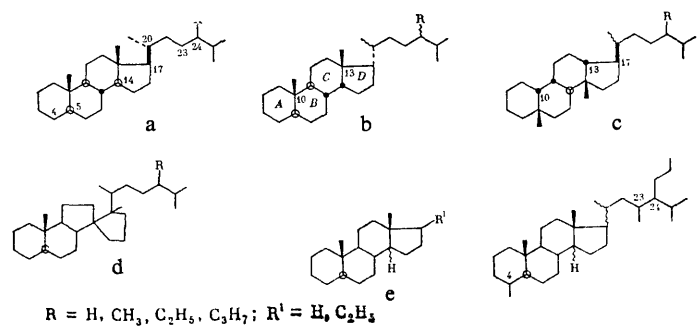
4. Tetracyclic isoprenoids

Tetracyclic isoprenoids constitute the largest and most interesting group of isoprenoid petroleum hydrocarbons. Sterane hydrocarbons (Scheme VIII) play an especially major role, because these compounds contain a very large amount of information for the solution of a series of geochemical problems (more will be said about this below).

Furthermore, the steranes, formed from the chemically fairly labile steroids, undergo a series of interesting structural and stereochemical transformations in the Earth's core leading to the formation of a series of hydrocarbons which have no analogues in living nature and which are present only in petroleums. Such are, for example, isosteranes (the 14β,17β-epimers), rearranged steranes, etc.

Thus, as was already mentioned previously, petroleum is a source of completely new types of organic molecules; an example is the discovery of hydrocarbons of the adamantane series in petroleums. Scheme VIII presents the formulae of the principal sterane hydrocarbons discovered in petroleums[1,2,35–41] [a mixture of the (24*S*)- and (24*R*)-epimers for R = C_1-C_3]:

Scheme VIII



R = H, CH_3, C_2H_5, C_3H_7; R¹ = H, C_2H_5

† Here and henceforth the suffixes β and α denote the orientation of the hydrogen atom.

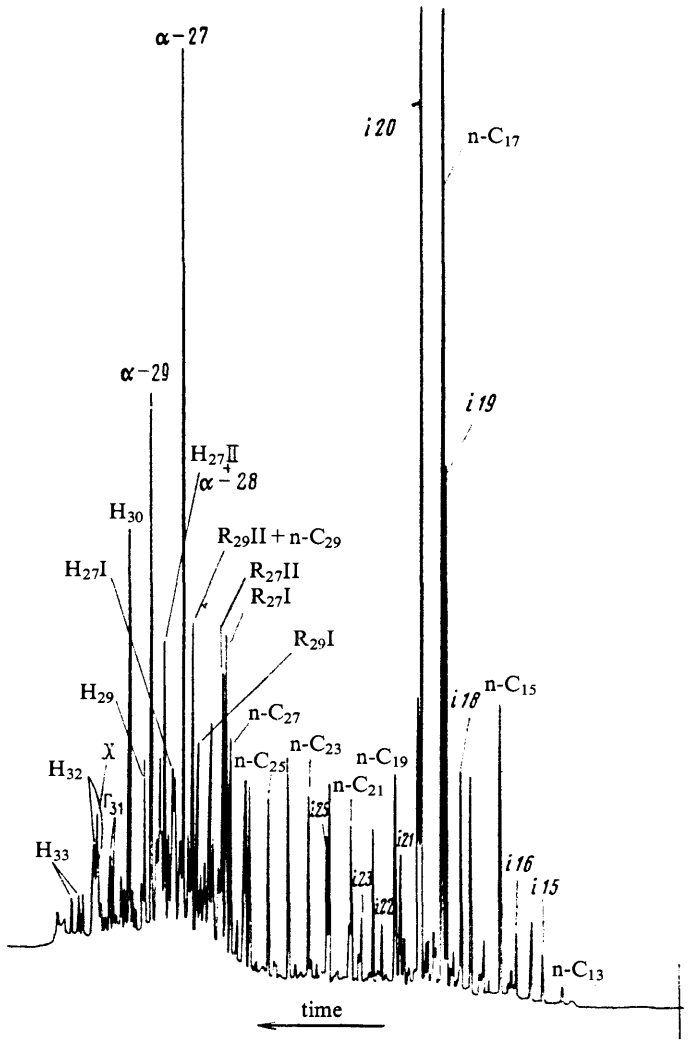


Figure 2. Chromatogram of a mixture of saturated hydrocarbons in the petroleum of the Vostochno-Vystupovichskoe deposit; the analytical conditions were the same as in Fig. 1; n, normal alkanes; *i*, isoprenoid alkanes; α-27, α-28, α-29, regular steranes (5α, 14α, 17α, 20*R*); R_{27}, R_{28}, R_{29}, rearranged steranes (13β, 17α, 20*S* and 20*R*); H, hopanes; in the $C_{31}-C_{35}$ doublet peaks, (22*S*)-epimers are eluted first; X, gammacerane; the numerals indicate throughout the number of carbon atoms in the molecule for R [I (20*S*) and II (20*R*)] and for H_{27} [I (18α-H) and II (17α-H)].

In terms of the steric structure, the hydrocarbons (VIIIa) belong to the series of biological steranes in which the most important chiral centres having the (5α, 14α, 17α, 20*R*)-configuration.[35] Fig. 2 presents a chromatogram of the saturated hydrocarbons of the petroleum from the Vostochno-Vystupovichskoe Deposit (Belorussia).‡ The peaks due to the C_{27}, C_{28}, and C_{29} (5α, 14α, 17α, 20*R*)-steranes (VIIIc) having the same composition are clearly seen.

The concentration of the stereochemically modified (5α, 14β, 17β, 20*S*)- and the corresponding (20*R*)-epimers of compound (VIIIb) in this petroleum is low. The isosteranes/α-steranes ratio is ~0.1. However, in other petroleums this ratio can reach 5 and more up to thermodynamic equilibrium value which is 7 (at 400 K).[1,35] The epimerisation of (5α, 14α, 17α, 20*R*)-steranes with formation of (5α, 14β, 17β, 20*S*)- and the corresponding (20*R*)-epimers is thermodynamically extremely favourable, since the change from the *trans*-junction of the *C/D* rings to the *cis*-junction removes all the strain characteristic of angularly substituted methyl-*trans*-hydrindans. As a result of the simultaneous epimerisation of the C(17) chiral centre, the hydrogen atoms at C(17)–C(20) and the angular methyl group [at C(13)] cease being eclipsed. At the same time, the quaternary C(10) and C(13) carbon atoms remain unaltered, which in fact preserves the high optical activity of the petroleum isosteranes formed. Apart from the epimerisation of the C(14) and C(17) centres, the epimerisation of C(20) also takes place and leads to the appearance on the chromatograms of doublet peaks of the

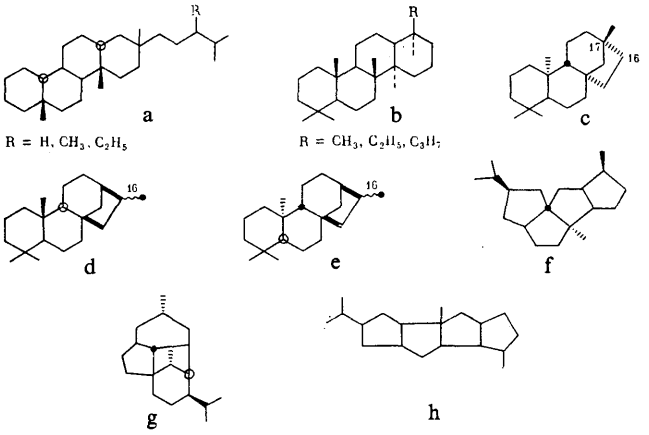
‡ Al A Petrov, Geologiya Nefti i Gaza, 1988, No. 10, p. 50.

hydrocarbons with the (α, β, β, 20*S*)- and (α, β, β, 20*R*)-configurations formed, whose thermodynamic stabilities are similar. The rearranged steranes (VIIIc) have the characteristic (10α, 13β, 17α)-configuration and also exist in the form of pairs of (20*S*)- and (20*R*)-epimers (these hydrocarbons are sometimes called diasteranes). The proportions of steranes with different molecular weights, the ratio of the α, α, α-steranes and isosteranes, as well as the relative concentrations of the rearranged steranes are some of the most important geochemical characteristics of the petroleums investigated.§ Apart from the steranes already examined, the spirosteranes (VIIId) as well as steranes with shorter substituents at C(17)—androstane and pregnane (VIIIe)—have also been determined in petroleums.[42] In addition, a series of C_{30} steranes (VIIIf), having either a propyl substituent at C(24) or methyl substituents at C(4), C(23), and C(24), have also been found in petroleum.[43] All these steranes can also exist in petroleum in the form of the biological α, α, α-epimers and in the form of their reaction products—(α, β, β, 20*S*)- and the corresponding (20*R*)-steranes with a rearranged skeleton.

Spirosteranes are formed via the acid rearrangement of steranes followed by saturation as a result of a redistribution of hydrogen. Steranes in petroleums are usually determined with the aid of gas chromatography-mass spectrometry on the basis of the principal fragment ions: m/z = 217 for the regular structures and m/z = 259 for the rearranged structures (m/z = 231 and 273 respectively for the 4-methylsteranes).

Hydrocarbons with the perhydrochrysene structure (IXa, b), in particular 17*D*-homosteranes (IXa) and 17, 21, secohopanes (IXb), also belong to tetracyclic isoprenoids.[1,29,44] (The dots designate quaternary and tertiary carbon atoms exhibiting a strong downfield shift in the ^{13}C NMR spectra.)

Scheme IX



17-*D*-Homosteranes, identified from the fragment ion with m/z = 287, are also products of the skeletal rearrangement of sterenes, proceeding via a carbonium ion mechanism, and can be regarded as compounds formed from diasteranes as a result of the expansion of the *D* ring.

§ Among the regular steranes, the most important hydrocarbons any structure are the (5α, 14α, 17α, 20*R*)-epimers (biosteranes), (5α, 14α, 17α, 20*S*)-epimers, (5α, 14β, 17β, 20*S*)-epimers, and the corresponding (20*R*)-epimers (geosteranes). Among the rearranged steranes, the (10α, 13β, 17α, 20*S*)- and the corresponding (20*R*)-epimers are most important. Data concerning the equilibrium of the epimers considered have been published in a monograph.[35]

The hydrocarbons with the structure (IXb)—the products of the degradation of the *E* ring of hopanes (see below)—are 17, 21-secohopanes having the $C_{24}-C_{27}$ composition.

The group of petroleum diterpanes comprising beyerane (IXc), phyllocladane (IXd), and kaurane (IXe) is very interesting.[45] The hydrocarbons (IXd, e) exist in the form of epimeric pairs (16α- and 15β-).

A remarkable group of tetracyclic C_{19} hydrocarbons (IXf–h), containing mainly five-membered rings, has been examined recently.[46] The compact packing of the carbon atoms make it possible to create a tetracyclic system consisting of only 14 carbon atoms. The key factor in the determination of the structure of the hydrocarbons (IXf–g) is the strong downfield shift in the ^{13}C NMR spectra (65–66 p. p. m. relative to TMS). The hydrocarbons (IXf–h) are most probably formed via the microbiological C_5 cyclisation of the unsaturated monocyclic isoprenoids, such as, for example, cembrene,[47] although, in principle, other pathways and sources are also possible. The relatively very high concentration of the hydrocarbons (IXf–h) in certain petroleums, reaching 1–2%, is noteworthy.

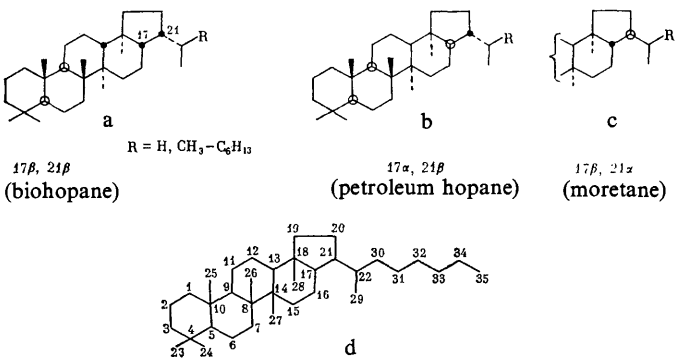
5. Pentacyclic isoprenoids

Together with tetracyclic hydrocarbons, pentacyclic hydrocarbons occupy one of the most important places in the chemistry of petroleum hydrocarbons. Compounds of this type belong to the class of triterpenoid hydrocarbons (triterpanes), although homologous properties are observed here also. It is possible to differentiate two main types of structures:

(a) hydrocarbons with the perhydropicene skeleton (all the rings are six-membered);

(b) hydrocarbons with the cyclopentanoperhydrochrysene skeleton. Hydrocarbons of the second type are much more common in petroleums.

Scheme X



We shall begin the examination of pentacyclic hydrocarbons with the important homologous series of hopane hydrocarbons (Scheme X). Studies by Ourisson's school (France) have played an outstanding role in the determination of the structure and stereochemistry of petroleum hopanes. Ourisson has justly referred to these hydrocarbons as "ubiquitous",[48] because they are present in almost all caustobioliths: in petroleums, coals, shale, peat, etc.[1] The hopane series hydrocarbons are formed in the microbiological processing of natural organic compounds in the early stages of their fossilisation. The pentacyclic tetrahydric alcohol bacteriotetrol (see below), which forms part of the composition of the lipid component of membranes of ancient bacteria, is the source of the hopanes

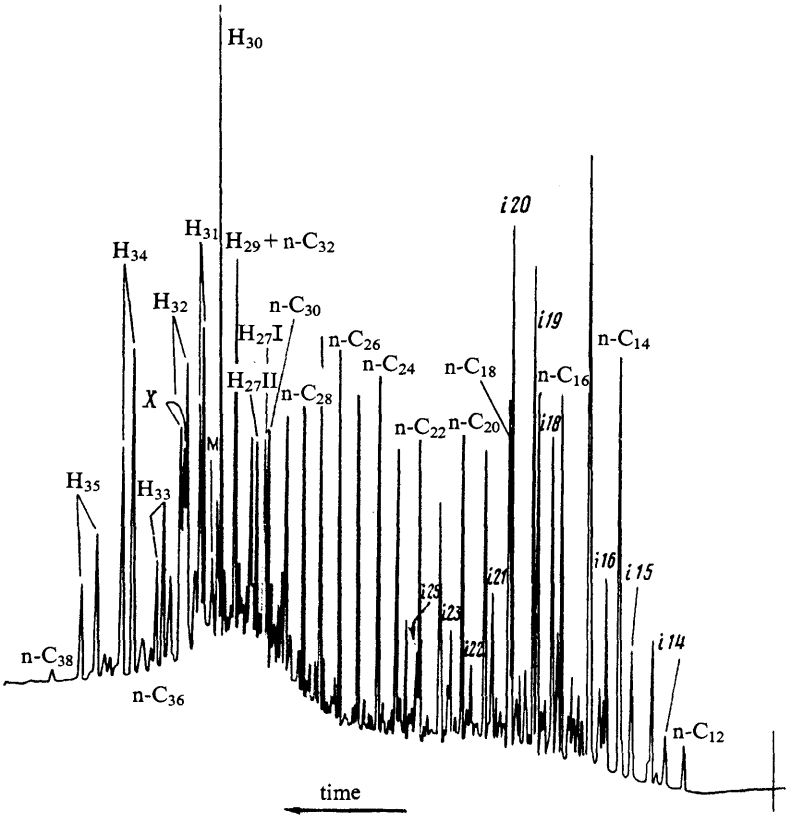


Figure 3. Chromatogram of a mixture of saturated hydrocarbons from the Zapadno-Slavan'skoe deposit; the chromatographic conditions were the same as in Fig. 1; the legend is the same as in Fig. 2. M = moretane.

themselves. We may also note that the studies by the school of the famous English organic geochemist Eglinton have played a no less important role in the determination of the structures of other isoprenoid biomarkers (chemofossils) and in establishing organic geochemistry as an independent scientific discipline.[49,50]

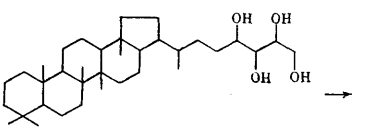
A large number of studies have been published on petroleum hopanes.[1,2,51–55]

Scheme X presents the formulae of hopanes having different stereochemistry: (a) biohopane; (b) petroleum hopane; (c) moretane, which is also encountered in petroleums. The numbering of carbon atoms is indicated in the formula (Xd).

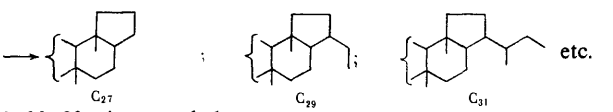
The principal factor determining the energy gain in the isomerisation of the 17β,21β-epimers to the 17α,21β-epimers is again the greater stability of the *cis*-fused angular methylhydrindan. In addition, the change in the configuration of the C(17) chiral centre removes the strain present in biohopane (17β), which arises because the 17–16 and 21–22 bonds (*cis*-orientation) are eclipsed. Calculations have shown that only 3% of biohopane, 12% of moretane, and 85% of petroleum hopane may be present under equilibrium conditions at 400 K.[1] The composition of hopanes in petroleums is very closely represented by the above figures.

As already stated, the tetrahydric C_{35} alcohol bacteriotetrol is believed to be the source of hopanes (Scheme XI).

Scheme XI



C_{35}
bacteriotetral



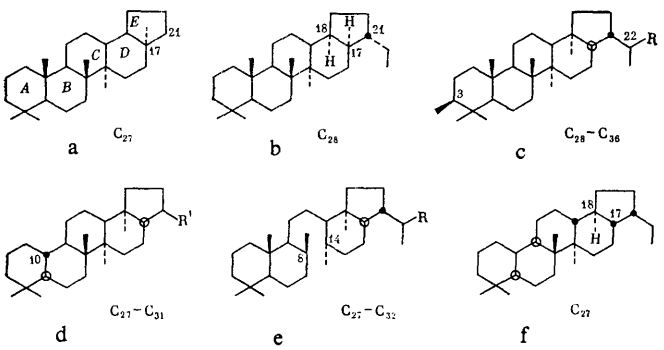
C_{27} 22, 29, 30-trisnormethylhopane; C_{29} adiantane; C_{31} homohopane

The degradation of the main chain of this compound gives rise to the homologous series of $C_{27}-C_{35}$ hopanes (naturally with the exception of the C_{28} hopane).

The minor series of $C_{36}-C_{40}$ hopanes with higher molecular weights has been described.[56] Their aliphatic chains have no additional branches. Dimeric forms of hopanes and saturated

codimers of hopenes and sterenes have also been found.[57,58] The C(22) atom in C_{31} and higher hydrocarbons is chiral and readily undergoes epimerisation. For this reason, the $C_{31}-C_{35}$ petroleum, hopanes emerge on the chromatograms in the form of doublets consisting of the (22*S*)- and (22*R*)-epimers; the (22*R*)-configuration is characteristic of biohopane [the (22*S*)-epimers are naturally absent from biohopanes]. Fig. 3 presents a chromatogram for the petroleum from the Zapadno-Slavan'skoe deposit.¶ This petroleum is exceptionally rich in hopanes. The $C_{27}-C_{35}$ hopane peaks are clearly seen, including the doublet peak due to the $C_{31}-C_{35}$ 17α,21β-hopanes. The hopanes in petroleums are determined usually by mass fragmentography on the basis of the most important fragment ion with $m/z = 191$. Apart from the main ("classical") hopanes examined above, numerous representatives of hopanes with a modified skeleton have been found in petroleums.[1,53,59-63] Some of these compounds are presented in Scheme XII. (We draw attention to the fact that in the names of hydrocarbons the lost methyl group has a number assigned to it as the usual nomenclature for gopanes—see Scheme XI.)

Scheme XII



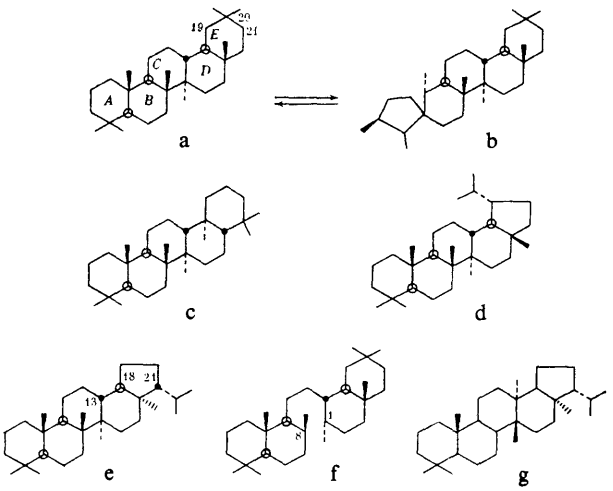
Thus the structure (XIIa), i.e. 17-methyl-22,29,30-trisnormethylhopane, is formed via the rearrangement of the usual C_{27} hopane. The rearrangement proceeds only in the C_{27} hopane, i.e. the hydrocarbon having no substituent at C(21). The structure (XIIb), i.e. 28,30-bisnormethylhopane, was first discovered in Sivinskaya petroleum [Perm Priural'e (Sub-Ural Region)].[1] In constrast to the remaining hopanes, here there is no methyl substituent at C(18). Since the angular methyl group (in the *D*/*E* rings) is absent, the system with a *D*/*E trans*-junction between the rings is more stable. In petroleums, this hydrocarbon is present as two epimers having the following steric structures: 17α,18α,21β and 17β,18α,21α; the structures (XIIc), i.e. 3-methylhopanes, present as a homologous series, have an additional methyl substituent in the *A* ring. The principal fragment ion in this series of hydrocarbons has $m/z = 205$. The chirality of the C(22) atom is manifested in this case starting from C_{32} hydrocarbons. On the other hand, a characteristic feature of the hydrocarbons in the homologous series (XIId) is the loss of the methyl group at C(10). The C(22) atom acquires chiral properties in this case starting with C_{30} hydrocarbons and the principal fragment ion in the mass spectra has $m/z = 177$. These hydrocarbons are mainly present in highly biodegradated petroleums.

The homologous series (XIIe) is represented by the so called 8,14-secohopanes, which are formed via the degradation of the most labile 8—14 bond. Their stereochemistry is the same as that of hopanes. The hydrocarbon (XIIf) is 25,28,30-trisnormethylmoretane.

Whereas the origin of hopanes is attributed mainly to the activity of micro-organisms, petroleums contain also other triterpanes (with the C_{30} composition), whose origin has a direct bearing on the plant materials involved in Continental genesis.[49,64-70]

The structures of some of these compounds are presented in Scheme XIII. All the hydrocarbons illustrated in Scheme (XIII) are triterpanes and contain 30 carbon atoms. Demethylated structures are encountered more rarely.

Scheme XIII

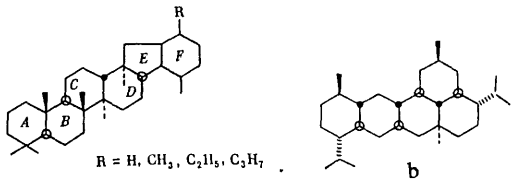


The hydrocarbons (XIIIa) and (XIIIb) (oleanane and spirotriterpane), belonging to the first group, are closely related via the carbonium ion 1,2-rearrangement. Lupane (XIIId), formed as a result of the contraction of the *E* ring with formation of the 19—21 bond and dissociation of the 20—21 bond, is closely related to them. The hydrocarbon (XIIIc) (gammacerane) has been found in large amounts in the petroleum produced by Continential genesis (China, Indonesia, Australia). The hydrocarbon neohopane (isohopane) (XIIIe) is usually present in brown coal, although it is found in small amounts also in petroleums. The hydrocarbon 8,14-secooleanane (XIIIF) is formed as a result of the degradation of the strained 8—14 bond of oleanane similarly to the 8—14-secogopanes examined previously. Fernane (XIIIg) is present in lichens, mosses, and peat.

All the hydrocarbons examined in Scheme (XIII) (including hopane) can be formed as a result of the cyclisation of squalane present in different conformations.[71] Like steranes, all the petroleum triterpanes exhibit a high optical activity, because they each contain four chiral centres formed by non-epimerising quaternary carbon atoms.

In conclusion of this Section, one should consider the homologous series of hexacyclic $C_{32}-C_{35}$ terpenoids discovered recently in petroleums[72] and also dicadinane—a C_{30} pentacyclic triterpenoid[73] (Scheme XIV).

Scheme XIV



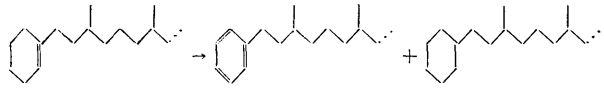
¶ Al A Petrov, *Geologiya Nefti i Gaza*, 1988, No. 10, p. 50.

The hydrocarbons of the first series (XIVa) are formed from bacteriotetrol simultaneously with benzohopanes having a similar structure (with the aromatic *F* ring). This reaction will be examined in greater detail in the next Section.

Bicadinane (XIVb) can be regarded as the product of the dimerisation of cadinene (eudesmane). The presence of two isopropyl groups leaves no doubt about its isoprenoid nature. Bicadinane has certain structural features characteristic of the tetracyclic C_{19} diterpenoids considered above.

IV. Aromatic isoprenoids

Aromatic isoprenoid compounds are usually absent from natural bioorganic objects. Therefore this Section will deal with the secondary products formed as a result of the redistribution of hydrogen (on clays) in hydrocarbons whose six-membered rings contain multiple bonds. Thus the aromaticity of these hydrocarbons is a secondary feature.

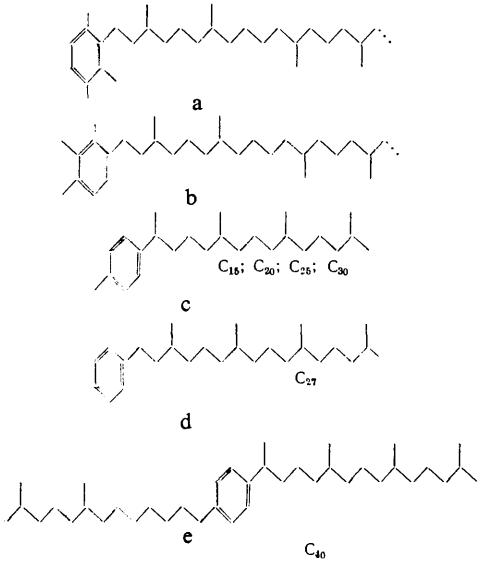


However, the character of the hydrocarbons examined below leaves no doubt about the isoprenoid nature of the compounds from which they have been formed. As will be shown below, overall the aromatic isoprenoid hydrocarbons are very similar in their structure (naturally with certain exceptions) to their alicyclic analogues.

1. Monocyclic hydrocarbons

Scheme (XV) presents the formulae of hydrocarbons [represented mainly by the $C_{10}-C_{30}$ homologous series (XVa, b)] containing a benzene ring and an aliphatic isoprenoid chain.

Scheme XV

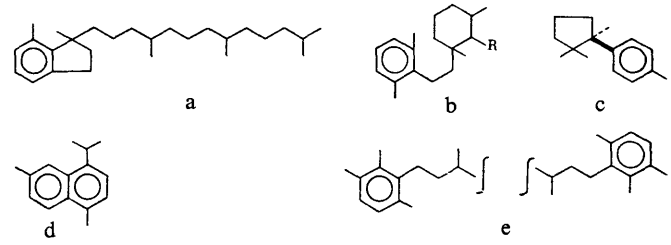


The structure of the hydrocarbons (XVa) and also the absence of the C_{12}, C_{17}, C_{23}, and C_{28} homologues from this series leaves no doubt that we are dealing here with aromatic derivatives of carotane. Hydrocarbons of the series (XVb) having a similar structure are present at lower concentrations. Apart from aromatic derivatives of carotane, $C_{15}-C_{30}$ methylalkylbenzenes (XVc), having a regular isoprenoid chain, have been found in petroleum. In contrast to aromatic carotenoids, C_{15}, C_{20}, C_{25}, and C_{30} hydrocarbons clearly predominate here, i.e. these hydrocarbons are sesquiterpanes, diterpanes, sesterterpanes, and triterpanes. A C_{27} hydrocarbon (XVd), having a regular isoprenoid chain, is present in certain petroleums at very high concentrations. An interesting aromatic phytadiene "dimer" (XVe) has been described.[75]

2. Bicyclic hydrocarbons

The C_{27} indan homologue (XVIa), with a regular isoprenoid chain, has been reliably identified in a number of petroleums[74] (Scheme XVI).

Scheme XVI

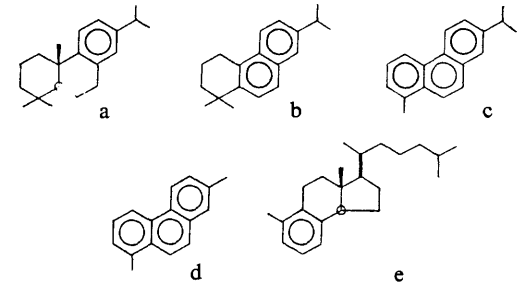


A group of phenylethylcyclohexanes (XVIb), formed via the degradation of the middle ring of the tricyclic isoprenoids (VIIa), has also been described.[57] The interesting hydrocarbon cuparene (XVIc) is a representative of the rarely encountered group of aromatic sesquiterpenoids.[2] Among naphthalene derivatives, cadalane (XVId) is undoubtedly isoprenoid in character.[76] A biaromatic analogue (XVIe) of β-carotane has been described. The hydrocarbon has been called isorenieratene.

3. Tricyclic hydrocarbons

Tricyclic aromatic isoprenoids are relatively less abundant in petroleums. Scheme (XVII) presents the formulae of four hydrocarbons formed on aromatisation of diterpenoids: dehydroabietane (XVIIa), simonellite (XVIIb), retene (XVIIc), and pimanthrene (XVIId).[78] The structure (XVIIe) is formed on degradation on the *A* ring in regular steranes (sterols).[79]

Scheme XVII



4. Tetracyclic hydrocarbons

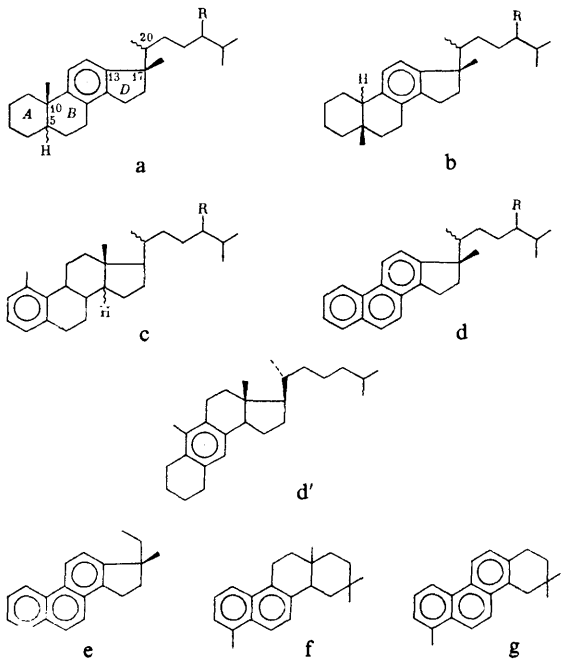
This group of compounds is extremely abundant in petroleums because the interaction of sterols with clays results in the formation, apart from saturated steranes, also of their aromatic analogues having from one to three aromatic rings in the molecule.[80,81]

A fairly large amount of attention has been devoted in the scientific literature to aromatic petroleum steranes.[1,2,82-90]

It has been found that the *C* ring is preferentially aromatised in steranes (steranes with the aromatic *A* ring are less common). Subsequently the *B* and *A* rings are aromatised simultaneously in *C*-aromatic steranes, which leads to triaromatic steranes containing the phenanthrene system. On aromatisation of the *A* ring, the angular methyl group at C(13) migrates to the C(17) atom. On exhaustive aromatisation, the methyl group at C(10) is usually eliminated. Monoaromatic steranes (*C* ring) have been identified in the mass spectra from the fragment with $m/z = 253$ (abstraction of an aliphatic group). In the mass spectra of steranes with an aromatic *A* ring, the principal fragment ion has $m/z = 211$. Triaromatic steranes are characterised by a fragment ion with $m/z = 231$ (also with abstraction of an aliphatic group).

Scheme (XVIII) presents the formulae of the most important aromatic steranes identified in petroleums as well as the formulae of certain other tetracyclic compounds.[91]

Scheme XVIII



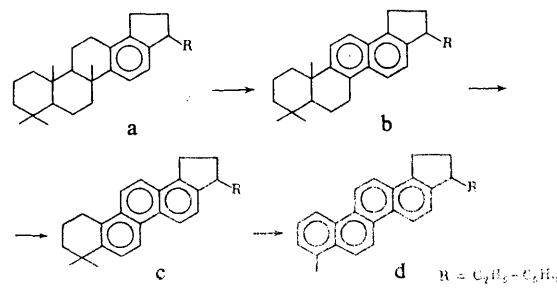
Monoaromatic steranes (XVIIIa) are present in the form of four epimers: 5α,20*R*; 5α,20*S*; 5β,20*R*; 5β,20*S*. In contrast to saturated steranes, in this case the 5β-isomers are more stable (because of the distortion of the *B* ring).[84] The structures (XVIIIa, d) are the most common in petroleums. Their ratio is widely used as an important correlation factor determining the degree of catagenic maturity of the petroleum. Since the exhaustive aromatisation process is accompanied by the degradation of the side chain in steranes, the petroleums contain, apart from the $C_{26}-C_{28}$ steranes [structures of the type (XVIIId)], a series of triaromatic steranes with shorter aliphatic chains, for example, compound (XVIIIe).[89]† Partly aromatised molecules of the pentacyclic triterpanes (XVIIIf, g), which have undergone degradation (*E* rings), have been found in petroleums.[91]

† The sterane (XVIIId′) with an aromatic *B* ring belongs to the class of the rarely encountered anthrasteroids.[89]

5. Pentacyclic hydrocarbons

The formation of pentacyclic aromatic petroleum isoprenoids is wholly associated with the aromatisation of triterpenoids, especially hopane and its homologues. Aromatic derivatives of adiantane, hopane, and homohopanes have been described.[92,93] The aromatisation of the rings takes place gradually in the sequence $D \rightarrow C \rightarrow B \rightarrow A$ with the simultaneous loss of methyl substituents (Scheme XIX).

Scheme XIX

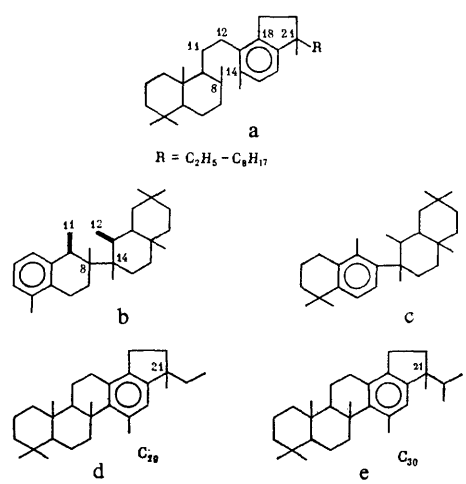


Another group of aromatic hydrocarbons formed from hopanes has also been discovered.[94-96] It has been shown that the aromatisation (of the *D* ring) takes place with the simultaneous dissociation of the most labile 8–14 bond. This results in the formation of tetracyclic monoaromatic 8,14-secohopanes of type (XXa) [we may note the interesting 1,3-migration of the methyl group from C(18) to C(21)[96] (Scheme XX)].

An example of other secotriterpanes (XXb, c), formed from oleanane (β-amyrin) with dissociation of the 11–12 bond, has been quoted.[76]

Interesting pentacyclic hopanes (XXd, e) with an aromatic *D* ring have been discovered in Soviet petroleums.[94] As in the case of secohopanes, their formation probable involved the migration of the methyl group from the C(18) atom to the C(21) atom. An intense fragment ion with $m/z = 363$ is characteristic of the mass spectra of these hydrocarbons. It is formed as a consequence of the elimination of the aliphatic substituent at C(21), similar to the elimination of the substituent in monoaromatic steranes ($m/z = 253$) or in secohopanes ($m/z = 365$).

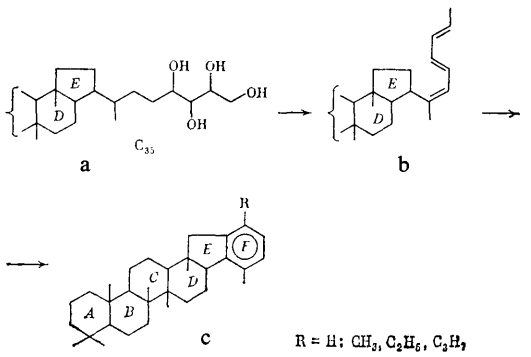
Scheme XX



6. Hexacyclic hydrocarbons

A series of hexacyclic hydrocarbons with one aromatic ring can be obtained from bacteriohopane with the simultaneous formation of hydrocarbons of the hopane series[96–98] (Scheme XXI). These hydrocarbons have been called benzohopanes.

Scheme XXI



The dehydration of the tetrol (XXIa) on clays leads to a series of polyenes (XXIb), capable of intramolecular cyclisation with formation of an aromatic *F* ring. This entails the partial degradation of fragments of the aliphatic chain. In addition to compounds (XXIc), their saturated heterocyclic analogues, described previously, are also formed simultaneously. It is striking that only $C_{32}-C_{35}$ hexacyclic compounds have been found in petroleums in both cases.

V. Conclusion

We shall now describe certain conclusions which arise from the data examined. The large number of studies carried out in recent years on the chemistry and geochemistry of petroleum have demonstrated an appreciable content of aliphatic, alicyclic, and aromatic isoprenoids in the test objects. The structures of all the compounds identified are directly related to those of their biological precursors.

The number of isoprenoid hydrocarbons in petroleums reaches 300 items and their overall concentration is in many instances 20–25% relative to the petroleum hydrocarbons. We may note that the sulphur- and oxygen-containing components of petroleum are also made up mainly of the same structural fragments with a clear predominance of isoprenoid structures.[99,100] All these findings undoubtedly confirm the bioorganic nature of the petroleum, which is a product of the transformation of the lipid component of ancient living matter: algae, bacteria, and higher plants. Petroleum hydrocarbons, which preserve information about the composition and structure of their bioorganic precursors because of their relative chemical stability, have therefore been called biological labels or chemofossils. They are sometimes also referred to as relict compounds.

However, the role of biological labels is not limited to the conclusion that petroleum is bioorganic in origin. They are much more important in modern geochemical methods used in prospecting for petroleum deposits.[1,2,101–104] Thus the characteristics of the qualitative and quantitative distribution of isoprenoid hydrocarbons in petroleums are used to determine the type of organic matter: marine (seaweed, plankton), continental, and highly modified by microbiological action. Typical parameters of the marine matter are, for example, high concentrations of steranes (especially with the C_{27} composition) and phytane. On the other hand, in the petroleums generated from continental (plant) organic matter pristane predominates, there are no steranes, and at the same time triterpanes, such as, for example, oleanane, and diterpanes, such as phyllocladane and kaurane, are present. The intense microbiological processing of organic matter is also indicated by the high concentrations of gopanes and the presence of irregular aliphatic isoprenoids with "head to head" fragments, etc. Isoprenoid petroleum hydrocarbons can be used also to determine the paleo-conditions for the accumulation of deposits and the transformation of organic matter into petroleum. Thus T-shaped isoprenanes and gammacerane arise in highly saline media. Rearranged steranes are usually absent from carbonate deposits (rocks), which are in fact most often formed in terrigenic (argillaceous) deposits. In addition, the proportions of aliphatic isoprenoids, steranes, and hopanes excellent "fingerprints" of particular petroleums,[1,2] which make it possible to determine the source from which they have been formed and the ways in which petroleums have migrated in the Earth's core.

Finally, the change in the stereochemistry of hopanes and especially steranes is widely used to determine the degree of "maturation" (catagenic modification) of organic matter in the regions and deposits up to the petroleum level which have been investigated. This is based on the fact that the initial (immature) organic matter always has the natural (biological) configuration of the labile chiral centres, for example C(17), C(21), and C(22) in hopanes and C(14), C(17), and C(20) in steranes. Petroleums usually consist of a catagenically fairly mature product (corresponding to the E–D stage on the coal metamorphism scale) which has been stereochemically modified. The formation of appreciable petroleum deposits is therefore possible, in principle, only in those places where the organic matter is characterised by the presence of 17α,22β-hopanes and (14β,17β,20*S*)- and the corresponding (20*R*)-steranes.

The distribution of isoprenoid hydrocarbons is also used for the chemical (geochemical) classification of petroleums and also for the estimation of the degree of microbiological transformation of petroleum.[1,2] Thus the practical importance of isoprenoid petroleum hydrocarbons (as well as other biomarkers) is very great. There is no doubt that these compounds have great potential possibilities and that there are good prospects for their wide scale practical use.

References

1. Al A Petrov *Uglevodorody Nefti* (Petroleum Hydrocarbons), Izd. Nauka, Moscow, 1984, 286 pp
2. A Mackenzie *Advances in Petroleum Geochemistry*, Acad. Press, London, 1984, Vol. 1, p. 115
3. P I Sanin *Usp. Khim.*, 1976, **45**(8) 1361 [English translation in *Russ. Chem. Rev.*, 1976(8)]
4. L S Golovkina, G V Rusinova, Al A Petrov *Usp. Khim.*, 1984, **53**(9) 1493 [English translation in *Russ. Chem. Rev.*, 1984(9)]
5. R Dean, E Whitehead *Tetrahedron Lett.*, 1961, 768
6. G I Safonova *Reliktovye Struktury v Uglevodorodakh Neftei Razlichnykh Stratigraficheskikh Podrazdelenii* (The Relict Structures in the Hydrocarbons of Petroleums from Different Stratigraphic Subdivision), Izd. Nedra, Moscow, 1980, 260 pp
7. J Albaiges, G Borbon, P Salagre *Tetrahedron Lett.*, 1978, 595
8. J Albaiges *Advances in Organic Geochemistry: Physics and Chemistry of the Earth*, Pergamon Press, Newcastle-on-Tyne, 1979, Vol.12, p. 19

9. R Patience, D Yon, G Ryback, J Maxwell *Advances in Organic Geochemistry: Physics and Chemistry of the Earth*, Pergamon Press, Newcastle-on-Tyne, 1979, Vol.12, p. 287
10. R Patience, S Rowland, J Maxwell *Geochim. Cosmochim. Acta*, 1978, **42** 1871
11. P Brooks, J Maxwell, J Cornforth, et al. *Advances in Organic Geochemistry*, Enadisma, Madrid, 1975, p. 81
12. N S Vorob'eva, Z K Zemskova, Al A Petrov *Neftekhimiya*, 1982, **22** 587
13. N S Vorob'eva, Z K Zemskova, Al A Petrov *Neftekhimiya*, 1987, **27** 308
14. B Chappe, W Michaelis, P Albrecht *Physics and Chemistry of the Earth*, 1979, Vol. 12, p. 265
15. J Moldowan, W Seifert *Science*, 1979, **204** 912
16. N S Vorob'eva, Z K Zemskova, Al A Petrov *Neftekhimiya*, 1986, **26** 579
17. D Yon, J Maxwell, G Ryback *Tetrahedron Lett.*, 1982, **23** 2143
18. S Rowland, D Yon, C Lewis, J Maxwell *J. Org. Geochem.*, 1985, **8** 207
19. J Moldowan, W Seifert *J. Chem. Soc., Chem. Commun.*, 1980, 912
20. S Brassell, G Eglinton, Juamo Fu *The XII International Meeting on Organic Geochemistry. Jülich*, Pergamon Press, 1985, p. 38
21. C Largen, A Kadonri, S Derenne, E Casadevall *The XII International Meeting on Organic Geochemistry. Jülich*, Pergamon, 1985, p. 22
22. N S Vorob'eva, Z K Zemskova, K Poladov, et al. *Neftekhimiya*, 1985, **25**(6) 25
23. I M Sokolova, S S Berman, E S Gervits, et al. *Neftekhimiya*, 1981, **21** 20
24. N S Vorob'eva, Z K Zemskova, Al A Petrov *Neftekhimiya*, 1980, **20** 483
25. P Hall, A Douglas *Advances in Organic Geochemistry*, Wiley, Chichester, 1983, p. 576
26. G R Kagramanova, S D Pustil'nikova, T I Pekhk, et al. *Neftekhimiya*, 1976, **16** 18
27. R Alexander, R I Kagi, R Noble, J Volkman *J. Org. Geochem.*, 1984, **6** 61
28. R Philip, T Gilbert, J Friedrich *Geochim. Cosmochim. Acta*, 1981, **45** 1173
29. N S Vorob'eva, Z K Zemskova, Al A Petrov *Neftekhimiya*, 1978, **18** 855
30. N F Aquino, J Trendel, A Restle, et al. *Advances in Organic Geochemistry*, Wiley, Chichester, 1983, p. 659
31. A Ekweozor, O Strausz *Advances in Organic Geochemistry*, Wiley, Chichester, 1983, p. 746
32. W Seifert, J Moldowan *Geochim. Cosmochim. Acta*, 1981, **45** 783
33. J Connan, A Restle, P Albrecht *Advances in Organic Geochemistry: Physics and Chemistry of the Earth*, Pergamon Press, Newcastle-on-Tyne, 1979, Vol. 12, p. 1
34. R Noble, R Alexander, R I Kagi *Advances in Organic Geochemistry*, Organic Geochemistry, 1986, Vol. 10, p. 825
35. Al A Petrov *Stereokhimiya Nasyshchennykh Uglevodorodov* The Stereochemistry of Saturated Hydrocarbons), Izd. Nauka, Moscow, 1981, 256 pp
36. A Ensminger, G Joly, P Albrecht *Tetrahedron Lett.*, 1978, 1575
37. L Mulheirn, G Ryback *Advances in Organic Geochemistry*, Enadisma, Madrid, 1975, p. 173
38. W Seifert, J Moldowan *Geochim. Cosmochim. Acta*, 1979, **43** 111
39. A Mackenzie, R Patience, J Maxwell, et al *Geochim. Cosmochim. Acta*, 1980, **44** 1709
40. J Curiale *Org. Geochem.*, 1987, **11** 233
41. O A Aref'ev, M N Zabrodina, V M Makushina, Al A Petrov *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1980, (3) 135
42. A M Kuliev, Al A Petrov, A M Levshina, et al. *Azerb. Khim. Zh.*, 1984, (2) 48
43. J Moldowan *Geochim. Cosmochim. Acta*, 1984, **48** 2767
44. J Trendel, A Restle, J Connan, P Albrecht *J. Chem. Soc., Chem. Commun.*, 1982, 304
45. R Noble, R Alexander, R I Kagi, J Knox *Geochim. Cosmochim. Acta*, 1985, **49** 2141
46. N S Vorob'eva, Z K Zemskova, T I Pekhk, Al A Petrov *Neftekhimiya*, 1986, **26** 291
47. M Kaneda, F Takahashi, J Jitaka, et al. *Tetrahedron Lett.*, 1972, 4609
48. A Van Dorsselaer, A Ensminger, C Spyckerelle, et al. *Tetrahedron Lett.*, 1974, 1349
49. G Eglinton, M I J Murphy *Organic Geochemistry* (Translated into Russian), Izd. Nedra, Leningrad, 1974, 487 pp
50. S Brassell, G Eglinton, J Maxwell *Biochem. Soc. Trans.*, 1983, **11** 575
51. E Whitehead *Advances in Organic Geochemistry*, Technip, Paris, 1973, p. 225
52. A Ensminger, A Van Dorsselaer, C Spyckerelle *Advances in Organic Geochemistry*, Technip, Paris, 1973, p. 215
53. W Seifert, J Moldowan *Geochim. Cosmochim. Acta*, 1978, **42** 77
54. G Ourisson, P Albrecht, M Rohmer *Pure Appl. Chem.*, 1979, **51** 709
55. W Seifert, J Moldowan *Geochim. Cosmochim. Acta*, 1979, **43** **111**
56. K Rullkötter, P Philp *Nature (London)*, 1981, **292** 616
57. T Jena, G V Chilingar (Editors), *Oil Shale* (Translated into Russian), Izd. Nedra, Leningrad, 1980, 262 pp
58. H Olert, D Severin, H Windhager *Brennst. Chem.*, 1973, **26** 392
59. J Rullkötter, D Wendisch *Geochim. Cosmochim. Acta*, 1982, **46** 1545
60. J Moldowan, W Seifert, E Arnold, J Clady *Geochim. Cosmochim. Acta*, 1984, **48** 1651
61. J Volkman, R Alexander, R Kagi, G Woodhouse *Geochim. Cosmochim. Acta*, 1983, **47** 785
62. G P Kayukova, S D Pustil'nikova, N N Abryutina, et al. *Neftekhimiya*, 1981, **21** 803
63. P Grantham, J Posthuma, K De Groot *Advances in Organic Geochemistry*, Pergamon Press, Oxford, 1980, p. 29
64. P Grantham, J Posthuma, A Baak *Advances in Organic Geochemistry*, Wiley, Chichester, 1983, p. 675
65. C Ekweozor, J Okogun, D Ekong, J Maxwell *Chem. Geol.*, 1979, **27** 11
66. J Hills, G Smith, E Whitehead *Nature (London)*, 1968, **219** 243
67. J Rullkötter, D Leythaeuser, D Wendisch *Geochim. Cosmochim. Acta*, 1982, **46** 2507
68. J Shi, A Mackenzie, R Alexander, et al. *Chem. Geol.*, 1982, **35** 1
69. A Mackenzie, S Brassell, G Eglinton, J Maxwell *Science*, 1982, **217** 491

70. N S Vorob'eva, Z K Zemskova, Al A Petrov *Khim. Tverd. Topliva*, 1984, (5) 40
71. R Clayton *Quart. Rev.*, 1965, **29** 168
72. J Connan, D Dessort *Org. Geochem.*, 1987, **11** 103
73. H Cox, J de Leuw, P Schenk, et al. *Nature (London)*, 1986, **319** 316
74. S B Ostroukhov, O A Aref'ev, V M Makushina, et al. *Neftekhimiya*, 1982, **22** 723
75. B Simoneit, A Burlingame *Advances in Organic Geochemistry*, Technip, Paris, 1973, p. 629
76. J Bendoraitis *Advances in Organic Geochemistry*, Technip, Paris, 1973, p. 209
77. J Schaefle, B Ludwig, P Albrecht, G Ourisson *Tetrahedron Lett.*, 1977, 3673
78. B Simoneit, J Grimalt, T Wang, R Cox *Org. Geochem.*, 1986, **10** 877
79. T Peakman, P Farrimond, S Brassell, J Maxwell *The XII International Meeting on Organic Geochemistry. Jülich*, Pergamon Press, 1985, p. 43
80. O Sieskind, G Joly, P Albrecht *Geochim. Cosmochim. Acta*, 1979, **43** 1675
81. S D Pustil'nikova, N N Abryutina, G P Kayukova, et al. *Geokhimiya*, 1982, (1) 144
82. W Seifert, R Carlson, J. Moldowan *Advances in Organic Geochemistry*, Wiley, Bergen, 1983, p. 710
83. A Mackenzie, C Hoffman, J Maxwell *Geochim. Cosmochim. Acta*, 1981, **45** 1345
84. V G Zubenko, N S Vorob'eva, Z K Zemskova, et al. *Neftekhimiya*, 1981, **21** 323
85. V G Zubenko, S D Pustil'nikova, N N Abryutina, Al A Petrov *Neftekhimiya*, 1986, **20** 490
86. J Moldowan, F Fago *Geochim. Cosmochim. Acta*, 1986, **50** 343
87. J Riolo, P Albrecht *Tetrahedron Lett.*, 1985, **26** 2701
88. J Riolo, G Hussler, P Albrecht, J Connan *Advances in Organic Geochemistry*, Org. Geochem., 1986, **10** 981
89. A Yu Kolesnikov, I A Matveeva, G N Gordadze, Al A Petrov *Neftekhimiya*, 1986, **26**, 583; H Hussler, P Albrecht, *Nature (London)*, 1983, **304** 262
90. B Ludwig, G Hussler, P Albrecht *Tetrahedron Lett.*, 1981, **22** 3313
91. C Spyckerelle, A Greiner, P Albrecht, G Ourisson *J. Chem. Res.*, 1977, 330
92. A Greiner, C Spyckerelle, P Albrecht *Tetrahedron*, 1976, **32** 257
93. S Wakeham, G Schaffner, W Geiger *Geochim. Cosmochim. Acta*, 1980, **44** 451
94. V G Zubenko, G N Gordadze, Al A Petrov *Neftekhimiya*, 1979, **19** 833
95. J Schmitter, W Sucrow, P Arpino *Geochim. Cosmochim. Acta*, 1982, **46** 2345
96. G Hussler, J Connan, P Albrecht *Org. Geochem.*, 1984, **6** 39
97. S B Ostroukhov, O A Aref'ev, Al A Petrov *Neftekhimiya*, 1983, **23** 152
98. G Hussler, P Albrecht, G Ourisson, M Cesario *Tetrahedron Lett.*, 1984, **25** 1179
99. V F Kam'yanov, V S Aksenov, V I Titov *Geteroatomnye Komponenty Nefti* (Heteroatomic Components of Petroleum), Izd. Nauka, Novosibirsk, 1983, 238 pp
100. J Valisolalao, N Perakis, B Chappe, P Albrecht *Tetrahedron Lett.*, 1984, **25** 1183
101. B P Tissot, D H Welte *Petroleum Formation and Occurrence* (Translated into Russian), Izd. Mir, Moscow, 1981, 501 pp
102. Al A Petrov *Geologiya Nefti i Gaza*, 1985, (10) 29
103. D McKirdy, A Aldridge, P Ypma *Advances in Organic Geochemistry*, Wiley, Chichester, 1983, p. 99
104. W Seifert, J Moldowan *Geochim. Cosmochim. Acta*, 1978, **42** 77

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Thermostable and fire-resistant polymers based on chloral and its derivatives

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ABSTRACT. The possible ways of using chloral and its derivatives as monomers for the synthesis of fire-resistant and thermostable carbochain and heterochain polymers are examined. Questions concerning the synthesis from chloral of the polyfunctional monomers used to prepare polyheteroarylenes with specific properties are given an especially detailed consideration.

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I. Introduction

The development of raw materials for the synthesis of polymers and materials derived from them is a key problem which in many respects determines the successful and intensive development of the chemistry and technology of high-molecular-weight compounds. The problem of ensuring the supply of monomers for the development of polymers with specific properties—fire resistance, thermal stability, etc.—in which considerable progress has been made during the last decade, is especially acute.[1]

The use of chloral, which is produced on a large scale,[2,3] its output in 1970 in the USA being at the level of 50 000 tonnes annually, as the raw material for the synthesis of monomers of this kind is therefore of considerable interest. Chloral is the starting material for the synthesis of pharmaceuticals, especially pure chloroform, herbicides (sodium trichloroacetate, dichloral-urea) and insecticides of the type of chlorophos.[3] However, the principal application of chloral has always been the manufacture of DDT [4]—a widely used insecticide, whose world production in 1956 was 80 000 tonnes.[5] Between 1942 and 1974, 4.5 million tonnes of DDT were used in the fight against agricultural pests throughout the world[6] and during the antimalarial compaign over a period of many years the application of DDT saved more than 1 billion people from malaria.[7] Furthermore, it helps to eradicate diseases such as the plague, typhoid, sleeping sickness, yellow fever, leishmaniasis, colorado tick fever, etc.[7]

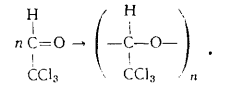
During the last 20–25 years, an acute controversy has developed concerning the toxic effect of DDT on the human organism which it enters as a result of being incorporated in the "food chain", including plants and animals used by man, as a result of which the World Health Organisation forbade the use of this preparation as an insecticide or in any other way leading to the possibility of its being incorporated in the "food chain". Furthermore, many pests (about 200 species) have developed resistance to DDT as a result of its frequent application. Consequently in all the major states a programme for the gradual replacement of DDT has been put in train and in 1963 its manufacture and the associated manufacture of chloral already began to decrease.[3,7] Nevertheless the output of these products has continued to be considerable (mainly for the use of DDT in developing countries[7]) and the manufacturing capacity for chloral and DDT available in the world is capable of meeting the highest requirements for these products.

In view of the foregoing, the use of chloral and DDT for the synthesis of polymers with specific properties appeared extremely attractive.

The promising nature of this aspect has been partly demonstrated in a number of studies[8–11] but none of them reflect the set of possibilities inherent in the use of these compounds—direct or indirect—in the chemistry and technology of polymers. Within the framework of this review, we have attempted to consider as widely as possible the ways of utilising chloral and DDT for the preparation of thermostable and fire-resistant polymers.

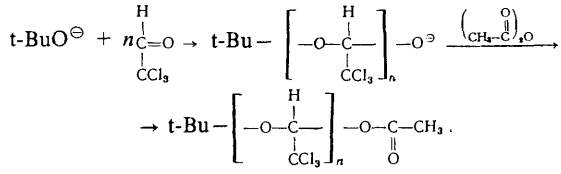
II. Chloral homopolymers and copolymers

Since the polymerisation of aldehydes, involving the partial dissociation of a carbon–oxygen bond, is a familiar reaction in the synthesis of polymers,[12] it is quite natural that the polymerisation of chloral became the first application of this product in the chemistry of polymers.[12–15] Vogl showed that chloral can polymerise via both anionic and cationic mechanisms:

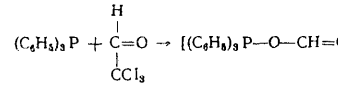


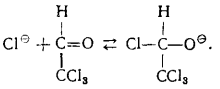
The tendency of aldehydes to polymerise is correlated with the polarisation of the double bond of the carbonyl group, which is reflected in the position of the C=O band in the IR spectrum. Aldehydes in which the absorption frequency of the carbonyl group is above 1750 cm^{-1} and especially chloral readily polymerise via an anionic mechanism on treatment with nucleophiles.[16] The most widely used initiators are alkali metal alkoxides, tertiary amines, tertiary phosphines, quaternary ammonium and phosphonium salts, as well as organometallic compounds. Even when comparatively weak nucleophiles are employed, the anionic polymerisation takes place at a high rate and leads to the formation of polychloral in a high yield. For example, the block polymerisation of chloral using 0.2 mol% of lithium t-butoxide as the initiator leads to the

formation of polychloral in 85% yield after 3 min.[17] A study of the mechanism of chain propagation by stopping the polymerisation at early stages of the process showed that it proceeds via the mechanism[18,19]



When triphenyl phosphite is used as the initiator,[20] the polymerisation reaction proceeds, according to Hoffmann and Diehr,[21] in conformity with the following scheme:





In the presence of anionic initiators, chloral is polymerised by a special method. It consists in carrying out the initiation at a temperature above the limiting value followed by the polymerisation after cooling below the limiting temperature.[14,15,17] This process makes it possible to obtain polychloral in the form of desirable materials.

The cationic polymerisation of chloral can be initiated only by strong Lewis and Brønsted acids (BF_3, CH_3SO_3H, H_2SO_4); the rate of polymerisation is then significantly lower—when 2 mol% CH_3SO_3H is used as the initiator at −5 °C for 300 h, the degree of conversion is only 40%. A noteworthy exception is observed in polymerisation initiated by $AlCl_3$ and $SbCl_2$; in these cases, polychloral was obtained in a high yield, but there are doubts about the purely cationic nature of this process which might have been initiated also by chlorine.[12]

Polychloral is completely insoluble in organic solvents because of its isotactic structure,[12,22] demonstrated by X-ray diffraction, ^{13}C NMR, and ^{35}Cl NQR and caused by the large bulk of the trichloromethyl side groups. The same fragments which are responsible for the high chlorine content in polychloral give rise also to the virtual incombustibility of this polymer.

The mechanical, electrical, and thermal properties of polychloral have been examined.[23] The polymer is characterised by moderate crystallinity; its density is 1.9 g cm^{-3} and its refractive index is $n_D^{25} = 1$. Its thermal expansion coefficient is 4×10^{-5} K^{-1}. Polychloral fibres have a tensile strength of the order of 40 mPa and an elongation on rupture of the order of 25%. The coefficient of friction of polychloral, both static and dynamic, is 0.55.

The dielectric constant of polychloral at room temperature is 2.8, its scattering factor is 0.003, and its electrical resistivity is 4×10 Ω cm.

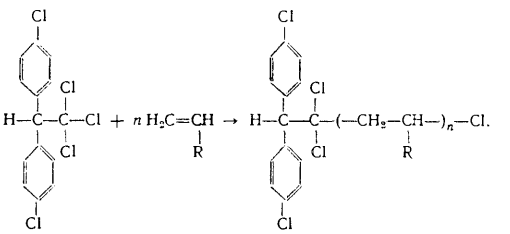
The thermal stability of polychloral obtained as a result of polymerisation is low (220 °C); as for other polyacetals, regardless of the methods of polymerisation subsequent treatment leads to the formation of more stable end groups. Thus the comparatively low thermal stability of the polychloral obtained by the anionic mechanism is due to the presence of alkoxy-end groups with which the depolymerisation process begins. The mechanism of the degradation of the polychloro-compound has been investigated in fair detail.[24] Thermogravimetric analysis of polychloral showed that the unstabilised polychloral is degraded at comparatively low temperatures. The bimodal and even trimodal character of the differential thermogravimetric analysis curves indicate the presence of two or three polychloral fractions with different end groups.[24]

The methods for the introduction of more stable end groups during and after the polymerisation of chloral include the use of the corresponding chain transfer agents, decomposing counterions etc. as well as different versions of the treatment of the polymer already obtained. Thus, when the polymerisation is initiated by triphenylphosphine and the polymer is subsequently treated with PCl_5 in CCl_4, polychloral acquires a greater thermal stability. On heating in an atmosphere of nitrogen at a rate of 20 K min^{-1}, this type of polychloral begins to degrade at 250 °C and the maximum rate of degradation is attained at 340 °C. Thus correctly stabilised polychloral has the same thermal stability as the industrial (i.e. stabilised) polyoxymethylene.

Polychloral does not melt without decomposition. Its hypothetical melting point (~460 °C), which is far removed from its degradation temperature, has been obtained by extrapolating the melting points of chloroal–formaldehyde complexes.[23]

The copolymers of chloral with other monomers have attracted much attention among investigators; copolymers of this product with a wide variety of comonomers have been described in the patent literature. However, one should note that the copolymerisation reactions of chloral with mono- and di-chloroacetaldehydes,[25] aliphatic and aromatic isocyanates,[26–28] ketones, formaldehyde, and trioxane have been studied in greatest detail. The copolymers of chloral with monochloroacetaldehyde are soluble in chloroform, while its copolymers with dichloroacetaldehyde are insoluble. None of the copolymers melt below the thermal degradation temperature and their thermal stabilities are intermediate between those characteristic of the corresponding homopolymers.

Yet another possible application of chloral in polymerisation processes is associated with the presence in it of the trichloromethyl group, which plays the role, under certain conditions, of an active centre at which radical processes take place. Thus the telomerisation of ethylene, propene, butene, and a number of other polymers using DDT has been examined:[29]



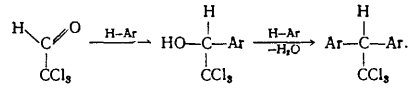
The presence of trichloromethyl substituents in the chloral homopolymers and copolymers leads to the possibility, by analogy with the process examined above,[29] of modifying these polymers by the graft polymerisation reactions. According to a number of investigators,[30–32] such reactions should proceed especially effectively in the presence of metal carbonyls. The radical formation process in the systems considered usually involves electron transfer from the transition metal to the halogeno-derivative; the metal then passes to a higher oxidation state and the halogen-derivative decomposes into ionic and radical fragments.[32]

Despite the availability of the starting material, the chloral homopolymers and copolymers as well as their modification products have not found practical applications. The condensation polymers, obtained from chloral derivatives and DDT, are more promising in this respect.

III. Chloral-based condensation monomers

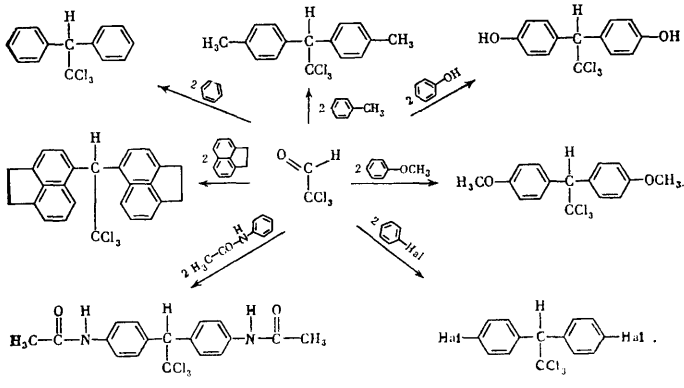
The majority of syntheses of condensation monomers using chloral are based on the well known reactions of this compound with aromatic hydrocarbons, aromatic alkyl-substituted hydrocarbons, and aromatic hydrocarbons containing various functional groups[2] with subsequent reactions of the diaryltrichloroethanes obtained in this way via the central chloroethane fragments and the aromatic rings.

The condensation reactions between chloral and aromatic hydrocarbons and their derivatives, leading to the formation of diaryltrichloroethane derivatives, are carried out in the presence of an acid catalyst and proceed with formation of intermediate carbinols:[33]

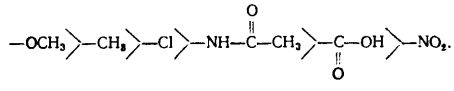


Concentrated H_2SO_4 or its monohydrate, HCl, HF, P_2O_5, H_2PO_4, Lewis acids, and a number of other acid agents are usually employed as catalysts.[2]

In a series of numerous reactions of chloral with aromatic hydrocarbons and their derivatives, the greatest interest attaches, from the standpoint of the synthesis of condensation monomers, to the reactions of chloral with benzene,[34] toluene,[35] acenaphthene,[36] phenol,[37] anisole,[38] acetanilide,[39] and halogenobenzenes—especially chlorobenzene[40] and fluorobenzene.[41] Thes reactions take place in accordance with an idealised scheme and lead to the formation of the target 2,2-diaryl-1,1,1-trichloroethanes in high yields:

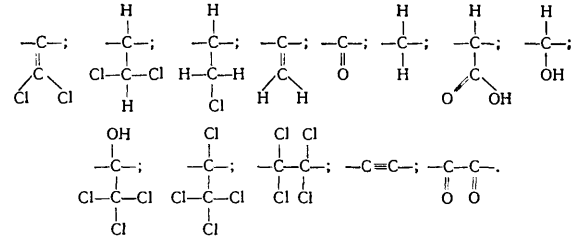


The ease of the reaction of substituted benzenes with chloral varies, in the first place, as a function of the electronic influence of the substituents. According to Yasue and Takai,[42] the reactivity of aromatic rings in reactions with chloral diminishes in the following sequence as a function of the nature of the substituent:

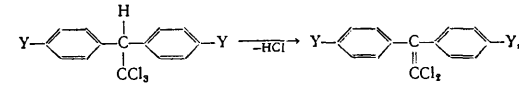


The reactions of 2,2-diaryl-1,1,1-trichloroethanes are carried out in the following ways: (a) the reactions of central 1,1,1-trichloroethane groups; (2) the substitution of the hydrogen atoms in the aromatic rings of diarylchloroethanes and their derivatives with respect to the central group; (3) the reactions of the functional groups, introduced into the aromatic rings of diaryltrichloroethanes and their derivatives with respect to the central group.

The central trichloroethane groups can undergo various reactions leading to their transformation into groups such as 1,1-dichloroethylene, 1,1-dichloroethane, 1-chloroethane, ethylene, carbonyl, methylene, carboxy-, hydroxy-, trichloroethanol, 1,1,1,2-tetrachloroethane, 1,1,2,2-tetrachloroethane, acetylene, α-dicarbonyl, etc.:



In a series of numerous reactions of the 1,1,1-trichloroethane groups, their dehydrochlorination reactions have been most thoroughly investigated,[43] especially in relation to the following series:

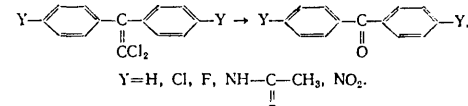


Y=H, Cl, CH_3, OCH_3, OH, NH_2.

The main dehydrochlorinating agents are alcoholic alkali,[35,40] liquid ammonia,[44] methylamine,[44] LiCl in dimethylformamide (DMF),[45] MOH or M_2CO_3 (M = K or Na) in DMF,[46] and tertiary and heterocyclic amines.[4]

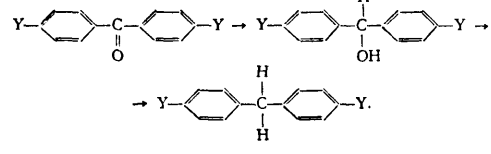
A semiquantitative kinetic study of the dehydrochlorination of various 2,2-diaryltrichloroethanes by KOH in 90% ethanol at the boiling points of the solutions has been carried out[47] and it has been shown that the process proceeds quantitatively and that only one mole of HCl is split off at 80 °C. The kinetics of the dehydrochlorination reaction of diaryltrichloroethanes (which are related to DDT) using NaOH were investigated in a later study.[48] It was found that these processes are second order reactions and proceed via the E_2 mechanism.

In a series of different reactions of the 1,1-dichloroethylene groups, the most thoroughly investigated and most widely used process is their oxidation to keto-groups:[49,50]



Y=H, Cl, F, NH—C(=O)—CH_3, NO_2.

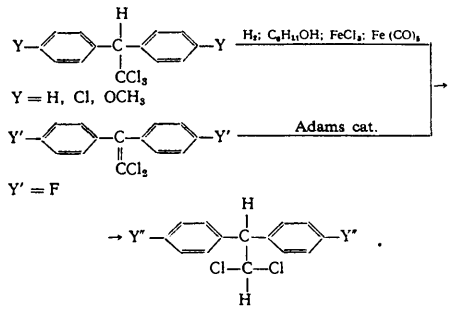
The commonest oxidants of the 1,1-dichloroethylene groups are CrO_3/AcOH, HNO_3/AcOH, and $K_2Cr_2O_7$/AcOH. The diaryl ketones obtained in this way are reduced to the corresponding diphenylmethanols[51,52] and diarylmethanes:[53,54]



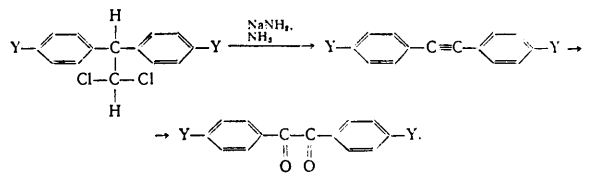
Sodium amalgam[51] and $LiAlH_4$ [52] are used to reduce diaryl ketones to diphenylmethanols; the reduction of diaryl ketones to diarylmethanes is achieved successfully by catalytic hydrogenation using Pd/C [53] or NiRe [54] as catalysts.

Reactions of the 1,1,1-trichloroethane group such as its hydrolysis with formation of 1,1-diarylacetic acids and their subsequent decarboxylation also lead to derivatives of the diphenylmethane series;[55] the same sequence of reactions can be achieved with compounds of the 2,2-diaryl-1,1-dichloroethylene series.[55]

An interesting aspect of the reactions of 1,1,1-trichloroethane groups consists of their reduction processes.[56] In particular, the reduction of 2,2-diaryl-1,1,1-trichloroethanes to 2,2-diaryl-1,1-dichloroethanes has been achieved in cyclohexanol at 110–150 °C using $FeCl_3$ or $Fe(CO)_5$ as catalysts.[55,56] Analogous products have been obtained by reducing 2,2-diaryl-1,1-dichloroethylenes in the presence of the Adams catalyst:[41]

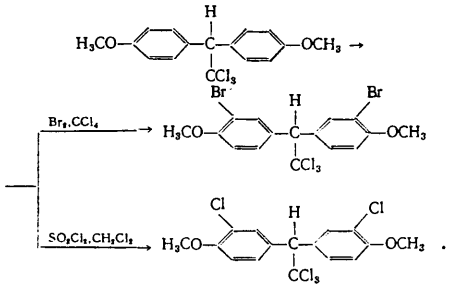


1,2-Diarylacetylenes, subsequently oxidised to benzils,[59] have been obtained by dehydrochlorinating 1,1-dichloroethanes on treatment with $NaNH_2$ in liquid ammonia[57] and also by catalytic dehydrochlorination in the presence of $Mo(CO)_6$:[58]

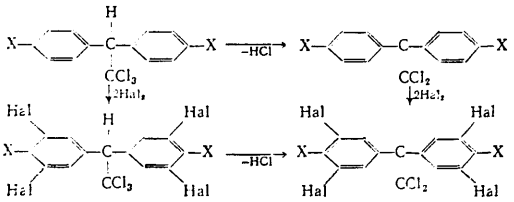


These reactions take place with a change in the carbon skeleton of the molecules, but the isomerisation mechanisms have not been established to this day. A number of reactions of 2,2-diaryl-1,1,1,2-tetrachloroethanes, obtained by chlorinating 2,2-diaryl-1,1,1-trichloroethane derivatives,[50] include a similar isomerisation:[60–65]

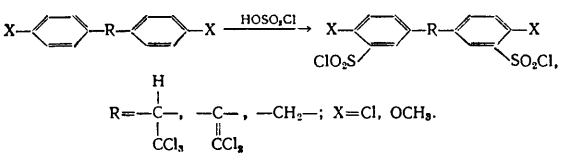
In a series of reactions involving the substitution of hydrogen atoms in the aromatic rings of diaryltrichloroethanes and their derivatives substituted in the central group, the halogenation,[66–69] sulphonylchlorination,[70,71] and nitration[72–75] processes occur most widely. The halogenation of 1,1,1-trichloro-2,2-di(*p*-methoxyphenyl)ethane, namely bromination with bromine in CCl_4 and chlorination with SO_2Cl_2 in methylene chloride, has been described:[66]

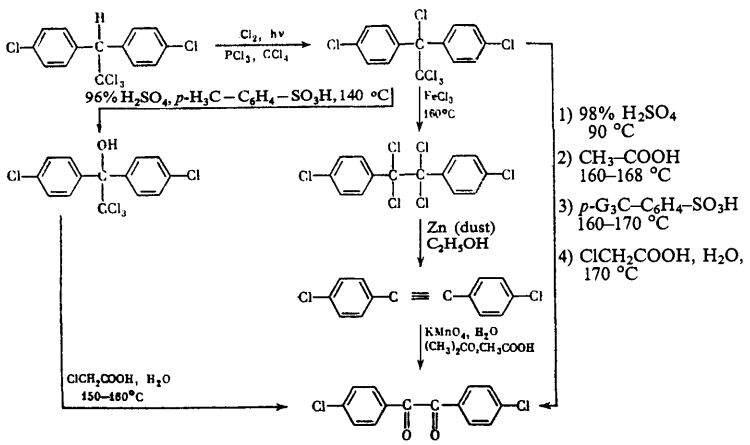


Bisphenols containing an even greater number of chlorine atoms have been obtained by halogenating 1,1,1-trichloro-2,2-di-(4-hydroxyphenyl)ethane with subsequent dehydrochlorination[67–69] or, in the reverse sequence, by dehydrochlorination and then halogenation:

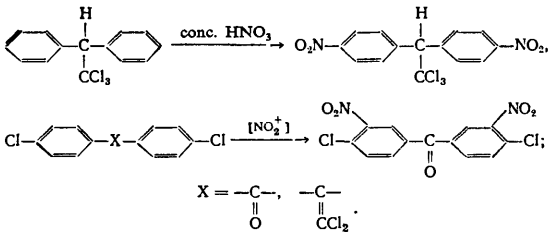


The sulphonylchlorination of the simplest chloral derivatives—DDT, 1,1-dichloro-2,2-di(*p*-chlorophenyl)ethylene, 4,4′-dichlorodiphenylmethane, and 1,1-dichloro-2,2-di(*p*-methoxyphenyl)ethylene [70–71]—led to the corresponding disulphonyl chlorides:

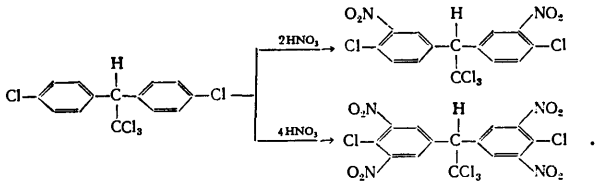




The nitration of diaryltrichloroethanes and their derivatives substituted in the central group has been achieved for a wide range of objects—1,1,1-trichloro-2,2-diphenylethane,[72] 1,1-dichloro-2,2-di(*p*-chlorophenyl)ethylene,[73] 4,4′-dichlorobenzophenone,[73] and DDT:[74,75]



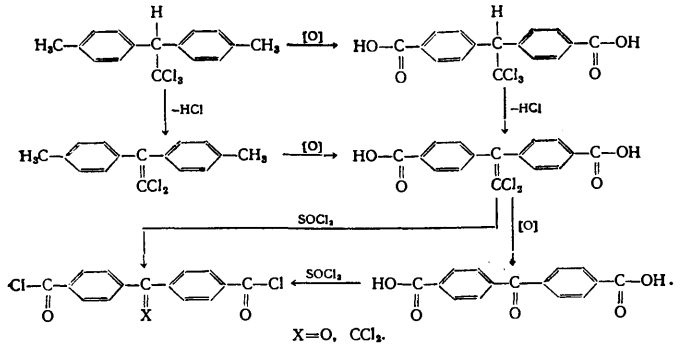
Depending on the conditions under which they are carried out, the latter processes lead to 1,1,1-trichloro-2,2-di(4-chloro-3-nitrophenyl)-ethane or 1,1,1-trichloro-2,2-di(4-chloro-3,5-dinitrophenyl)ethane:



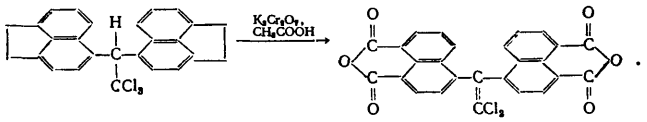
On reaction with caustic alkalis in alcoholic solutions, these compounds are converted into the corresponding dichloroethylene products, which are then oxidised to benzophenone derivatives.[75]

The reactions of the functional groups introduced at various stages of the processes into the aromatic rings of diaryltrichloroethanes and their derivatives substituted in the central group have developed considerably. In particular, diaryltrichloroethanes containing alkyl substituents in the aromatic rings have been oxidised with formation of the corresponding dicarboxylic[76] and tetracarboxylic[36] acids. Thus the oxidation of 1,1,1-trichloro-2,2-di(*p*-tolyl)ethane afforded 2,2-di(*p*-carboxyphenyl)-1,1,1-trichloroethane,[76] which was then made to undergo reactions involving the central group with formation of 2,2-di(*p*-carboxyphenyl)-1,1-dichloroethylene[77] and benzophenone-4,4′-dicarboxylic acid.[78] The same dicarboxylic acids have been obtained by oxidising 1,1-dichloro-2,2-di(*p*-tolyl)ethylene.[77,78]

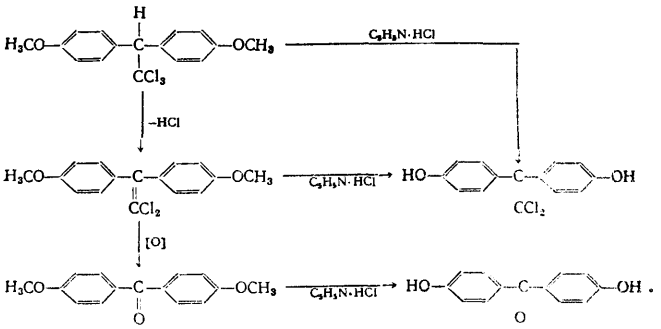
The dicarboxylic acids obtained were converted into the corresponding dichlorides:[77,78]



2,2-Di(4-acenaphthenyl)-1,1,1-trichloroethane was oxidised in a glacial acetic acid using $K_2Cr_2O_7$ or $Na_2Cr_2O_7$ as oxidants.[36] The simultaneous occurrence of the oxidation reactions of the alkylene fragments of the acenaphthenyl units, the conversion of the *peri*-dicarboxy-groups into anhydrides, and the dehydrochlorination of the trichloroethane "bridges" to the 1,1-dichloroethylene bridges were then observed:



The principal reactions of 1,1,1-trichloro-2,2-di(*p*-methoxyphenyl)ethane and its derivatives substituted in the central group involve the conversion of the methoxy-groups into hydroxy-groups on treatment with pyridine hydrochloride:[68,79]

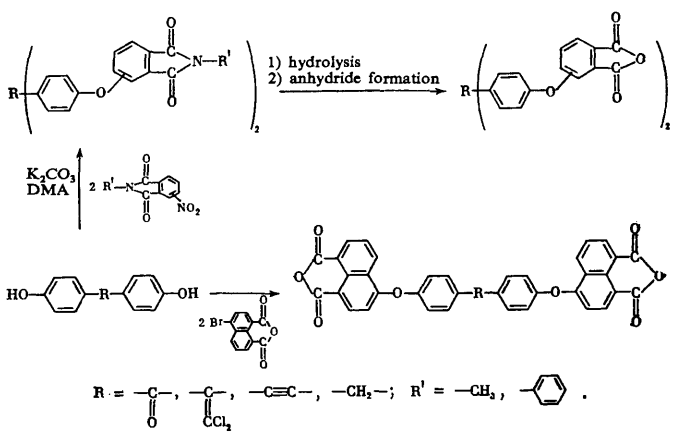


The dehydrochlorination of the 1,1,1-trichloroethane groups to 1,1-dichloroethylene groups takes place simultaneously under the reaction conditions (210 °C).

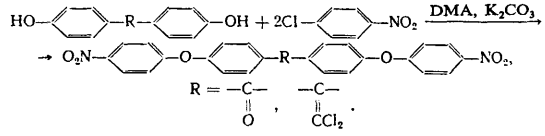
Similar reactions have been used to convert 2,2-di(3-halogeno-4-methoxyphenyl)-1,1,1-trichloroethane into 2,2-di(3-halogeno-4-hydroxyphenyl)-1,1-dichloroethylene:[66]



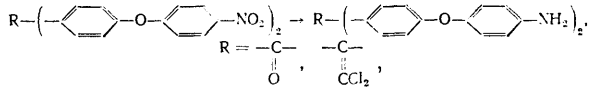
The reactions of the hydroxy-groups of bisphenols involve primarily their conversion into bisphenoxides, which interact vigorously with activated aromatic halogeno- and nitro-compounds. Thus the reaction of bisphenoxides with *N*-substituted 4-nitrophthalimides yielded diimides containing ether linkages; the hydrolysis of these diimides led to the formation of bisphthalic acids, which were then converted into bisphthalic anhydrides.[80–82] Bisnaphthalic anhydrides containing ether linkages were obtained by the reaction of bisphenoxides containing methylene and carbonyl central groups with 4-bromonaphthalic anhydride:[83]



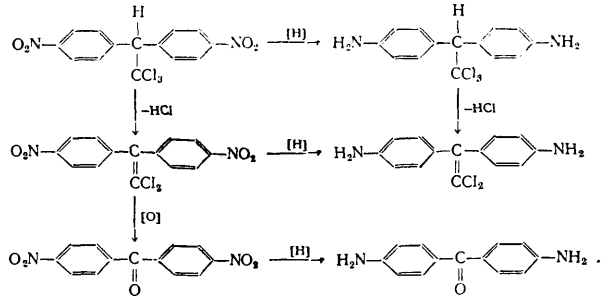
Aromatic dinitro-compounds, each containing two diaryl ether units, have been obtained by the reaction of bisphenoxides with *p*-chloronitrobenzene in dimethylacetamide (DMA) in the presence of K_2CO_3:[84]



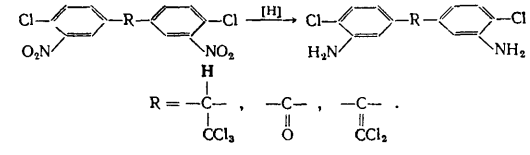
The reduction of nitro-groups to amino-groups has been the main pathway in the chemical reactions of nitro-groups present in various derivatives of chloral and DDT. The catalytic reduction of 4,4′-di(*p*-nitrophenoxy)arylenes to the diamines,[84] i.e.



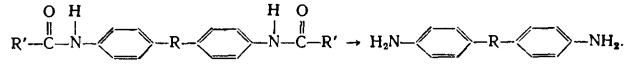
has not been the only reaction of this kind. The simpler dinitro-chloral derivatives 1,1,1-trichloro-2,2-(*p*-nitrophenyl)ethane,[72] 1,1-dichloro-2,2-di(*p*-nitrophenyl)ethylene,[72] and 4,4′-dinitrobenzophenone[74] have also been reduced catalytically:



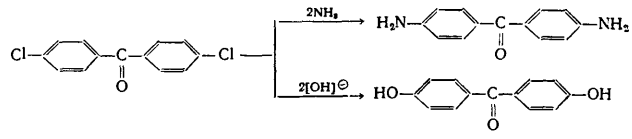
The same type of reaction has been carried out likewise for di(4-chloro-3-nitrophenyl)arylenes:[75,85,86]



An alternative method of synthesis of aromatic diamines from chloral derivatives is the hydrolysis of the bisamides:[87]



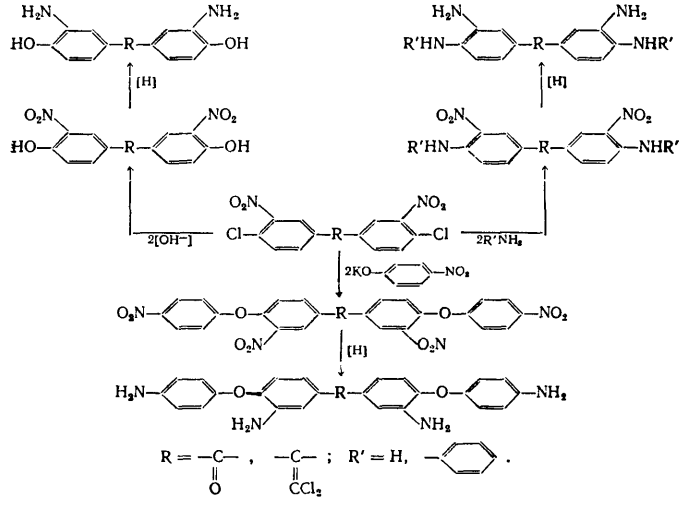
The reactions involving the substitution of halogen atoms in activated aromatic dihalogeno-compounds also constitute an extremely effective approach to the synthesis of diamines. A simple method of synthesis of diamines, for example from 4,4′-dichlorobenzophenone,[73,88] using NH_3 and different catalysts, has thus arisen:



The hydrolysis of the same compound[89,90] with aqueous NaOH using different catalysts, for example CuCl and Cu_2O,[90] led to the formation of 4,4′-dihydroxybenzophenone.

The introduction of nitro-substituents increases sharply the mobility of the chlorine atoms in the aromatic rings of DDT and the products of its reactions via the central group, making them more reactive even compared with the chlorine atoms in di(4-chlorophenyl) sulphone.[91] This fact determines the possibility of the successful use of such products directly in polycondensation processes and also of carrying out various reactions involving the chlorine atoms. In particular, the reactions of such compounds with ammonia and aromatic amines, leading to the corresponding bis(*o*-nitroanilines) and bis(*o*-nitrodiphenylamines), are of considerable interest.[86,92] The chlorine atoms in compounds of this kind are very readily hydrolysed by alkalis;[73] this has been used, in particular, to synthesise 4,4′-dihydroxy-3,3′-dinitrobenzophenone,[73] and they also interact with potassium *p*-nitrophenoxide, forming, for example, 3,3′-dinitro-4,4′-di(*p*-nitrophenoxy)benzophenone.[93]

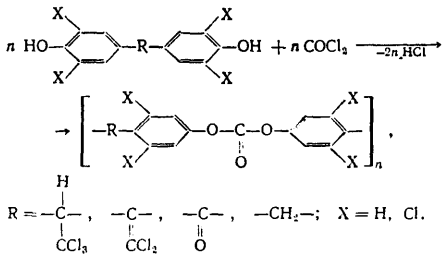
The reduction of the nitro-groups in dinitrodiamines leads to the formation of unsubstituted[86] and *NN*′-diphenyl-substituted[92] bis(*o*-phenylenediamines); the reduction of nitro-groups in bis(*o*-nitrophenols) affords bis(*o*-aminophenols),[73] while the reduction of nitro-groups in 3,3′-dinitro-4,4′-di(*p*-nitrophenoxy)-benzophenone leads to the formation of 3,3′-diamino-4,4′-di(*p*-aminophenoxy)benzophenone:[93]



Analysis of the entire foregoing data enables one to claim that a wide range of varied di- and tetra-functional monomers have been obtained from chloral and DDT. Some of them are of considerable interest from the standpoint of the properties of the polymers based on them and also from the standpoint of their availability and potential cost.

IV. Condensation polymers based on chloral derivatives

In the series of condensation polymers based on chloral and DDT derivatives, polycarbonates obtained in accordance with the scheme



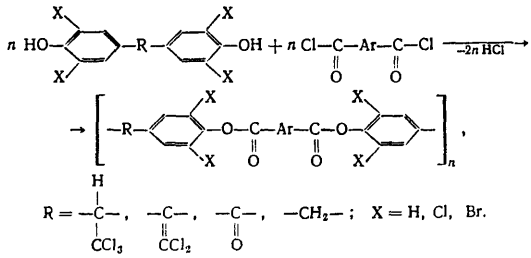
were the first to attract the attention of investigators.[94-98] Since polycarbonates based on 4,4'-dihydroxybenzophenone and di(4-hydroxyphenyl)methane were examined previously,[94-98] in the present review attention is concentrated on polymers derived from bisphenols containing 1,1,1-trichloroethane and 1,1-dichloroethylene central groups.

The first mention of the use of 1,1,1-trichloro-2,2-di(*p*-hydroxyphenyl)ethane and 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene to obtain polycarbonates (as comonomers of bisphenol A) dates back to 1964,[99] when a group of Polish investigators synthesised copolycarbonates by interfacial polycondensation. The subsequent research by the same group of investigators[68,69] led to a series of interesting results, referring, in particular, to the synthesis of homopolycarbonates from 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)-ethylene.[69] Comparison of the properties of homopolycarbonates based on 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene, 1,1,1-trichloro-2,2-di(*p*-hydroxyphenyl)ethane, and bisphenol A[100,101] showed that the homopolymer based on 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene is characterised by a more interesting set of thermal and deformation-strength properties. At approximately 20 °C, the thermal stability of this polymer exceeds that of the industrial polycarbonate obtained from bisphenol A and is superior to it as regards its strength characteristics and, by virtue of the large content (25%) of chlorine, as regards its fire resistance. Further increase in the chlorine content in polycarbonates leads, on the one hand, to a further increase of the thermal stability and fire resistance, but, on the other hand, it entails a sharp diminution of the elasticity of the polymers. Furthermore, systems containing 1,1,1-trichloroethane groups are characterised by a reduced thermal stability—after prolonged exposure to temperatures in the range 100–300 °C they evolve HCl, which is probably associated with the dehydrochlorination of the trichloroethane groups.

The valuable set of properties of the polycarbonates based on 1,1-dichloro-2,2-di(*p*-hydroxyphenol)ethylene combined with the high hydrolytic stability of chlorine-containing polycarbonates[102] have been responsible for the further development of studies in this field,[44,103-108] which were completed by the development of a high-quality thermoplastic.

The thermal stability of the unstabilised and stabilised homopolycarbonates and copolycarbonates as well as their fire resistance have attracted special attention.[109] The study of the chemical composition of the gases evolved on combustion of this polycarbonate[110] and tests on mice using the technique involving the pyrolysis of the polymers in air[111,112] showed that they are characterised by the smallest combustibility, smoke evolution, and toxicity among all the known thermoplastics.

Together with the polycarbonates considered above, polyarylates obtained from the same bisphenols and aromatic dicarboxylic acid dichlorides have aroused considerable interest:[113]

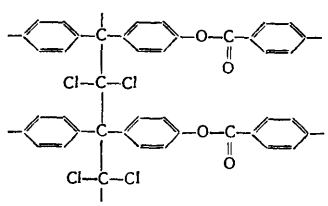


By virtue of the considerations described above in relation to polycarbonates, in the present review attention is concentrated on polyarylates derived from bisphenols containing 1,1,1-trichloroethane and 1,1,1-dichloroethylene central groups, in particular from 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene.[108,114-118] The synthesis of these polymers using the dichlorides of the commonest aromatic dicarboxylic acids—isophthalic and terephthalic—as acid components was achieved by interfacial polycondensation[108,114-16] and also by the acceptor-catalytic polyesterification in solution.[108,118] Polyarylates have been obtained as homopolymers as well as copolymers using bisphenol A as the comonomer.[119,120] The polyarylates obtained are satisfactorily soluble in chlorinated hydrocarbons; they form films and coatings with effective mechanical, dielectric, and optical properties.[116,121] Homopolyarylates based on 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene are characterised by significantly better thermal and electrophysical characteristics than polymers based on other bisphenols.

In terms of their thermal stability and fire resistance, polyarylates based on 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene are superior to industrial polyesters and polycarbonates. The maximum temperature of the long-range use of polyarylate is 180 °C, whilst that of the short-term use is 260 °C. The onset of thermal degradation in air is observed at 360 °C according to the results of dynamic thermogravimetric analysis (DTGA), the weight loss after 150 h at 200 °C amounting to 1%. Their dielectric and mechanical properties do not change after heating at 180 °C for 1000 h.

The properties of polyarylate films can be significantly improved by heat treatment for 2–5 h at 180–250 °C. Thus the heat-treated films become much more chemically stable and lose their solubility in chlorinated hydrocarbons.

These changes in properties are probably associated with the partial "cross-linking" via the dichloroethylene groups:[108,118]



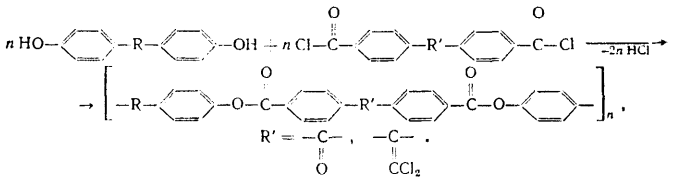
which has also been noted for polycarbonates.[104]

Polyarylates sensitive to UV radiation[122,123] as well as electret[124] and coloured[125] polyarylates have been obtained from 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene.

The attempts to use the polyarylates synthesised as pigmented and non-pigmented coatings[126] to protect pipes transporting hot liquids at 150–200 °C showed that, after use for 2 years, these coatings retain excellent thermal and chemical characteristics as well as good adhesion to metallic surfaces.

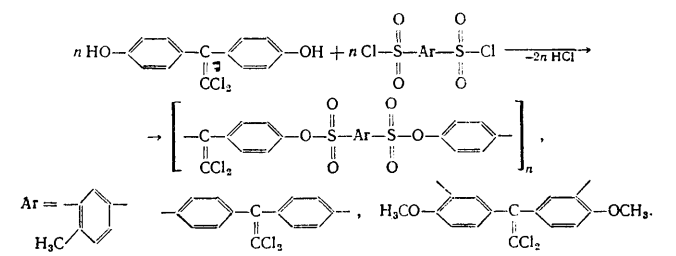
The polyarylates can also be used as constructional materials in the production of components for electrotechnical and radiotechnical purposes.

Together with the bisphenol derivatives of chloral and DDT, the dichlorides of aromatic dicarboxylic acids—benzophenone-4,4'-dicarboxylic acid and 2,2-di(*p*-carboxyphenyl)-1,1-dichloroethylene, which are also chloral derivatives, have been used to synthesise polyarylates:



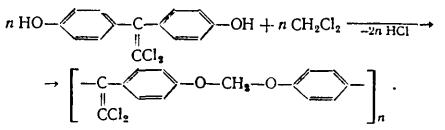
Since polyarylates based on the dichloride of benzophenone-4,4'-dicarboxylic acid were examined in detail previously,[113] in the present review attention is concentrated on polymers based on the dichloride of 2,2-di(*p*-carboxyphenyl)-1,1-dichloroethylene.[118,127–133] These polymers were obtained by interfacial polycondensation[127,128] and acceptor-catalytic polycondensation[118,128–131] methods. According to a number of workers,[118,127–133] the polyarylates synthesised dissolve readily in methylene chloride, chloroform, tetrachloroethane, tetrahydrofuran (THF), and other solvents. Films characterised by a higher fibre resistance and capacity for long term use at 200 °C have been obtained by casting from solutions of these polymers in chloroform. According to Taova et al.,[133] the 1,1-dichloroethylene group has a positive influence on the thermal characteristics of polyarylates.

Together with polyarylates, polysulphonates obtained by the reaction of bisphenols with disulphonyl chlorides have also attracted much attention of investigators; here at least one of the comonomers was a chloral or DDT derivative. In particular, the interaction of 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene with various disulphonyl chlorides, carried out under the conditions of interfacial polycondensation using phase transfer catalysts afforded polysulphates with comparatively high molecular weight characteristics:[108,117,134,135]



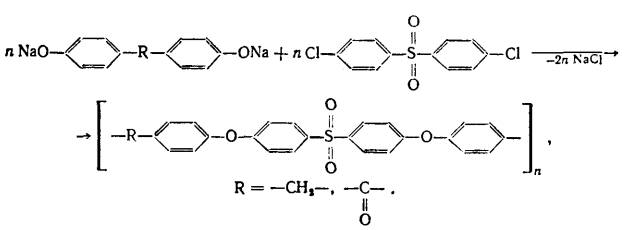
Polysulphonates are superior to the corresponding polyarylates in the first place as regards solubility; in the series of polymers represented by the scheme above,[37] the highest solubility is that of the polysulphonate based on the 1,1-dichloro-2,2-di(3-chlorosulphonyl-4-methoxy)ethylene; this polymer is readily soluble in acetone, cyclohexanone, and xylene,[134] which is due to the presence in it of *ortho*-methoxy-substituents and *meta*-phenylene rings in the main chains of the macromolecules. Polysulphonates with the highest molecular weights are obtained using triethylbenzylammonium chloride or bromide as the phase transfer catalyst. The polysulphonates then form films characteristic by a high fibre resistance as a consequence of the presence in the polymer of a large amount of chlorine and sulphur. The film forming properties of polysulphonates improve significantly when part of the disulphonyl chloride is replaced by isophthaloyl chloride (20 mol%) or terephthaloyl chloride (30 mol%).[136] The thermal decomposition of polysulphonates modified in this way begins at 330 °C; the modification improves the adhesion properties of the polysulphonates, their solubility in the available organic solvents, their resistance to the action of acids and alkalis, and their elastic properties. The mechanical properties of the modified polysulphonates do not change at a temperature of approximately 180 °C.

Together with the synthesis of various types of polyesters, chloral and DDT derivatives have been used successfully to synthesise polyethers. Thus 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene has been used to synthesise polyformals—the products of the condensation of bisphenols with methylene chloride:[137]



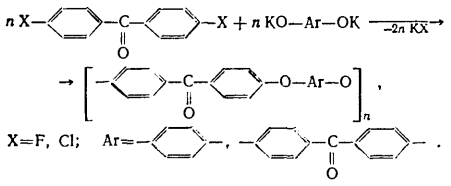
A polyformal was synthesised by the reaction of 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene with methylene chloride in *N*-methyl-2-pyrridinone (MP) in the presence of NaOH.[137] The polyformal thus obtained contained 10–15% of cyclic oligomers. Comparison of the characteristics of the polyformal with those of the analogous polymer obtained from bisphenol A showed that their mechanical properties are comparable but the system containing the 1,1-dichloroethylene group is more heat resistant (by approximately 25 °C) and more fire resistant. The glass point of the polyformal synthesised from 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene is 120 °C and its oxygen index is 43.

The first attempts to synthesis fully aromatic polyethers using chloral and DDT derivatives as the monomers were associated with the development of processes for the interaction of di(4-chlorophenyl) sulphone with different bisphenols,[138,139] especially with di(4-hydroxphenyl)methane and 4,4'-dihydroxybenzophenone:

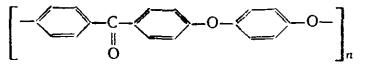


Later studies in this field were associated with the use of 1,1-dichloro-2,2-di(*p*-hydroxyphenyl)ethylene as the bisphenol.[140,141] In the series of these polymers, systems based on 4,4'-dihydroxybenzophenone, characterised by the glass point T_g = 205 °C, attracted most attention by investigators. The possibility of using chloral and DDT derivatives as dihalogeno-components of the reaction attracted even more interest. In particular, polyethers based on 4,4'-dichloro- and 4,4,'-difluorobenzophenone are of considerable

interest.[142,143] These polymers are obtained in accordance with the scheme[144–146]



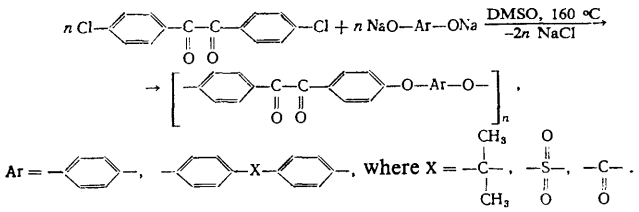
The crystallinity of the polymers formed, referred to as polyetherketones, makes it necessary to synthesise them at high temperatures (up to 335 °C) in solvents such as sulpholan[144] and diphenyl sulphone.[145] One of the representatives of polymers of this class, corresponding to the formula



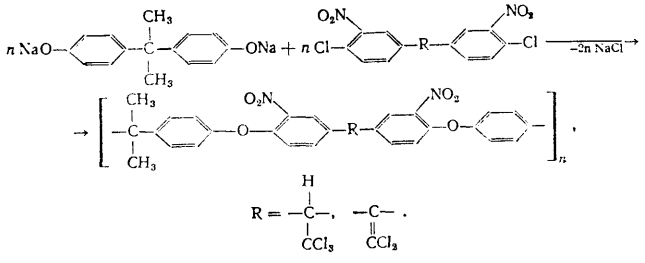
and characterised by T_g = 145 °C and the melting point T_m = 334 °C, was first introduced by the ICI Company in 1982.[143]

Using 4-hydroxythiophenol as the diol component, polythioetherketones were obtained.[147] These are crystalline polymers with $[\eta] \geqslant 0.4$ dl g^{-1} and having a high thermal and chemical stability and effective mechanical properties. The use of *p*-dimercaptobenzene led to polysulphideketones[148] with good thermal characteristics.

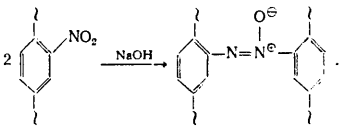
The attempt to use a DDT derivative such as 4,4′-dichlorobenzil as the dihalogeno-reactant[149] led to the formation of oligomeric polyethers, which has the consequence, according to Lesiak and Nowakowski,[149] of the reduced reactivity of 4,4′-dichlorobenzil due to the non-coplanarity of its molecules:



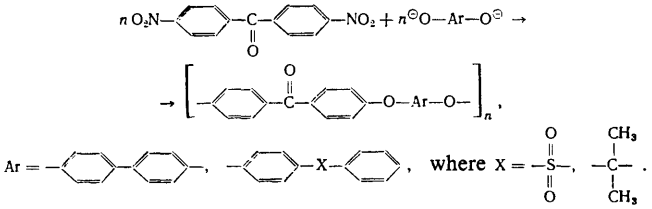
Polymers with extremely low molecular weights have been obtained by the reaction of bisphenol A with 1,1-dichloro-2,2-di(*p*-chlorophenyl)ethylene and 1,1,1-trichloro-2,2-di(*p*-chlorophenyl)ethane;[91,150] high-molecular-weight polyethers have been synthesised only as a result of the activation of the chlorine atoms by introducing nitro-substituents into the monomers:[91,150]



However, it is noteworthy that, when the polycondensation is carried out at high temperatures (more than 80 °C), insoluble products are formed. According to Adam and Husein,[91] this is a consequence of side reactions involving nitro-groups—for example, their coupling in an alkaline medium with formation of intermolecular azoxy-"cross-links":

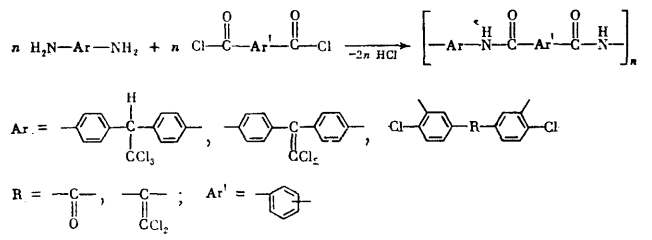


An alternative nucleophilic aromatic nitro-substitution process[151] led to the formation of high-molecular-weight unsubstituted aromatic polyethers based on chloral derivatives: the interaction of 4,4′-dinitrobenzophenone with alkali metal bisphenoxides under the conditions of nucleophilic aromatic nitro-substitution, i.e.



afforded polyetherketones with [η] for solutions in *N*-MP in the range 1.07–1.32 dl g^{-1}.[152] The polyetherketones synthesised are readily soluble in DMF, DMA, and MP. They have melting points in the range 195–255 °C, appreciably below their decomposition temperatures. These are the reasons why materials with a high thermal stability can be obtained from polyetherketones.

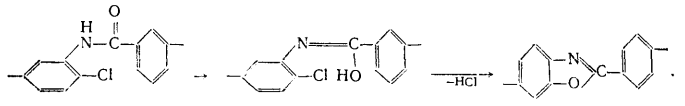
Aromatic polyamides have been obtained both from diamino-derivatives of chloral and DDT,[153–156] i.e.



and from the acid dichloride of 2,2-di(*p*-carboxyphenyl)-1,1-dichloroethylene.[157–159]

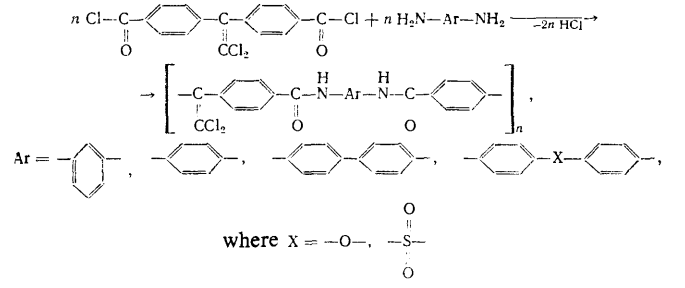
The initial studies on the synthesis of polyamides from the diamino-derivatives of chloral and DDT were performed using 2,2-di(*p*-aminophenyl)-1,1,1-trichloroethane and 2,2-di(*p*-aminophenyl)-1,1-dichloroethylene[153,154] under the conditions of polycondensation in solution[153] and interfacial polycondensation.[154] This yielded comparatively high-molecular-weight and fire-resistant but sparingly soluble polymers. The change to diamines with less symmetrical structures—3,3′-diamino-4,4′-dichlorobenzophenone and 2,2-di(3-amino-4-chlorophenyl)-1,1-dichloroethylene[155,156]—led to the possibility of obtaining polyamides with improved solubility in organic solvents. A detailed study of the dependence of the principal characteristics of polyamides on their structure[155,156] showed that polymers with 1,1-dichloroethylene groups dissolve somewhat better than systems with carbonyl groups in the main macromolecular chain and that the introduction of chlorine into the aromatic rings imparts a greater fire resistance to the polymers than the introduction of the same amount of chlorine in the form of dichloroethylene groups. Polyamides containing carbonyl groups are less fire

resistant than the analogous systems containing 1,1-dichloroethylene groups but are more heat resistant and more thermostable than the latter. An interesting feature of polyamides containing chlorine atoms as *ortho*-substituents relative to the amide group is their ability to undergo intramolecular dehydrochlorination at elevated temperatures (> 300 °C), which leads to the formation of benzoxazole rings:[160,161]



Overall the polyamides considered are of definite practical interest due to the availability of the initial compounds and to their set of valuable properties of the polymers.

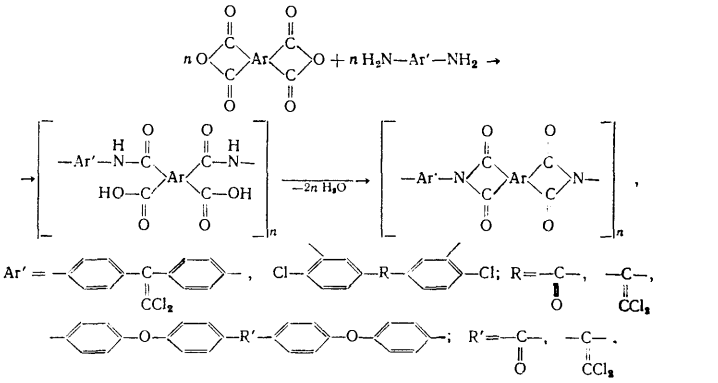
Polyamides based on the acid dichloride of 2,2-di(*p*-carboxyphenyl)-1,1-dichloroethylene,[157–159] obtained in accordance with the scheme



using low-temperature polycondensation in solution[157] and emulsion polycondensation[159] methods, are also extremely interesting from the practical point of view.

The polyamides obtained are high-molecular-weight polymers readily soluble in DMA and MP and with limited solubility in DMF, hexamethylphosphoramide (HMP), and pyridine. They all have a relatively high heat resistance and thermal stability—their softening temperatures reach 310 °C and the temperatures corresponding to a 10% weight loss are in the range 360–405 °C. The high chlorine content in the polyamides (~ 13–18%) is responsible for the self-quenching capacity of these systems. Films obtained from them are not inferior as regards strength to films based on the polyamide of the "phenylon" type. The polyamide obtained using *meta*-phenylenediamine and known under the name "Dneprolon-M" is especially promising.[158]

The use of chloral and DDT derivatives for the synthesis of linear heterocyclic polymers has attracted much attention of investigators in recent years. Among them, the commonest are aromatic polyimides,[1] many of which have been obtained from compounds such as 4,4'-diaminobenzophenone, di(4-aminophenol)methane, etc. i.e. monomers which, as has been shown above, can be obtained from chloral and DDT. Since the methods of synthesis and properties of such polymers have already been examined in detail,[1] in the present review attention is concentrated on polymers which had not been described hitherto. Polyimides based on aromatic diamino-derivatives of chloral and DDT have been obtained by their interaction under mild conditions with the dianhydrides of tetracarboxylic acids in dipolar aprotic solvents with subsequent catalytic conversion of poly(*o*-carboxy)amides into imides in accordance with the scheme



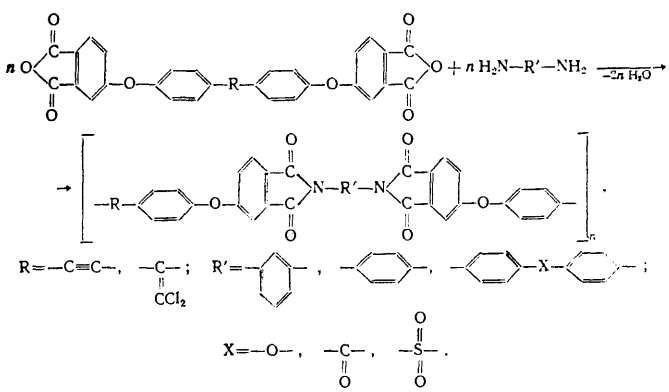
Chloral and DDT derivatives such as 2,2-di(4-aminophenyl)-1,1-dichloroethylene,[162] 3,3'-diamino-4,4'-dichlorobenzophenone, and 2,2-di(3-amino-4-chlorophenyl)-1,1-dichloroethylene[155] have been used in a number of studies[155,156] as the diamines. The commonest bisphthalic anhydrides—the anhydrides of pyromellitic and benzophenone-3,3'-4,4'-tetracarboxylic acids and the 3,3',4,4'-tetracarboxy-derivative of diphenyl sulphone—served as the comonomers of these diamines. The polymers based on 2,2-di(4-aminophenyl)-1,1-dichloroethylene were obtained in the form of comparatively high-molecular-weight {[η] = 1.0–1.4 dl g^{-1}}, heat-resistant (T_{soft} > 280 °C), and fire-resistant [oxygen index (OI) = 36–40] systems which are, however, soluble only in H_2SO_4 and a 3 : 1 tetrachloroethane (TCE)–phenol mixture. The transition from these polymers to polyimides based on 3,3'-diamino-4,4'-dichloroarylenes[155] led, by analogy with a similar structural change in polyamides (see above), to the formation of systems with a significantly greater solubility in organic solvents. Analysis of the dependence of the properties of these polymers on their structure showed that polyimides based on 2,2-di(3-amino-4-chlorophenyl)-1,1-dichloroethylene exhibit the highest solubility and fire resistance, while the best thermal characteristics are those of polyimides based on 3,3'-diamino-4,4-dichlorobenzophenone. The improved capacity of such polymers for being worked into articles is determined not only by their solubility in organic solvents but also by the comparatively mild pressing conditions. Polyimides of this type with the most rigid chains, namely polypyromellitimides, which can be worked by pressing at a temperature exceeding 350 °C, behave under these conditions as thermoreactive systems; intermolecular HCl elimination processes take place during pressing, which results in the formation of "cross-linked" structures characterised by an increased heat resistance.

Diamines containing ether linkages and other groups, for example 4,4-di(*p*-aminophenoxy)benzophenone, have been used to synthesise polyimides.[84] The polyimides obtained from this monomer are high-molecular-weight crystalline systems, whose structure is similar to that of polymers regarded as promising film and constructional materials.[163,164]

Aromatic tetraamino-derivatives of DDT, especially 3,3',4,4'-tetraaminobenzophenone, have been used to obtain polyimides containing *N*-phthalimide *ortho*-substituents.[165] The synthesis of such polyimides reduces to treating the tetraamines with twice the molar amounts of cyclic dicarboxylic acid anhydrides and equimolar

amounts of the dianhydrides of tetracarboxylic acids with subsequent catalytic conversion of the prepolymers thus obtained into imides. The difference between the nucleophilicities of the reaction centres of the aromatic tetramines makes it possible to vary the isomeric composition of the polyimides by altering the sequence in which the mono- and di-anhydrides are introduced into the reaction.[165] When 3,3',4,4'-tetraaminobenzophenone, phthalic anhydride, and various bisphthalic anhydrides were used as the initial compounds, polyimides containing *N*-phthalimide *ortho*-substituents were obtained; these polymers are readily soluble in amide and phenolic solvents and this is combined with high thermal stabilities and heat resistances, differing little in this respect from polyamides based on other di(*o*-phenylenediamines).[165] Fundamentally different results were obtained when 3,3'-diamino-4,4'-di(*p*-aminophenoxy)benzophenone was used as the initial tetramine.[93] The synthesis of polyimide with the initial introduction of phthalic anhydride yields polymers containing predominantly the *N*-(*p*-phenoxy)phthalimide *ortho*-substituents. These polymers exhibit a solubility, unique for polymers of this class, in DMF, DMA, MP, HMP, dimethyl sulphoxide (DMSO), phenolic solvents, tetrachloroethane, chloroform, and cyclohexanone. Their softening temperatures are in the range 245–290 °C and the temperatures corresponding to a 10% weight loss, determined by the DTGA method, are 440–490 °C.

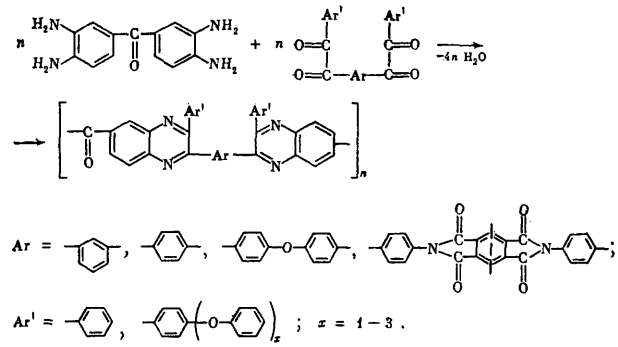
A series of polyimides have also been obtained from non-traditional tetracarboxylic acid dianhydrides derived from chloral and DDT. Thus the synthesis of polyimides from the dianhydrides of di(*o*-dicarboxyphenoxyphenyl)acetylene and 1,1-di(*o*-dicarboxyphenoxyphenyl)-2,2-dichloroethylene has been described. The dianhydrides were made to react with aromatic and aliphatic diamines in organic solvents or in the melt in accordance with the scheme



Polymers based on *m*-phenylenediamine, having T_g = 219–247 °C, temperatures of the onset of thermal degradation in the range 470–500 °C (in air) and 470–545 °C (in N_2), and OI = 45–56 and giving rise to coke residues in the range 64–73%, have been studied in greatest detail.

Polyquinoxalines based on DDT derivatives, in the first place on 3,3',4,4'-tetraaminobenzophenone,[166–170] whose interaction with various bis(α-diketones) has been achieved in accordance with the scheme below, have attracted much attention of investigators.

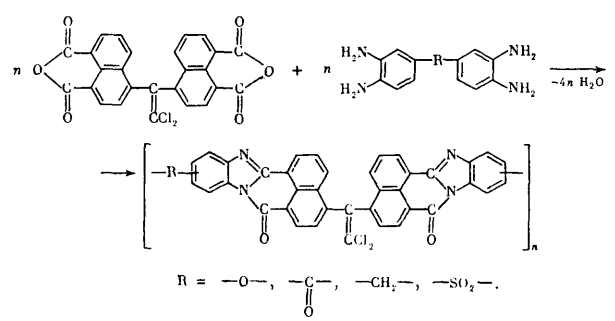
Scheme



High-molecular-weight polymers have been obtained under the usual conditions[167] of the synthesis of polyquinoxalines—low-temperature polycondensation in protic solvents or in the presence of protic additives. Their heat resistance exceeds by 10–25 °C the analogous systems based on di(3,4-diaminophenyl) ether and they have a high thermal stability under the conditions of dynamic and isothermal thermogravimetric analysis being at the same time readily soluble in phenolic and chlorinated solvents, which makes it easy to work them and convert them into articles. In particular, strong films have been obtained from them. They lose between 5.8 and 32.1% of the initial weight depending on their structure and the duration of thermal ageing at 316 °C.

Carboplastics and adhesives capable of being used for a long time at 316 °C and superior, as regards the retention of their strength characteristics during thermal ageing, to the analogous systems based on 3,3'-diaminobenzidine have been obtained from polyphenylquinoxalines synthesised from 3,3',4,4'-tetraaminobenzophenone.[168,169]

Finally, chloral and DDT derivatives have been used by a number of investigators also for the synthesis of ladder polyheteroarylenes, among which polynaphthoylenebenzimidazoles have been studied in greatest detail. In particular, polymers of this type have been obtained by the reaction of the dianhydride of 2,2-di(4,5-dicarboxynaphthyl)-1,1-dichloroethylene with bis(*o*-phenylenediamines) in phenolic solvents (phenol, *m*-cresol), preferably using benzoic acid as the catalyst:



A characteristic feature of the polynaphthoylenebenzimidazoles thus obtained is ready solubility not only in acid but also in phenolic solvents, which makes it easier to work them and convert them into articles.

The list of uses, presented in this review, of chloral and DDT derivatives in the synthesis of new polymers and materials based on them indicates exceptionally interesting possibilities in the development of this field. The ease of reaction of chloral and DDT

derivatives via the central group, via the functional groups in the aromatic rings, etc. makes it possible to obtain a large number of a wide variety of monomers which are in their turn responsible for a valuable set of properties of the polymers based on them. The possibility of synthesising from available starting materials of high-molecular-weight compounds with improved thermal stability and fire resistance and combined with an improved solubility and capacity for being worked may provide an important stimulus for the intensification of studies in the field under consideration.

References

1. V V Korshak *Termostoikie Polimery* (Thermostable Polymers), Izd. Khimiya, Moscow, 1969
2. F I Luknitskii *Chem. Rev.*, 1975, **75**(3) 259
3. L A Oshin (Editor), Handbook *Promyshlennye Khlororganicheskie Produty* (Industrial Organochlorine Products), Izd. Khimiya, Moscow, 1978
4. N N Mel'nikov, V A Nabokov, E A Pokrovskii *DDT—Svoistva i Primenenie* (DDT—Properties and Applications), GNTIKhL, Moscow, 1954
5. P Karrer *Lehrbuch der Organischen Chemie* (Translated into Russian), GNTIKhL, Leningrad, 1960
6. N N Mel'nikov, A I Volkov, O A Korotkova *Pestitsidy i Okruzhayushchaya Sreda* (Pesticides and the Environment), Izd. Khimiya, Moscow, 1977
7. Z Poller *Chemistry on the Way to the Third Millenium* (Translated into Russian), Izd. Mir, Moscow, 1982
8. T Lesiak, J Nowarkowski *Polimery*, 1980, **25**(3) 81
9. T Lesiak, J Nowarkowski *Polimery*, 1981, **26**(1) 1
10. V V Korshak, A L Rusanov, S Kh Fidler, et al *Plastmassy*, 1984, (10) 32
11. E R Kekharsaeva et al. *Plastmassy*, 1985, (2) 9
12. O Vogl *Encyclopedia of Polymer Science and Engineering*, Wiley, New York, 1985, Vol. 1, p. 623
13. O Vogl, US P. 3 454 527, 1969
14. O Vogl, H C Miller, W H Sharkey *Macromolecules*, 1972, **5**(5) 656
15. O Vogl, K Hatada *J. Polym. Sci., Polym. Lett. Ed.*, 1975, **B13** 609
16. O Vogl, W M D Brayant *J. Polym. Sci.*, 1964, **A2**(10) 4633
17. K Hatada et al. *Vysokomol. Soedin., Ser. A*, 1977, **19**(9) 1987
18. O Vogl *Chemist*, 1985, **62**(9) 16
19. A Abe, K Tasaki, K Inomata, O Vogl *Macromolecules*, 1986, **19**(11) 2707
20. O Vogl, US P. 3 775 371, 1973
21. H Hoffmann, H J Diehr *Tetrahedron Lett.*, 1962, **13** 583
22. G Wasai, T Iwata, M Kuragano, et al *Kogyo Kagaku Zasshi*, 1964, **67** 1920
23. P Kubisa, L S Corley, T Kondo, et al. *Polym. Eng. Sci.*, 1981, **21** 829
24. L S Corley, O Vogl *J. Macromol. Sci., Chem.*, 1980, **14** 1105
25. G H McCain, D E Hudgin, I Rosen, *ACS Polymer Prepr.*, 1965, **6** 659
26. G Odian, L S Hiraoka *J. Polym. Sci.*, 1970, A1, **8**(5) 1309
27. P Kubisa, T Teshirogi, K Hatada, et al. *Makromol. Chem.*, 1980, **181**, 2267
28. P Kubisa, L S Corley, O Vogl, *J. Macromol. Sci., Chem.*, 1980, **181** 2267
29. E C Ladd, US P. 2 609 402; *Chem. Abs.*, 1953, **47** 11 252
30. R Kh Freidlina, A B Belyavskii *Dokl. Akad. Nauk SSSR*, 1959, **127**(6) 1027
31. R Kh Freidlina, A B Belyavskii *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1961, (1) 177
32. C H Bamford, in *Reactivity, Reaction Mechanisms, and Structure in Polymer Chemistry* (Edited by A D Jenkins et al.) (Translated into Russian), Izd. Mir, Moscow, 1977
33. F D Chattaway, R J K Muir *J. Chem. Soc.*, 1934 701
34. A Bayer *Ber. Bunsenges. Phys. Chem.*, 1872, **5** 25
35. O Fisher *Ber. Bunsenges. Phys. Chem.*, 1874, **7** 1191
36. V V Korshak, A L Rusanov, et al. *Dokl.Akad.Nauk SSSR*, 1988, **299**(1) 131
37. M Ter Meer *Ber. Bunsenges. Phys. Chem.*, 1874, **7** 1200
38. E Jager *Ber. Bunsenges. Phys. Chem.*, 1874, **7** 1197
39. E Graef, A Burger *J. Am. Chem. Soc.*, 1946, **68** 2400
40. O Zeidler *Ber. Bunsenges. Phys. Chem.*, 1874, **7** 1180
41. H L Bradlow, C A Werf *J. Am. Chem. Soc.*, 1947, **69** 662
42. M Yasue, Y Takai *Yakugaku Zasshi*, 1957, **77** 829; *Chem. Abs.*, 1957, **52** 116
43. M Trojna, J Hubacek *Chem. Listy*, 1957, **51** 752
44. M R McLaury, et al *J. Polym. Sci., Polym. Chem. Ed.*, 1980, **18**(8) 2501
45. W K S Cleveland, J I Webb, C M Orlando US P. 4 117 018, 1978
46. P L Kinson, C B Guinn, US P. 4 073 814, 1978
47. B Brand, S Busse-Sundermann *Ber. Bunsenges. Phys. Chem.*, 1942, **75**(12) 1819
48. S J Cristol *J. Am. Chem. Soc.*, 1945, **67**(9) 1494
49. H Haller, P Bartlett, N Drake, et al *J. Am. Chem. Soc.*, 1945, **67**(9)
50. O Grummitt, A Buck, A Jenkins *J. Am. Chem. Soc.*, 1945, **67**(1) 155
51. H Wichelhaus *Ber. Bunsenges. Phys. Chem.*, 1889, **22** 988
52. L H Conover, D S Tarbell *J. Am. Chem. Soc.*, 1950, **72**(8) 3586
53. H L Bradlow, C A Werf *J. Am. Chem. Soc.*, 1947, **69**(6) 1254
54. M Levine, S C Temin *J. Org. Chem.*, 1957, **22**(1) 85
55. W C White, T R Sweeny *US Public Health Rpts.*, 1945, **60** 66; *Chem Abs.*, 1945, **39** 1676
56. E C Chukovskaya, R Kh Freidlina, N A Kuz'mina *Synthesis*, 1983, (10) 773
57. A I Kovredov, Zh S Shaugumbekova, A V Kazantsev, L I Zakharkin *Zh. Obshch. Khim.*, 1979, **49**(7) 1534
58. N A Kuz'mina et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, (6) 1443
59. S S Tomar, N K Ray, S K Mukerjee *Agric. Biol. Chem.*, 1974, **38** 1067
60. W L Walton *J. Am. Chem. Soc.*, 1947, **69**(6) 1544
61. O Neilands, J Kreieberga, US P 3 935 239; *Chem. Abs.*, 1976, **85** 5370
62. I N Uspenskaya, G V Motsarev *Khim. Promst.*, 1975, (3) 181
63. H F Wilson, W E Craig US P 2 812 280; *Chem. Abs.*, 1958, **52** 7357
64. G T Barry, R Boyer *Can. J. Res.*, 1943, **26B** 518
65. W Voegtli, H Muhr, P Läuger *Helv. Chim. Acta*, 1954, **37**(6) 1627
66. T Lesiak, J Nowakowski, Polish P. 216 194, 1979
67. S Porejko, Z K Brzozowski, S Maczenski, Z Wielgosz, Polish P. 48 893, 1964
68. S Porejko et al *Chim. Ind. (Milan)*, 1964, **92**(3) 243
69. S Porejko, Z Wielgosz *Polimery*, 1968, **13**(2) 55
70. J Nowakowski *Zh. Org. Khim.*, 1981, **17**(7) 1482

71. Z K Brzozowski, B Zurakowska *IUPAC Macro-83, Bucharest,* 1983, VIII-26, p. 343
72. S Kirkwood, P H Phillips *J. Am. Chem. Soc.*, 1947, **69**(4) 934
73. G S Mironov, V A Ustinov, M I Farberov *Zh. Org. Khim.*, 1972, **8**(7) 1509
74. J Forest, O Stephenson, W A Waters *J. Chem. Soc.*, 1946, (5) 333
75. O G Backeberg, J L O Marais *J. Chem. Soc.*, 1945, **54**(11) 803
76. V T Dorofeev, V N Sokolenko USSR P. 793 989; *Byull. Izobret.*, 1981, (1) 92
77. A M Kharaev, E R Kekharsaeva, G B Shustov, V T Dorofeev *Polikondensatsionnye Protsessy i Polimery* (Polycondensation Processes and Polymers), Izd. Kabardino-Balkar. Gos. Univ., Nal'chik, 1984, p. 51
78. V T Dorofeev, A A Matnish'yan, M G Mordzon, S G Grigoryan *Reaktivy i Osobo Chistye Veshchestva* (Reagents and Specially Pure Substances), Izd. NIITEKhim, Moscow, 1980, No. 6
79. T Lesiak, J Nowakowski, Polish P. 219 827, 1979
80. B G Clayton, F G Wiliams, US P. 3 944 517
81. B G Clayton, F G Williams, US P. 3 956 222
82. T Takekoshi, J E Kochanowski, J S Manello, M J Webber *J. Polym. Sci., Polym. Chem. Ed.*, 1985, **23**(6) 1759
83. Z Jedlinski, U Gaik, B Kowalski, Polish P. 131 685
84. V V Korshak, A L Rusanov, Yu N Margalitadze, N Z Makharashvili *Vysokomol. Soedin., Ser. B*, 1988, **30**(3) 114
85. T Lesiak, J Nowakowski *J. Prakt. Chem.*, 1979, **321**(6) 921
86. P Montagne *Ber. Bunsenges. Phys. Chem.*, 1915, **48** (10) 1027
87. A Burger, E Graeff, M S Bailey *J. Am. Chem. Soc.*, 1946, **68**(9) 1725
88. V V Voronenkov, E A Lazurin *Zh. Org. Khim.*, 1971, **7**(8) 1764
89. G S Mironov, I V Budnii, K A Chernyakovskaya, M I Farberov *Zh. Org. Khim.*, 1972, **8**(3) 597
90. V A Ustinov, G S Mironov, V V Kepeikin, et al., USSR P. 529 149; *Chem. Abs.*, 1976, **85** 192378
91. G A Adam, N Husein *Br. Polym. J.*, 1979, 190
92. F Consonna *Gazz. Chim. Ital.*, 1904, **34** 374
93. V V Korshak et al. *Dokl. Akad. Nauk SSSR*, 1986, **289**(2) 367
94. H Schnell *Chemistry and Physics of Polycarbonates* (Translated into Russian), Izd. Khimiya, Moscow, 1967
95. O V Smirnova, S B Erofeeva *Polikarbonaty* (Polycarbonates), Izd. Khimiya, Moscow, 1972
96. V V Korshak, S V Vinogradova *Neravnovesnaya Polikondensatsiya* (Non-equilbrium Polycondensation), Izd. Nauka, Moscow, 1972
97. D W Fox *Encyclopedia of Chemical Technology*, Wiley, New York, 1982, Vol. 18, p. 479
98. D W Fox *ACS Polym. Prepr.*, 1986, **27**(1) 474
99. Z Dobkowski, B Krajewski, Z Wielgosz *Polimery*, 1970, **15**(8) 428
100. Z Sobiczewski, Z Wielgosz *Plast. Kautsch.*, 1968, **15** 176
101. Z Sobiczewski, Z Wielgosz, K Janicka *Plast. Kautsch.*, 1969, **16** 99
102. Z Boromowska, Z Wielgosz *Polimery*, 1970, **15** 12
103. S Porejko, Z Wielgosz *Polimery*, 1971, **16** 495
104. S Porejko, Z Wielgosz *Polimery*, 1972, **17** 76
105. Z Boromowska, Z Wielgosz *Polimery*, 1975, **20** 1
106. W K S Cleveland, I L Webb, C M Orlando, US P. 4 117 018, 1978
107. A Factor, C M Orlando *J. Polym. Soc., Polym. Chem. Ed.*, 1980, **18**(2) 579
108. Z K Brzozowski *Polimery*, 1984, **29** 415
109. K N Sannes, A Factor, US P. 4 118 370, 1978
110. J C Cornahan, A M Colley *ACS Polym. Prepr.*, 1972, **20**(2) 353
111. G L Nelson, E J Hixson, E P Denike *J. Combust. Toxicol.*, 1978, **5** 222
112. C J Hilado, C L Slattengren, A Fryst, et al. *J. Combust. Toxicol.*, 1976, **3** 270
113. V V Korshak, S V Vinogradova *Poliarilaty* (Polyarylates), Izd. Nauka, Moscow, 1964
114. Z K Brzozoski, J Kielkiewicz, Z Gozlowski *Angew. Makromol. Chem.*, 1975, **44** 1
115. J Kielkiewicz, S Porejko *Angew. Makromol. Chem.*, 1979, **78** 75
116. Z K Brzozowski, J Kaczorowski, C Traczewski *Prepr. Int. Symp. Macromolec. Helsinki*, 1972, Vol. 4, Sec. 3, p. 373
117. Z K Brzozowski *XXXI IUPAC Macromolecular Symposium. Merseburg (GDR), 1987*, Microsymp. I. Abstracts, p. 60
118. A M Kharaev et al *Vysokomol. Soedin., Ser. A*, 1986, **28**(6) 1325
119. Z K Brzozowski, J Kielkiewicz, S Porejko, J Kaczorowski, US P. 3 887 522, 1975
120. Z K Brzozowski, J Kielkiewicz, S Porejko, J Kaczorowski, B. P. 1 384 975, 1975
121. Z K Brzozowski, J Petrus, J Dubczynski *J. Macromol. Sci., Chem.*, 1979, **A13**(17) 887
122. Z K Brzozowski *Chem. Prum.*, 1976, **26** 315
123. Z K Brzozowski, B Jozwik *J. Photochem.*, 1986, **35**(3) 341
124. Z K Brzozowski, J Kielkiewicz, K Bukat, et al. *II Internat. Conf. Symp.*, 1979, 3B
125. Z K Brzozowski, J Kielkiewicz, K Goslanka *Plast. Kautsch.*, 1979, 26
126. Z K Brzozowski, S Porejko, J Kaczorowski, J Kielkiewicz US P. 3 856 558, 1975
127. A K Mikitaev et al. *Vysokomol. Soedin., Ser. B*, 1983, **25**(12) 916
128. A I Kharaev, E R Kekharsaeva, G B Shustov, V T Dorofeev *Polikondensatsionnye Protsessy i Polimery* (Polycondensation Processes and Polymers), Izd. Karbardino-Balkar. Gos. Univ., Nal'chik, 1984, p. 51
129. S V Plyasovskaya, M A Voronina, L D Khokhlyavina *Vopr. Khim. Khim. Tekhnol.*, 1983, **72** 43; *Chem. Abs.*, 1984, **101** 171863
130. A M Kharaev et al. *Vysokomol. Soedin., Ser. A*, 1986, **28**(6) 1325
131. A K Mikitaev et al *Vysokomol. Soedin., Ser. A*, 1984, **26**(6) 1207
132. E R Kekharsaeva, A K Mikitaev, G B Shustov, et al. *Plast. Massy*, 1985, (7)
133. A Zh Taova, S F Koshieva, A M Kharaev, Z M Betrozova *Polkondensatsionnye Protsessy i Polymery* (Polycondensation Processes and Polymers), Izd. Kabardino-Balkar. Gos.Univ., Nal'chik, 1985, p. 133; *Ref. Zh. Khim.*, 1986, 14S347
134. Z K Brzozowski, B Zurakowska *IUPAC Macro-83, Bucharest,* 1983, VII-26, p. 343
135. Z K Brzozowski, B Jozwik, K Wojhar, P Priffer *IUPAC Macro-83, Bucharest*, 1983, CII-27, p. 347
136. Z K Brzozowski, P Kaminski *Pr. Nauk. Inst. Technol. Org. i Tworzyw. Sztucz. Wrocl.*, 1985, (39) 25; *Ref. Zh. Khim.*, 1986, 15S189
137. F J Williams, A S Hay, H M Relles, et al. *New Monomers and Polymers* (Edited by B M Culbertson et al.), Plenum Press, New York–London, 1984
138. R N Johnson *J. Polym. Sci.*, 1967, A1, **5**(4) 1237

139. A S Hay *Adv. Polym. Sci.*, 1967, **4** 496
140. Z K Brzozowski, G Rokicki, B Pogorzelska-Marciniak *Angew. Makromol. Chem.*, 1976, **43** 59
141. Z K Brzozowski, J Kielkiewicz *Polimery*, 1973, **18** 315
142. R A Clendinning, A G Farnham, R N Johnson *ACS Polymer Prepr.*, 1986, **27**(1) 478
143. J B Rose *ACS Polymer Prepr.*, 1986, **27**(1) 480
144. R N Johnson et al. *J. Polym. Sci.*, 1967, A1, **5**(9) 2375
145. T A Attwood, P C Dawson, J L Freeman, et al. *Polymer*, 1981, **22** 1096
146. D R Kelsey US P. 4 638 944
147. I Fukawa, H Komeda, H Sakurai *Japanese Appl.* 61-143 438; *Ref. Zh. Khim.*, 1987, 12S521
148. I Fukawa, H Komeda, H Sakurai *Japanese Appl.* 61-200 127; *Ref. Zh. Khim.*, 1987, 17S440
149. T Lesiak, J Nowakowski *Vysokomol. Soedin.,Ser. B*, 1980, **22**(7) 498
150. G A Adam, M A Husoin, M M Barbooti *Thermochim. Acta*, 1980, **37** 173
151. T Takekoshi *Polymer J.*, 1987, **19**(1) 191
152. E Radlmann, W Schmidt, G E Nischk *Makromol. Chem.*, 1969, **130** 45
153. Z K Brzozowski, A Grabowska-Rostek, Z Przybysz *J. Macromol. Sci., Chem.*, 1981, **A16**(7) 1193
154. Z K Brzozowski, Z Przybysz, A Grabowska-Rostek *J. Macromol. Sci., Chem.*, 1981, **A16**(7)
155. V V Korshak, A L Rusanov, S Kh Fidler, et al. *Trudy X Mezhdunarodnogo Mikrosimpoziuma po Polikondensatsii. Solnechnyi Bereg (NRB). 1985* [Proceedings of X International Microsymposium on Polycondensation. Slanchev Brjag (Bulgaria). 1985], Izd. Bolg. Akad. Nauk 1986, p. 123.
156. V V Korshak, A L Rusanov, N Z Makharashvili, G V Kazakova *Plast Massy*, 1987, (11) 18
157. V T Dorofeev, V N Sokolenko, I A Oleksyuk, L A Seredina *Vysokomol. Soedin., Ser. B*, 1978, **20**(10) 737
158. A I Burya et al. *Vopr. Khim. Khim. Tekhnol.*, 1979, (57) 109
159. V T Dorofeev *Vysokomol. Soedin., Ser. B*, 1981, **23**(12) 925
160. A C Karydas, W T Whang, E M Pearce *J. Polym. Sci., Polym. Chem. Ed.*, 1984, **22**(3) 847
161. E M Pearce *Polym. Prepr. Jpn.*, 1983, **32**(5) 975
162. V V Korshak, A L Rusanov, S Kh Fidler, et al. *Vysokomol. Soedin., Ser. B*, 1985, **27**(3) 220
163. P M Hergenrother *Angew. Makromol. Chem.*, 1986, **145/146** 323
164. P M Hergenrother *Polymer J.*, 1987, **19**(1) 73
165. V V Korshak et al *Faserforsch. Textiltechn.*, 1978, **29**(11/12) 649
166. W Wrasidlo, J M Augl *Macromolecules*, 1970, **3**(5) 544
167. P M Hergenrother *J. Macromol. Sci. Rev.*, 1971, **C6**(1) 1
168. P M Hergenrother *J. Appl. Polym. Sci.*, 1974, **18** 1779
169. P M Hergenrother *Polym. Eng. Sci.*, 1976, **16**(5) 303
170. J M Augl, J V Duffy *J. Polym. Sci.*, 1971, **A9** 1343

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Porphyrin–quinone compounds as synthetic models of the reaction centre in photosynthesis

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ABSTRACT. **Data on the synthesis, steric structure, and photochemical properties of porphyrin–quinone compounds as synthetic models of the reaction centre in photosynthesis are examined and described systematically.**

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I. Introduction

The electron transfer from the electronically excited chlorophyll molecule or its dimer via intermediate acceptors to the primary quinone-type acceptor is a key step in photosynthesis.[1–4] The efficiency of charge separation in photosynthesis is close to unity. One of the factors ensuring such efficiency is the high degree of the structural organisation of the photosynthetic apparatus. However, the complex structure of the reaction centres of photosynthesising organisms makes it difficult to understand the mechanisms of charge separation in photosynthesis. This and also the attempts to create, by analogy with photosynthesis, artificial systems for the utilisation of solar energy have stimulated the synthesis and study of various compounds which are models of the reaction centres in photosynthesis, such as covalently bound porphyrins with different structures: porphyrin–polymer complexes,[5–7] porphyrin dimers,[8,9] porphyrin–quinone compounds,[10,11] etc.

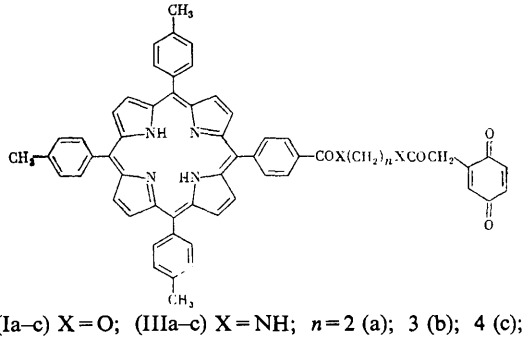
The electron transfer from the porphyrin, whose molecular structure is similar to that of chlorophyll, to a covalently bound quinone models the primary charge separation stage in photosynthesis. The high electron-accepting capacity of quinones has been demonstrated in a number of studies on the flash photolysis of solutions containing electron-donating additives and quinones.[12–22] However, attempts to model charge separation processes in photosynthesis with the aid of homogeneous solutions have encountered considerable problems. The most important of these is the extremely low, compared with photosynthesis, efficiency of the separation of the oxidised and reduced forms of the reactants in solutions. Despite the fact that effective quenching of the fluorescence of chlorophyll and its analogues by quinones has been observed in solutions, the attempts to detect radical-ions have been unsuccessful.[12,13] This is apparently due to the rapid recombination of the radical-ions as a result of the collisions between the radical-cation of the porphyrin (P^+) and the radical-anion of the quinone (Q^-) in solutions.

The attempts to use micelles,[23,24] liposomes,[25,26] and cyclodextran compounds[27] to stabilise the radical-ions and to elucidate the detailed mechanism of the photoseparation of charges have also failed to yield the desired result. This has in fact stimulated the synthesis and study of porphyrin–quinone compounds (P–Q), in which the porphyrin and the quinone are separated by a system of covalent bonds.

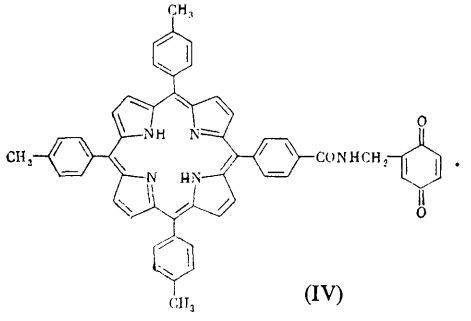
In terms of the character of the bond between the porphyrin and the quinone, all the P–Q compounds synthesised hitherto since 1978 can be divided into two main groups: (1) P–Q compounds with a flexible covalent bond and (2) P–Q compounds with a rigid bond between the porphyrin and the quinone. In addition, covalently bound triads, containing an electron-donating fragment together with P and Q, can be differentiated as an independent group.

II. Porphyrin–quinone compounds with a flexible covalent bond between the porphyrin and the quinone

P–Q derivatives with a flexible bond are the simplest and most readily available. There exist different ways of linking P and Q:



(Ia–c) X = O; (IIIa–c) X = NH; n = 2 (a); 3 (b); 4 (c);



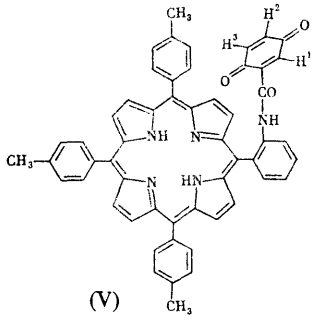
(IV)

Compounds (I) in which the porphyrin and quinone components are linked by a diol chain of different lengths were some of the first to be synthesised.[28,29] 5-(4-Chlorocarboxyphenyl)-10,15-20-tri(4-tolyl)porphyrin (II), obtained by the Rothemund reaction from pyrrole and a mixture of 4-toluic aldehyde and 4-carboxybenzaldehyde[30] and subsequent treatment with thionyl chloride, was condensed in the presence of pyridine with an excess of the alcoholic component obtained by esterifying 2,5-dimethoxyphenylacetic acid with ethane-1,2-diol (derivative a), propane-1,3-diol (derivative b), and butane-1,4-diol (derivative c) with formation of a porphyrin-dimethoxybenzene derivative. The yield of the product was ~60%. After removing the methyl protecting group with BBr_3 and oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), compound (I) was purified chromatographically on silica gel.

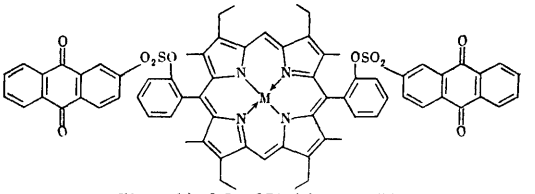
The replacement of the ester linkage by the hydrolytically more stable amide linkage leads to compound (III). It has been suggested[31] that the amide linkage makes the structure more rigid because of its greater similarity to the double bond. The conditions in the synthesis and purification of the derivative (III) are almost identical to those for compound (I), but the hydroquinone adduct was oxidised with PbO_2, which greatly simplified the isolation of the product (III). The yields in the stage involving the condensation of the porphyrin (II) with the amino-component were 40–50%.

In order to obtain the porphyrin-quinone (IV) with a shortened chain, the acid chloride (II) was treated with 2,5-dimethoxybenzylamine.[32] After removing the protecting group and oxidising the hydroquinone component, the product (IV) was obtained similarly to compound (III).

On formation of the amide bond between the two chromophores in the *ortho*-position in the benzene ring of the porphyrin, compound (V) is obtained with a still more rigid structure than compound (IV):[33]



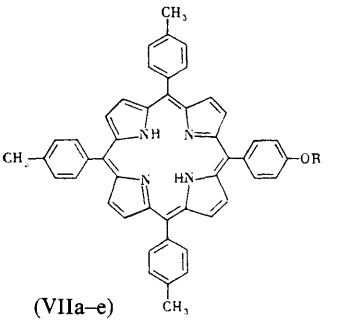
(V)



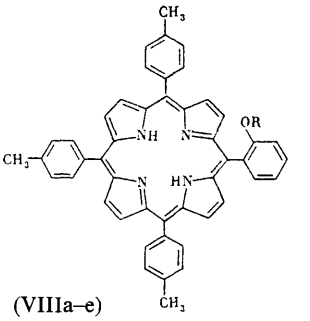
(VI a, b), M = 2H (a); Zn (b).

One equivalent of 5-(2-aminophenyl)-10,15,20-triphenylporphyrin, obtained by the Rothemund reaction from pyrrole and a mixture of benzaldehyde and 2-nitrobenzaldehyde and subsequent reduction with $SnCl_4$ in concentrated hydrochloric acid,[34] was treated with 10 equivalents of 1,4-diacetoxy-2-chlorocarbonylbenzene. The yield of the protected hydroquinone derivative was 76%. Selective hydrolysis with HCl in methanol (pH ~1) followed by oxidation with PbO_2 led to the product (V) in 75% yield.

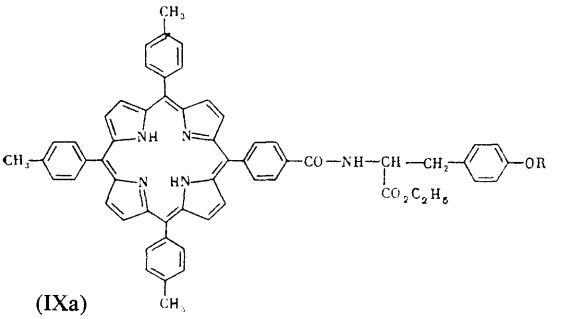
The fact that the sulphonyloxy-derivative involving the *ortho*-position of the phenyl residue in porphyrins has a rigorously defined "folded" conformation[35] led to the idea of synthesising the diquinone compound (VIa).[36] The structure (VIa) was synthesised by condensing 3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrrolylmethane with the corresponding aldehyde in the presence of toluene-*p*-sulphonic acid and subsequent oxidation with DDQ and isolation of the product by column chromatography on silica. The zinc complex (VIb) was obtained by treating the free base (VIa) with zinc acetate:



(VIIa–e)



(VIIIa–e)

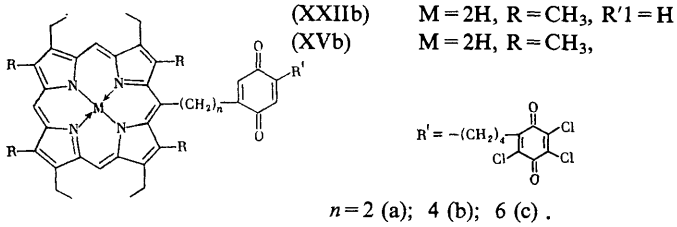


(IXa)

R =  (a),  (b),  (c),  (d),  (e).

A convenient method of synthesis of a large number of derivatives (VII)–(IX) has been developed on the basis of the photoinduced cross-condensation reaction between a phenol-containing porphyrin and a quinone.[37,38] 5-(4-Hydroxyphenyl)-10,15,20-tri(4-tolyl)-porphyrin was irradiated at a wavelength > 590 nm in the presence of a tenfold excess of 1,4-benzoquinone with formation of the condensation product (VIIa). No side products were then detected

by thin-layer chromatography (TLC) and ^{1}H NMR spectroscopy. Other P–Q derivatives (VIIb–e), (VIIIa–e), and (IXa) were obtained similarly. The yields were 90–94% for a relatively low degree of conversion (6–41%). The condensation took place via a stage involving the formation of the hydroquinone adduct and the subsequent oxidation to the P–Q compound by the excess of the initial quinone:



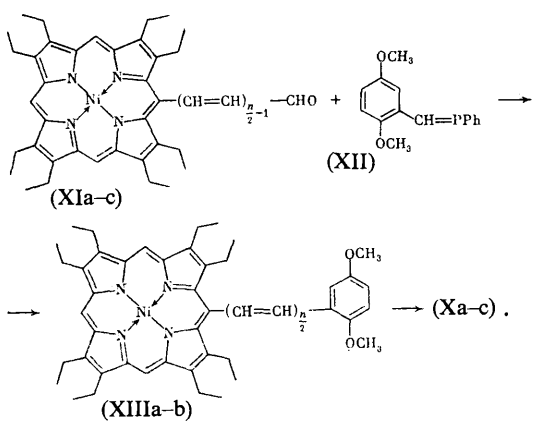
(D)(Xa–c) M = 2H, R = C_2H_5, R′ = H
(XIVa–c) M = Zn, R = C_2H_5, R′ = H
(XXIIb) M = 2H, R = CH_3, R′1 = H
(XVb) M = 2H, R = CH_3,

R′ = $-(CH_2)_4-$

n = 2 (a); 4 (b); 6 (c).

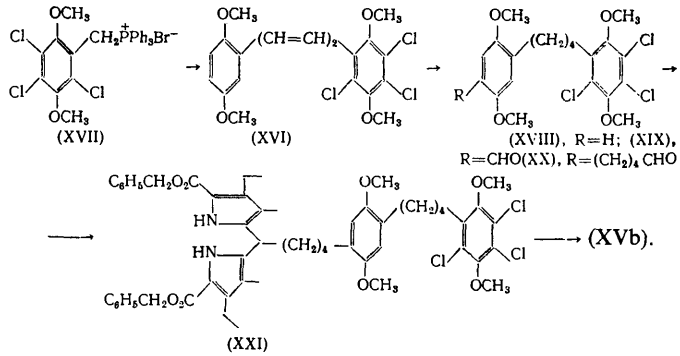
In order to avoid the possible influence of the heteroatom in the chain between the donor and the acceptor on the interaction between the chromophores and on the photoinduced intramolecular charge transfer and also the influence of the phenyl residues on the porphyrin ring, compounds (Xa–c) were synthesised. The chromophores were linked by polymethylene chains of different lengths (n = 2–6).[39] The synthesis was carried out as follows. The nickel complexes of octaethylporphyrins (XIa–c),[40,41] containing the formyl group in the *meso*-position, were condensed by the Wittig reaction with the triphenylphosphorane (XII), producing the dimethoxyphenyl complexes (XIIIa–c) in 82–95% yield (the Scheme 1). After removing the protecting group BBr_3, hydrogenation over Pd/C, and oxidation with DDQ, the yields of compounds (Xa–c) were 20–36%. The zinc complexes (XIVa–c) were obtained by treating the porphyrins (Xa–c) with zinc acetate.

Scheme 1



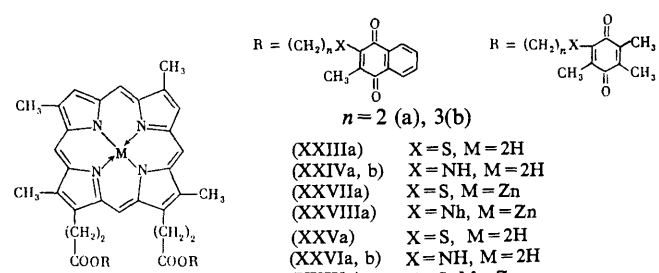
In natural photosynthesis, electron transfer takes place via many stages, which apparently promotes the stabilisation of the state with separated charges. The porphyrin (XVb), containing two series-connected acceptors with a corresponding oxidation-reduction potential (ORP) models such transfer.[42] The presence of two different quinones in this compound ensures a potential gradient in the molecule. The diquinone precursor (XVI) was obtained by the Wittig reaction from 2,5-dimethoxycinnamaldehyde and phosphonium bromide (XVII) (Scheme 2):

Scheme 2



After hydrogenation to compound (XVIII) over Pd/C, formylation by dichloromethyl methyl ether with formation of compound (XIX), and the lengthening of the chain by means of the Wittig reaction with the corresponding phosphonium salt, the aldehyde (XX) was condensed with 2-benzyloxycarbonyl-3-ethyl-4-methylpyrrole. The yield of the bipyrrole (XXI) was 85%. After removal of the benzyl protecting group from compound (XXI), the condensation of the product with 4,4′-diethyl-5,5′-diformyl-3,3′-dimethyl-2,2′-methylenebis(pyrrole) led to the corresponding aetioporphyrin derivative in 24% yield. Demethylation of the latter with BBr_3 and oxidation with DDQ afforded the diquinone derivative (XVb) (yield 24%).

In order to elucidate more accurately the influence of the second acceptor on the charge separation process, the aetioporphyrin (XXIIb), containing only one quinone residue, was synthesised[43] by a procedure similar to that used for compound (XVb):

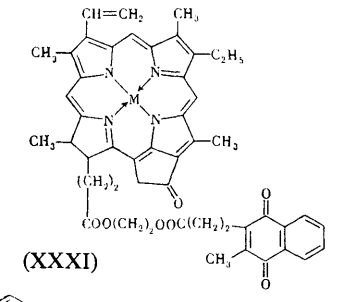


n = 2 (a), 3(b)

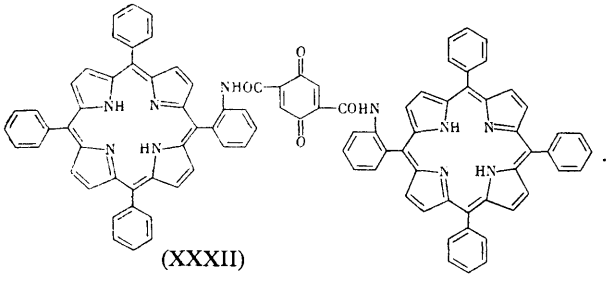
(XXIIIa) X = S, M = 2H
(XXIVa, b) X = NH, M = 2H
(XXVIIa) X = S, M = Zn
(XXVIIIa) X = Nh, M = Zn
(XXVa) X = S, M = 2H
(XXVIa, b) X = NH, M = 2H
(XXIXa) X = S, M = Zn
(XXXa) X = NH, M = Zn.

The present authors[44,45] synthesised P–Q compounds using for the first time deuterioporphyrin IX—a natural porphyrin. The hydroxyquinone derivatives were obtained by adding 2-mercaptoethanol, 2-aminoethanol, and 3-aminopropanol to 2-methylnaphthoquinone and 2,3,5-trimethylbenzoquinone. After purification, the yields were 55–91% for the sulphur containing quinones and 8–25% for the nitrogen-containing quinones. Compounds (XXIII)–(XXX) made it possible to investigate the influence of the nature of the heteroatom linked directly to the quinone fragment on the charge separation process. The condensation of hydroxyquinones with deuterioporphyrin IX using di-t-butyl pyrocarbonate and 4-dimethylaminopyridine led to the diquinone derivatives (XXIII)–(XXVI) in 76–89% yields. After compounds (XXIII)–(XXVI) had been treated

with zinc acetate, the corresponding zinc complexes (XXVII)–(XXX) were obtained:



(XXXI)



(XXXII)

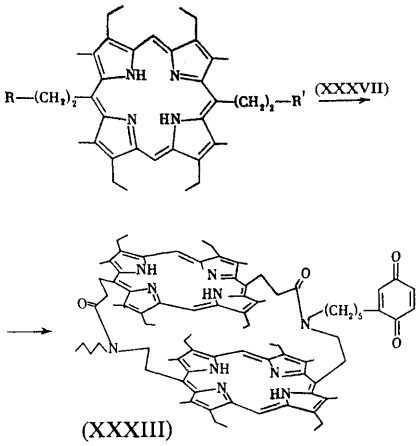
Compound (XXXI) has been synthesised[46] by a method in which carboxy-derivatives of pyrochlorophyll *a* and 2-methylnaphthoquinone were condensed via an ethylene glycol bridge.

It is known that one of the primary donors in bacterial photosynthesis is a chlorophyll "special pair".[47] The model compound (XXXII), in which two 5-(2-aminophenyl)-10,15,20-triphenylporphyrin derivatives are joined together by a bridge containing the benzoquinone structure, was therefore synthesised.[48] However, steric factors hinder the formation of the steric structure of the diporphyrin (XXXII) analogous to the structure of the natural chlorophyll dimer.

A more adequate model of the "special pair" is a rigid dimeric structure of the "surface to surface" type containing two porphyrin macrocycles connected by two covalent bonds.[49–52]

Compound (XXXIII),[53] in which two aetioporphyrin derivatives are linked covalently in the *meso*-position in the "surface to surface" orientation and benzoquinone is joined to the side chain, may make it possible to elucidate the role of the dimeric porphyrins in the stabilisation of the photoinduced state with separated charges. The synthesis was carried out in accordance with Scheme 3: Successive treatment of the di(methanesulphonate) (XXXIV), obtained by the method of Collman et al.,[54] with butylamine [involving the formation of compound (XXXV)] and with 1-(5-aminopentyl)-2,5-dimethoxybenzene led to the diamine (XXXVI) [the yields in the stages involving the formation of compounds (XXXV) and (XXXVI) were 38 and 67% respectively after chromatographic purification]. After the condensation of the amino-derivative (XXXVI) with the acid chloride (XXXVII) by the method of Collman et al.[54] (the yield in the condensation stage was 42%) and the removal of the methyl protecting group with BBr_3 followed by oxidation with DDQ (yield 28%), the P–Q dimer (XXXIII) was obtained. Compound (XXXIII) was purified by preparative TLC.

Scheme 3



(XXXIII)

(XXXIV), R = R' = OSO_2CH_3, (XXXV), R = OSO_2CH_3, R' = NHC_4H_9

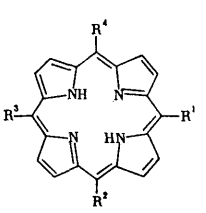
(XXXVI), R = NHC_4H_9, R' = $NH(CH_2)_5$–  , (XXXVII), R = R' = COCl.

III. Porphyrin–quinone compounds with a rigid bond between the porphyrin and the quinone

1. Polymer-based models

In P–Q compounds with a flexible linkage, there is an appreciable conformational mobility determined by external factors such as solvent polarity, the presence of external ligands, etc. This hinders the interpretation of the experimental results for the electron phototransfer in such systems. It therefore became necessary to create model structures in which the orientations of the donor and acceptor are known beforehand. One of the aspects of studies in this field involved the construction of a model of the photoreaction centre on a polymer base.[55] In this model, the porphyrin and quinone groups are distributed along a polymer chain and are separated by a known distance. The average distance between the chromophores can be regulated by altering the pH and the ionic strength of the solution. The copolymerisation of acrylic acid with 5-(10,15,20-tritolylporphyrinyl)phenyl methacrylate and 2-isopropenylanthraquinone led to the corresponding porphyrin-quinone polymer containing on average one porphyrin and three anthraquinone groups in the polymer chain.

2. Models with a rigid covalent bridge



(XXXVIII) $R^1 = R^2 = R^3 = R^4 = C_6H_3O_2$;

(XXXIX) $R^1 = C_6H_5$; $R^2 = R^3 = R^4 = C_6H_3O_2$;

(XL) $R^1 = R^2 = C_6H_5$; $R^3 = R^4 = C_6H_3O_2$;

(XLI) $R^1 = R^3 = C_6H_5$; $R^2 = R^4 = C_6H_3O_2$;

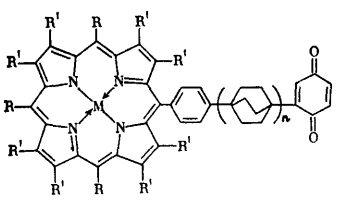
(XLII) $R^1 = R^2 = R^3 = C_6H_5$; $R^4 = C_6H_3O_2$;

(XLIII) $R^1 = R^2 = R^3 = C_6H_5$; $R^4 = C_6H_3O_2$;

(XLIV) $R^1 = R^2 = C_6H_5$; $R^3 = R^4 = C_6H_3O_2$;

(XLV) $R^1 = R^3 = C_{15}H_{21}$; $R^2 = R^4 = C_6H_3O_2$.

Another way of ensuring the rigidity of the structure is the formation of a C–C bond directly between the porphyrin and quinone components. The first models of this type (XXXIII)–(XLV) were obtained by the Rothemund condensation of pyrrole with an equimolecular amount of either 2,5-dimethyoxybenzaldehyde [in the case of compound (XXXVIII)] or with a mixture of the corresponding aldehydes [in the case of compounds (XXXIX)–(XLV)][56–58] and subsequent treatment with BBr_3 and DDQ. However, in contrast to natural systems, the distance between P and Q in compounds (XXXVIII)–(XLV) is small.

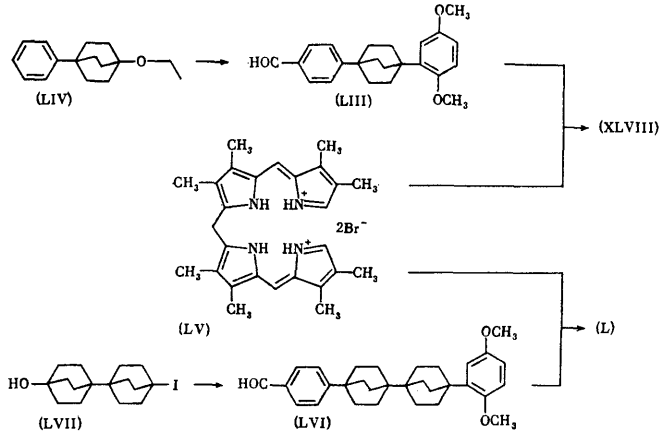


(XLVI) M = 2H, R = H, R' = CH_3, n = 0;
(XLVII) M = Zn, R = H, R' = CH_3, n = 0;
(XLVIII) M = 2H, R = H, R' = CH_3, n = 1;
(XLIX) M = Zn, R = H, R' = CH_3, n = 1;
(L) M = 2H, R = H, R' = CH_3, n = 2;
(LI) M = Zn, R = H, R' = CH_3, n = 2;
(LII) M = 2H, R = n-$CH_3C_6H_4$, R' = H, n = 1.

The structures (XLVI)–(LII), in which the P and Q fragments are linked by a rigid covalent bridge of variable length, are more suitable models of the reaction centres in photosynthesis.[59,60] In such compounds, there is a possibility of rotation only relative to the C–C bond. The models (XLVI)–(LII) are suitable for the investigation of the dependence of the efficiency of the charge separation on the distance between the donor and the acceptor.

The synthesis of these compounds is based on the method involving the condensation of linear tetrapyrroles and the corresponding aldehydes with formation of *meso*-substituted porphyrins (Scheme 4).[59]

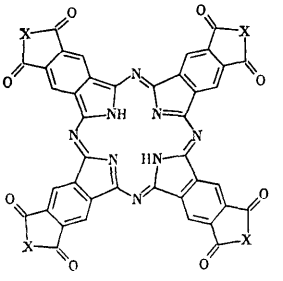
Scheme 4

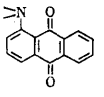
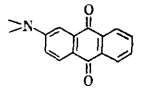


Arylbicyclo[2.2.2]octylbenzaldehyde (LIII), obtained from the ethyl ether of 4-phenylbicyclo[2.2.2]octanol (LIV), was condensed with *ac*-biladiene (LV) in 40% yield. Arylbibicyclo[2.2.2]octylbenzaldehyde (LVI), obtained from 4'-iodo-1,1'-bibicyclo[2.2.2]octan-4-ol (LVII), reacted similarly with *ac*-biladiene (LV) affording a yield of 30%. After the removal of the protecting group with BBr_3, oxidation with PbO_2, and chromatographic purification, the derivatives (XLVIII) and (L) respectively were obtained. Compound (XLVI) was synthesised similarly. Zinc was introduced by treating compounds (XLVI), (XLVIII), and (L) with zinc acetate to form the complexes (XLVII), (XLIX), and (LI) respectively.

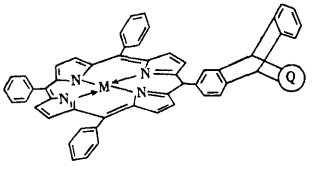
Compound (LII)[60] with the same type of bond but based on a tetraarylporphyrin was obtained by the Rothemund condensation of pyrrole with the appropriate amount of a mixture of 4-methylbenzaldehyde and 1-(4-formylphenyl)-4-(1,4-benzoquinonyl)-bicyclo[2.2.0]octane synthesised from 1-hydroxy-4-iodobicyclo-[2.2.2]octane in three stages.

Phthalocyanines, which are structural analogues of porphyrins, can also behave as electron donors in photochemical processes. The phthalocyanine-quinone compounds (LVIII) and (LIX), which possess only a rotational degree of freedom relative to the C–N bond, were obtained for the first time[61] by condensing the tetraanhydride (LX) with 1- or 2-aminoanthraquinone and subsequent purification by three reprecipitations from dimethylformamide with benzene. The yields of compounds (LVIII) and (LIX) were 38 and 77% respectively:

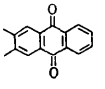


(LVII) X = 
(LIX) X = 
(LX) X = —O— .

In order to increase the rigidity of the linkage and to prevent the rotation of the chromophores relative to one another, the model compounds (LXI)–(LXIII), in which the porphyrin and quinone components are separated by a triptycene bridge, were synthesised:[62]



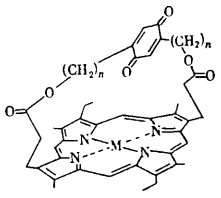
M = 2H (a); Zn (b)

(LXIa, b) Q = 
(LXIIa, b) Q = 
(LXIIIa, b) Q =  .

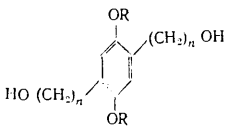
5-(2-Anthryl)-10,15,20-triphenylporphyrin, obtained in 25% yield by condensing a mixture of 2-anthraldehyde, benzaldehyde, and pyrrole, was refluxed in xylene with a fivefold excess of benzoquinone, which led to compound (LXIa) in 40% yield. For the synthesis of compound (LXIIa), the corresponding bicyclic naphthoquinone was obtained by the Diels–Alder addition of naphthoquinone to anthracene with subsequent oxidation *in situ*. After alkylation with dichloromethyl methyl ether and hydrolysis to the aldehyde (yield 30%), the product was condensed with benzaldehyde and pyrrole to form compound (LXIIa) in 15% yield. The derivative (LXIIIa) was obtained similarly by the Rothemund method in 18% yield. The bicyclic anthraquinone necessary for the synthesis of compound (LXIIIa) was obtained from triptycene acylated by phthalic anhydride and treated with polyphosphoric acid.

3. "Capped" porphyrin-quinones

P–Q derivatives, in which the quinone is rigorously oriented over the centre of the porphyrin ring, the so called "capped" porphyrin-quinones, are of considerable interest for the modelling of the charge separation process in photosynthesis. The linkage between the fragments is achieved by means of two or four covalent bridges located opposite one another. The advantages of such model systems consist in the possibility of controlling during synthesis the relative oxidation-reduction potentials of the fragments, the distances between them, and their mutual orientation:



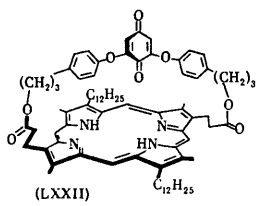
(LXVI) M=2H, n=2;
(LXVII) M=2H, n=3;
(LXX) M=Mg, n=2;
(LXXI) M=Mg, n=3.



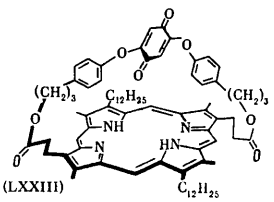
(LXVIII) R=CH_3, n = 2;
(LXIV) R=CH_2OCH_3, n = 2;
(LXIX) R=CH_3, n=3;
(LXV) R=CH_2OCH_3, n = 3.

The synthesis of such P–Q compounds is based on porphyrins with a symmetrical structure. The condensation of the acid chloride of mesoporphyrin II with the corresponding hydroquinone derivatives (LXIV) and (LXV) at high dilution in CH_2Cl_2 in the presence of Et_3N afforded "capped" porphyrins in 7 and 15% yields respectively. The subsequent removal of the protecting groups with BCl_3 and oxidation by PbO_2 led to compounds (LXVI) and (LXVII).[63,64] The quinone component was modified as follows: after the Friedel–Crafts chloromethylation in the 2- and 5-positions, 1,4-dimethoxybenzene was converted into the nitrile and the subsequent hydrolysis and esterification with ethanol gave rise to the diester which was reduced to the alcohol (LXVIII). In order to increase the chain length (to n = 3), 2,5-bis(dichloromethyl)-1,4-dimethoxybenzene was treated with diethyl malonate to form the tetraester, from which the ethoxycarbonyl groups were then removed under mild conditions by refluxing in dimethyl sulphoxide and the product was reduced to the diol derivative (LXIX). However, the methyl protecting group cannot be removed by known methods, without decomposing the structure, from the "capped" porphyrins obtained by condensing the acid chloride of mesoporphyrin II with the alcohols (LXVIII) and (LXIX). This problem was solved by replacing the methyl protecting group by the more labile methoxymethyl protecting group. After acylation and demethylation of the alcohol (LXVIII), the resulting hydroquinone was protected by methoxymethyl ether which was followed by deacylation to give the diol derivative (LXIV). The alcohol (LXIX) was modified analogously to give compound (LXV). Magnesium was introduced into the "capped" porphyrins (LXVI) and (LXVII) by Eschenmoser's method[65] with formation of the magnesium complexes (LXX) and (LXXI).

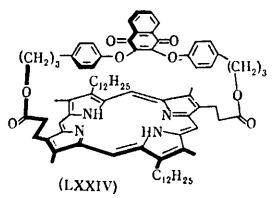
As for the linear P–Q compounds (VII) and (IX),[37,38] the method of photoinduced cross-condensation has been used to synthesise the "capped" porphyrins (LXXII)–(LXXIV) from the modified mesoporphyrin II.[66] The porphyrin component was obtained by condensing 1,5-di(2-chlorocarbonylethyl)-3,7-didodecyl-2,4,6,8-tetramethylporphyrin with 3-(4-hydroxyphenyl)-1-propanol, which led to the formation of the "capped" porphyrins (LXXII)–(LXXIV) on irradiation in the presence of the corresponding quinone derivatives:



(LXXII)



(LXXIII)



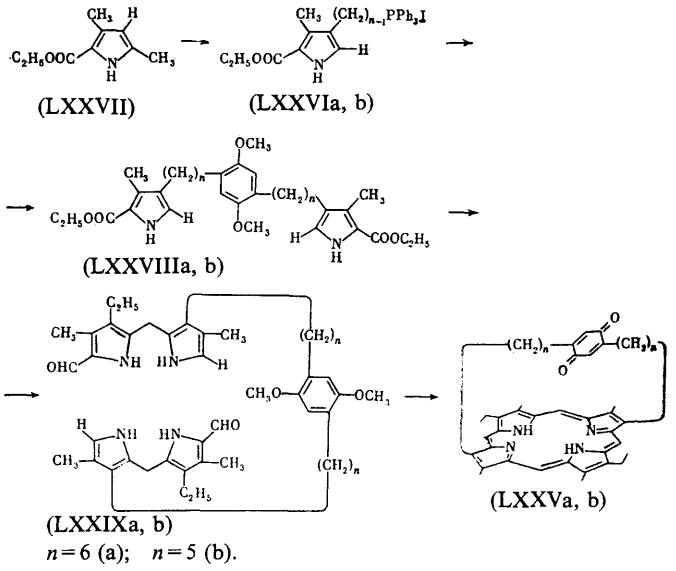
(LXXIV)

In order to achieve different spatial orientations of the donor and acceptor in the molecule relative to one another with the aim of elucidating the dependence of the rate of electron transfer on the relative disposition of the chromophores, the following quinones were selected: 2,6-dichloro-1,4-benzoquinone, 2,5-dichloro-1,4-benzoquinone, and 2,3-dichloro-1,4-naphthoquinone. The yields obtained in the photoreaction were 34, 42, and 8% of compounds (LXXII), (LXXIII), and (LXXIV) respectively. The low degree of conversion in these reactions was due to the formation of intermediate linear monoquinone derivatives, which cyclise after additional irradiation into the "capped" porphyrins (LXXII) and (LXXIII). In the synthesis of compound (LXXIV), the diquinone derivative was obtained as a side product in 10% yield.

The replacement of the ester linkage by an oligomethylene chain made it possible to create a more stable "capped" P–Q system (LXXVa,b).[67] The key stage of the synthesis (Scheme 5) is the double Wittig reaction of the pyrrole-substituted phosphonium salt (LXXVI), obtained from the pyrrole (LXXII) with a free β-position and 1,4-diformyl-2,5-dimethoxybenzene. The subsequent reduction of the corresponding alkenes leads to the oligomethylene-bridged bis(pyrroles) (LXXVIIIa,b) in 83% (for compound a) and 42% (for compound b) yields (after two stages). The condensation of the bis(pyrroles) (LXXVIIIa,b) having free α-positions with two equivalents of 5-chloromethyl-2-(2,2-dicyanoethylene)-4-ethyl-3-methylpyrrole afforded, after hydrolysis and decarboxylation, the substituted bis(dipyrrolylmethane) (LXXIX). The yield obtained in catalysed cyclisation at high dilution, which promotes the intramolecular reaction, was 20–60% after chromatographic purification, depending on the length of the oligomethylene chain. The demethylation BBr_3, which is allowed by the more stable C–C bond than the ester linkage in compounds (LXXVI) and (LXX), and

oxidation by PbO_2 lead to the porphyrins (LXXXa,b) (in 60 and 70% yields respectively):

Scheme 5



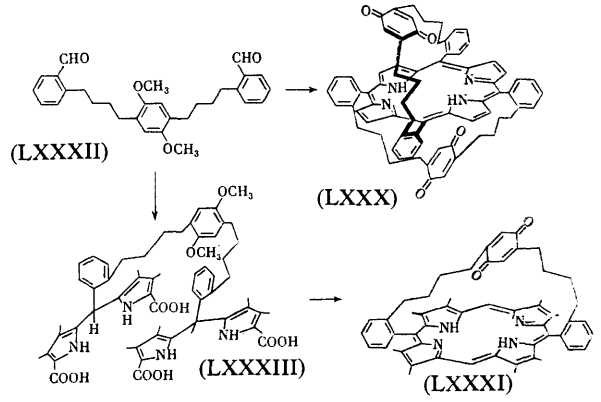
(LXXVII) (LXXVIa, b) (LXXVIIIa, b) (LXXIXa, b) (LXXVa, b)

$n=6$ (a); $n=5$ (b).

According to the strategy of the synthesis, the porphyrin cyclisation is carried out in the last stages, which ensures appreciable yields of the products even for a relatively short chain (n = 5). We may note that Scheme 5 permits the synthesis of "capped" model systems with different chain lengths ($n \geqslant 4$).

The wide variety of ways in which the porphyrin and quinone structures are linked together makes it possible to select the most suitable mutual orientation of the chromophores in the model system. Thus, apart from the compounds described above, the synthesis of the "capped" P–Q derivatives (LXXX) and (LXXXI), containing an oligomethylene chain in the *meso*-position in the porphyrin ring, has been achieved.[68,69] The starting material in the synthesis of compounds (LXXX) and (LXXXI) was the dialdehyde (LXXXII), obtained by the successive modification of 3,3′-(2,5-dimethoxybenzyl-1,4-phenylenedi)-1-propanol (Scheme 6):

Scheme 6

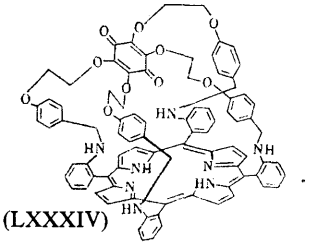


(LXXXII) (LXXX) (LXXXIII) (LXXXI)

The Rothemund condensation of the dialdehyde (LXXXII) with a twofold excess of pyrrole afforded the corresponding porphyrin derivative in 0.1% yield. Its subsequent demethylation with BBr_3 and oxidation with DDQ lead to the diquinone derivative (LXXX) in 41% yield.[68] The extremely low yield of the condensation reaction is due to the lack of specificity in its occurrence, which leads to a large number of cyclisation side products: oligomers and polymers.

Apart from the procedure described above, the dialdehyde (LXXXII) has been condensed with 2-ethoxycarbonyl-3,4-dimethylpyrrole (yield 78%). After subsequent transesterification with benzyl alcohol and catalytic hydrogenation, the corresponding bis(dipyrrolylmethane) (LXXIII) was obtained. The decarboxylation and subsequent condensation were carried out in dichloromethane in the presence of trichloroacetic acid and triethoxymethane (yield 11%). Demethylation with BBr_3 and oxidation with DDQ of the porphyrin fraction, freed chromatographically from oligomers and decomposition products, led to the "capped" P–Q compound (LXXXI) in 54% yield.

In order to synthesise a rigid structure in which the porphyrin and quinone planes are rigorously parallel, compound (LXXXIV) with four covalent bonds between the P and Q fragments has been synthesised:[70]



(LXXXIV)

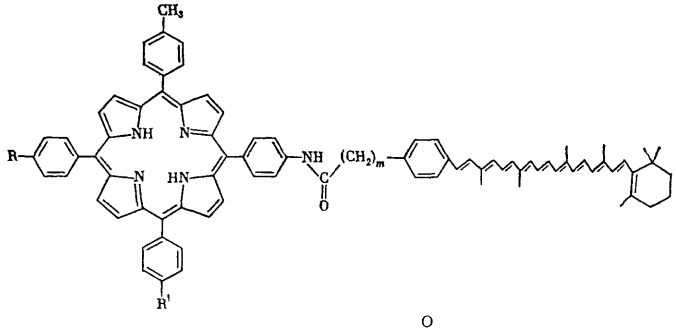
The introduction of an alkoxy-group into fluoranil by treatment with five equivalents of 4-(2-hydroxyethoxy)benzaldehyde in the presence of an excess of CsF led to 2,3,5,6-tetra[2-(4-formylphenoxy)ethoxy]benzoquinone (LXXXV) in 47% yield. The entropically favourable macrocyclisation of the tetraaldehyde (LXXXV) with the αααα-atropisomer of 5,10,15,20-tetra(2-aminophenyl)porphyrin, obtained by the isomerisation of the corresponding atropisomer in the presence of silica gel,[71] occurred with a yield of 85% and the reaction was catalysed by trifluoroacetic acid. The formation of the Schiff base was followed spectroscopically at 330 nm and the kinetic analysis of the reaction mixture was carried out with the aid of high performance liquid chromatography (HPLC). After chromatographic purification and reduction with $NaBH_4$, the "capped" P–Q compound (LXXXIV) was obtained.

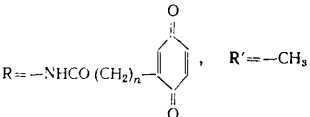
IV. Models with an additional donor (triads)

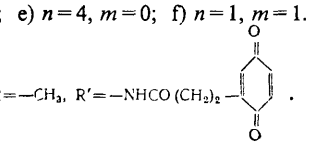
A new stage in the construction of model systems for the investigation of photosynthesis has been the synthesis of compounds containing a donor fragment together with the porphyrin and the quinone. During photosynthesis, the primary charge separation is accompanied by electron transfer from the primary donor to the oxidised chlorophyll-type photosensitiser.[1–4] The introduction of a donor into the P–Q compound made it possible to slow down the recombination of the light-separated charges by means of the dark reduction of the porphyrin radical-cation. Thus the triads make it possible to model more adequately the charge separation processes in photosynthesis.

The carotenoid structure with a system of conjugated double bonds, which participate directly in photosynthesis,[3,4] may serve as a suitable donor. The synthesis of the triads (LXXXVIa–f) and (LXXXVIIc), consisting of a tetraarylporphyrin linked covalently to

the carotenoid and quinone structures by a chain of atoms of different length (n = 0–4, m = 0, 1), has been described:[72,73]

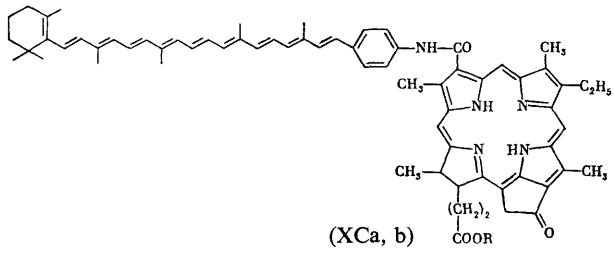


(LXXXVIa–e)  a) $n=0$, $m=0$; b) $n=1$, $m=0$; c) $n=2$, $m=0$; d) $n=3$, $m=0$; e) $n=4$, $m=0$; f) $n=1$, $m=1$.

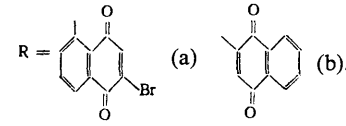
(LXXXVIIc) 

4-(β-apo-7′-carotenyl)benzoic acid (LXXXVIII), obtained by the Wittig reaction from β-apo-8′-carotenal and the corresponding phosphonium salt, was condensed with 5,15-di(4-aminophenyl)-10,20-di(4-methylphenyl)porphyrin (LXXXIX) (obtained by the Rothemund reaction) using dicyclohexylcarbodiimide and 4-dimethylaminopyridine. The same reagents were used in the condensation of carotenoporphyrin with 2,5-diacetoxyphenylacetic acid, while subsequent deacylation with KBH_4 and oxidation with PbO_2 led to the final structure (LXXXVIb). The triads (LXXXVIa,f) were obtained similarly from the corresponding modified hydroquinone derivatives.

However this synthetic scheme was unsuitable for the preparation of compounds (LXXXVIc–e) and (LXXXVIIc), because the corresponding hydroquinone derivatives readily formed lactones with the carboxy-group of the chain in the stage involving the synthesis of the quinone component. Another method of synthesis of the triads was as follows: 2,5-dibenzyloxybenzoic acid was methylated with CH_2N_2, reduced with $LiAlH_4$, and brominated with PBr_3. After malonate synthesis and the removal of the ethoxycarbonyl group, the acid chloride was obtained by treatment with $SOCl_2$ and condensed with the porphyrin (LXXXIX). After the removal of the benzyl protecting group by $(CH_3)_3SiI$ and oxidation by PbO_2, the P–Q obtained was condensed with the acid chloride (LXXXVIII) to form the triad (LXXXVIc). The derivatives (LXXXVId,e) and (LXXXVIIc) were synthesised similarly. By altering the length of the connecting unit between the porphyrin and quinone structures, it is possible to select a distance ensuring effective charge separation:



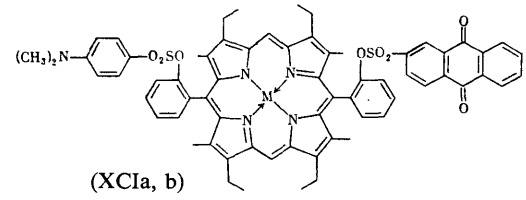
(XCa, b)



Similar triads (XCa,b), based on chlorophyll and naphthoquinone structures, were synthesised by the stepwise condensation of fragments of the system by a procedure similar to that used for compounds (LXXXVI a,b,f). The carboxy-derivative of methyl-pyrophaeophorbide *a* was condensed with aminocarotenoid by the acid chloride method. After the hydrolysis of the methyl ester by K_2CO_3 and esterification with 2-bromojuglone or lawsone, the corresponding products (XCa, b) were obtained.[74]

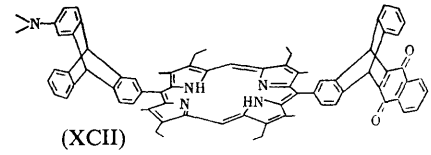
We may note that the (LXXXVI), (LXXXVII), and (XC) systems suffer from the same disadvantages as the models with a flexible covalent linkage between the donor and the acceptor.

The triad (XCIa), in which the secondary donor is a dimethylaniline derivative, was obtained by a procedure similar to that for the diquinone structure (VIa).[36] The zinc complex (XCIb) was obtained by treating the free base (XCIa) with zinc acetate.



(XCIa, b)
M = 2H (a); M = Zn (b).

In order to generate the three-component systems (XCII)[75] with a rigorously specified spatial orientation, a rigid triptycene bridge was used, as in compounds (LXI)–(LXIII). *NN*-Dimethylaniline was also chosen as the secondary donor in the triad (XCII). The condensation (catalysed by toluene-*p*-sulphonic acid) of a 1 : 1 mixture of the aldehyde of triptycenonaphthoquinone, obtained by the method of Wasielewski and Niemczyk,[62] and 2-formyl-6-nitrotriptycene, obtained in 95% yield by the Friedel–Crafts formulation of 2-nitrotriptycene with dichloromethyl methyl ether in the presence of $AlCl_3$, with two equivalents of di(3-ethyl-4-methylpyrrolyl)ethane led to a mixture of tetrahydroporphyrins, from which the final product (XCII) was obtained after oxidation with DDQ (overall yield of porphyrin 80%), reduction of the nitro-group with $SnCl_2$/HCl, chromatographic separation (yield 63%), and methylation of the amino-group with $CH_2O/NaBH_3CN$:



(XCII)

The methods of synthesis of all the model compounds examined are extremely varied. However, among them it is possible to distinguish two principal schemes for the construction of the covalent bond between the molecular fragments. The first involves the condensation of the system components with the simultaneous formation of the porphyrin ring.[36,42,56–60,62,67–69,75] The second involves the synthesis of porphyrin-quinones from synthetic[28,29,31–33,37–39,48,53,61,63,64,70,72,73] or natural[44–46,74] porphyrins and chlorins. An extremely large set of different porphyrin and

quinone structures of the model systems is necessary for the optimum selection of the corresponding donors and acceptors in photoinduced electron transfer reactions. The wide variety of the different forms of linkage between the chromophores has arisen because of the search for the most suitable conformations of the model systems and the optimum spatial orientation of their components for a high efficiency of the charge separation process.

V. Spatial disposition and mutual orientation of the fragments in model systems

The efficiency of electron transfer is known to depend significantly on the mutual orientation of the donor and acceptor. A study of the spatial organisation of P–Q compounds is therefore of considerable interest for the elucidation of the mechanism of electron transfer in such molecules.

The following methods are used to investigate the steric structure of P–Q derivatives: NMR spectroscopy, three-dimensional modelling, and X-ray diffraction analysis. The use of three-dimensional modelling is limited because of the presence of a large number of conformations for compounds with a flexible linkage. This method is used most effectively to determine the intramolecular distances between the fragments in structures with a rigid bond where the displacement of the chromophores relative to one another is difficult or almost impossible. Such data make it possible to calculate the probability and degree of overlap of the π-electron systems of the components, which determines the efficiency of the intramolecular electron transfer. Thus the distances between the donor and acceptor fragments have been determined with the aid of three-dimensional models in the porphyrin-quinones (XLVI)–(LII), (LXI)–(LXIII), and (XCII) with a rigid bond. For the three rigidly linked P–Q compounds (XLVI), (XLVIII), and (L), the distances between the chromophores are 6, 10, and 14 Å,[59] while the centres in the similar structure (LII) are at a distance of 16 Å.[60] The donor and acceptor in compounds (LXI), (LXII), and (LXIII) with a triptycene bridge are separated by 10, 10.5, and 11 Å, while the distance between the boundaries of the π-electron systems of the porphyrin and the quinone is >6–7 Å, which weakens significantly the direct overlap of the electron wave functions.[62] For the triad (XCII), the distance between the centres of the porphyrin and the quinone is 10.5 Å, that between dimethylaniline and the porphyrin is 10 Å, and that between dimethylaniline and the quinone is 25 Å.[75] For the "capped" porphyrin (LXXXIV), the distance between the parallel planes of the chromophores has been found to be ~10 Å.[70]

However, for the "capped" structures, this method is rarely used, because it does not permit an accurate determination of the distance between the chromophores. The reason for this is that the possibility of the vibration of the molecular fragments along the bonding axis and the presence of different conformational forms are not ruled out in systems of this kind. In order to investigate the intramolecular orientation of the chromophores and the spatial organisation of such model systems, ^{1}H NMR spectroscopy is employed. Appreciable upfield shifts of the signals due to the protons of the quinone ring [up to 4 p.p.m. for compounds (LXVI)–(LXXI) and (LXXV), up to 2.8 p.p.m. for compound (LXXII), and up to 2 p.p.m. for compounds (LXXX) and (LXXXI) in the ^{1}H NMR spectra relative to the unbound quinones are characteristic of the "capped" P–Q compounds (LXVI)–(LXXI), (LXXII), (LXXV), (LXXX), and (LXXXI)]. This is due to the influence of the ring current of the porphyrin.[63,66–69,76,77] The shifts of the signals for the P–Q compounds with a longer chain [compounds (LXVII) and (LXXVa)] compared with their analogues with a shortened bond [compounds (LXVI) and (LXXVb)] are greater by 0.2–0.65 p.p.m. This effect can be accounted for by the fact that the longer and flexible chain enables the quinone structure to approach the porphyrin more closely and to experience a greater influence of its π-electron system.[67,76,77] This hypothesis is confirmed by three-dimensional modelling[67] and the results obtained for other "capped" porphyrins.[76,78] Similar changes in the ^{1}H NMR spectrum are also characteristic of the proton signals of the methylene chain located above the plane of the porphyrin ring. The influence of the ring current on the chemical shift of these protons diminishes as the porphyrin is approached.[67,76] Thus the signals of the corresponding protons of the propionic residues in compounds (LXVI) and (LXVII) are located in the usual region, but, as a consequence of the rigidity of the structure, all four protons of the propionyl chain are non-equivalent and their signals are distributed in the form of four complex multiplets, each due to 2H, and not a simple AA'BB' system.[63,76]

Further studies on the conformational flexibility of the linkage in compounds (LXVI) and (LXVII) led to the observation of a linear temperature variation of the chemical shifts of the protons of the quinones and the nearest methylene groups. When the temperature is raised, the signals of the protons of the quinone and of its environment undergo a downfield shift [the shift constant is 4.5×10^{-3} p.p.m. K^{-1} for the quione proton and 5.1×10^{-3} p.p.m. K^{-1} for the nearest methylene group in compound (LXVII)]. Thus the distance between the fragments of the molecule increases with increase in temperature and diminishes on cooling.[76]

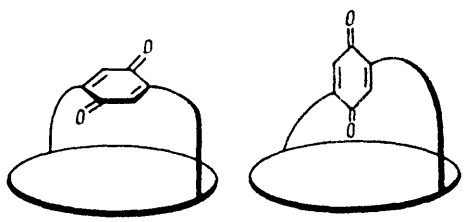


Figure 1. Schematic illustration of two extreme conformations of P and Q in "capped" porphyrin-quinones.[76]

The planes of the porphyrin and the quinone in the "capped" P–Q compounds (LXVI)–(LXXI), (LXXV), (LXXX), and (LXXXI) can be parallel or perpendicular to one another or they can occupy intermediate positions (Fig. 1). The necessary conformation of the fragments can be established in the course of specific synthesis.[66] Thus, when different substituted quinones were employed, "capped" P–Q structures with perpendicular (LXXII), parallel (LXXIII), and orthogonal (LXXIV) spatial orientations of the donor and acceptor were obtained. The molecular structure of the "sandwich" porphyrin (LXXX) has been determined by X-ray diffraction.[79] In compound (LXXX), having the S_4 symmetry, the two quinone rings are rigorously parallel to one another and to the plane of the porphyrin, while the centres of all three fragments coincide. The distance between the planes of the porphyrin and the quinones is

3.42 Å. It has been shown for compounds (LXVI) and (LXVII) that the real conformation constitutes a superposition of both limiting steric structures.[76] From this, it follows that there is virtually no coordination between the donor and acceptor parts in the free bases (LXVI) and (LXVII).[77] In the absence of external ligands, the magnesium complexes (LXX) and (LXXI) have structures in which the carbonyl group of the quinone is coordinated to the central metal ion resulting in the formation of a pentacoordinate intramolecular complex.[76,77] When an external ligand (pyridine[63,76] or 3,5-lutidine[77]) is added, a hexacoordinate complex is formed. This has been confirmed by the bonding constants found. The coordination of the ligand from the sterically unhindered side of the porphyrin plane entails appreciable upfield shifts of the quinone ring proton signals [by 0.6 p.p.m. for compound (LXX) and by 0.3 p.p.m. for compound (LXXI)] and the signals of the protons of the ligand itself. In contrast to magnesium complexes, in the presence of a ligand the zinc complexes have a geometry very similar to that of the free bases (LXVI) and (LXVII), which is due to the pentacoordination limit for zinc itself and the probability of the intramolecular bonding diminishes appreciably.[77]

The determination of the mutual orientation of the fragments for linear P–Q compounds with a flexible bond involves considerable difficulties because of their conformational lability. The time-average conformations of the triads (LXXXVIa–f) and (LXXXVIIc) in solution have been determined[73] from ^{1}H NMR data by conformational analysis on a computer. It was established that in all cases the triads have a linear structure and the quinone rings are arranged at an angle of 90° relative to the covalent bond. The spatial organisations of each of these molecules differ from one another by the orientations of the quinone and carotenoid components relative to the porphyrin plane, which depends on the length of the polymethylene chain (n = 0–4, m = 0–1). For a series of other linear P–Q compounds, only tentative conclusions concerning the mutual disposition of the quinone and porphyrin fragments have been reached with the aid of ^{1}H NMR spectroscopy. Depending on the length of the linkage and its location in the porphyrin ring, there are two possible versions of the steric structure: (1) the molecule has a linear form in which the chromophores are remote from one another and (2) the molecule is characterised by a folded configuration in which the quinone component is located above the plane of the porphyrin ring. However, in the second case it is also impossible to determine the exact position of the acceptor above the plane of the donor. Thus, in the structures (Ia–c),[29] (IIa–c),[31], (XXXIII),[53] and (XCa,b),[74] the porphyrin ring current does not exert an appreciable influence on the chemical shifts of the protons in the quinone component. This finding suggests a linear conformation of the molecule. Upfield shifts of the signals due to the protons of the quinone ring and its closest substituents have been observed for compounds (V),[33] (VIa,b), (XCIa,b),[36] (VIIIa–e),[38] (X)–(XVb),[39,42] and (XXXIIIa)–(XXXa,b).[44,45] This indicates a folded structure of the P–Q molecule. For the more rigid structure (V), the shifts are 0.1 p.p.m. for H(1), 2.0 p.p.m. for H(2), and 3.0 p.p.m. for H(3). This suggests that the H(3) hydrogen is closest to the porphyrin and the H(1) hydrogen is most remote. In the models (VIIIa–e), the maximum shifts are shown by compound (VIIIb), in which there is no substituent in the 3-position in the naphthoquinone component. It has been demonstrated by three-dimensional modelling that the quinone in the structure (VIIIb) can readily rotate about the C–O bond and can assume a position in which the porphyrin and quinone planes are parallel. The π–π interaction between the molecular fragments is then a maximum. For the derivatives (VIIIc–d), the rotation is hindered and the orthogonal conformation, in which the influence of the porphyrin ring current on the quinone is weakened, is optimal.

In the zinc complexes (XIVa–c), the signals of the quinone protons are displaced more ($\Delta\delta$ = 0.42–0.89 p.p.m. depending on the bond length) than in the free bases (Xa–c) ($\Delta\delta$ = 0.24 to 0.34 p.p.m.). This may be associated with the additional coordination of the quinone to the metal ion. For the diquinone derivative (XVb), these values are smaller ($\Delta\delta$ = 0.17 p.p.m.) because of the influence of the second quinone, which apparently prevents the localisation of benzoquinone above the porphyrin ring. Several changes have been observed also for the zinc complexes (VIb) and (XCIb). The addition of pyridine to a solution of the triad (XCIb) induced the formation of a pentacoordinate complex with the external ligand and the simultaneous breakdown of the interaction between the zinc atom and the carbonyl group of the quinone. The signals of the protons of the quinone component then shifted to the level of the free base (XCIa). In the natural P–Q compounds (XXIIIa)–(XXVIa,b), $\Delta\delta$ = 0.23–0.47 p.p.m. for the naphthoquinone-containing compounds (XXIIIa) and (XXIVa,b). The shift of the singlet signals of the methyl protons of the quinone residues in compounds (XXIIIa)–(XXVIa,b) is 0.27–1.43 p.p.m. Thus the molecular conformation in the P–Q compounds with a flexible linkage can be estimated from the shift of the protons of the quinone residues and the nearest substituents.

As stated above, information about the mutual disposition of the fragments of the P–Q molecule is of great interest for the understanding of the mechanisms of charge separation in these systems.

The photochemical properties of the model systems can be considered also on the basis of the available data for their structural features.

VI. Photochemistry of porphyrin–quinone compounds

Among the questions arising in the study of the photochemistry of porphyrin–quinone compounds, the most important are the following: (1) what structural features of the bridging chain determine the efficiency of the electron transport; (2) how should the bridge be constructed so that the direct electron transfer from *P to Q is rapid and the reverse transfer is slow; (3) in what way does the efficiency of the charge separation depend on the oxidation-reduction properties of P and Q. The solution of these problems in the photochemistry of P–Q compounds is of interest as regards the answer to the main question—what features of the organisation of the photosynthetic apparatus in photosynthesising organisms ensure a high efficiency of charge separation.

Considerable advances have now been achieved in the elucidation of the photochemical properties of P–Q compounds. It is possible to distinguish three main aspects of the study of the photochemistry of structures differing in the characteristics of the intramolecular electron transport processes: (1) the photochemistry of P–Q compounds with a flexible linkage; (2) the photochemistry of P–Q molecules with a rigid bridge; (3) the photochemistry of triad systems containing a porphyrin bound covalently to a quinone and an electron donor. The photochemical studies on P–Q compounds have developed in this sequence from the moment of their initiation. The transition from systems with a flexible linkage to P–Q compounds with a rigid bridge made it possible to investigate in greater detail the dynamics of charge separation between the porphyrin and the quinone without the complicating influence of conformational

movements manifested in the study of systems with a flexible linkage. The covalently bound triads constituted the next step towards more adequate modelling of the reaction centres of photosynthesing organisms. In these systems, it is possible to achieve fairly long lifetimes of the light-separated charges. Following the logic of the development of the research into P–Q compounds, we shall consider initially photochemical processes in systems with a flexible linkage.

1. Porphyrin–quinone compounds with a flexible linkage

In the first studies on the synthesis of P–Q compounds, attempts were already made to investigate their photochemical properties. Thus an appreciable quenching of the fluorescence of the porphyrin fragment by the quinone in dioxan and petroleum ether was noted[28,29] for compounds (Ia–c). In petroleum ether, the quenching efficiency proved to be higher than in dioxan. No data concerning the mechanism of the quenching of the fluorescence were obtained in the above studies.

The hypothesis that the quenching of the fluorescence of the porphyrin by the quinone in the P–Q compounds is caused by intramolecular electron transfer was first put forward by Tabushi et al.[33] and Dalton and Milgrom.[56] Since low concentrations of P–Q compounds were used in these studies, it was concluded that an intramolecular mechanism of the quenching of the fluorescence of the porphyrin fragment operates. However, data permitting the exclusion of an alternative explanation of the quenching of the fluorescence, involving intramolecular energy transfer, were not obtained either.[33,56]

It has been observed[56] that the Soret band in the spectrum of compound (XXXVIII) is much broader than in that of the free porphyrin. According to the authors, this indicates the formation of an intramolecular charge-transfer state in the P–Q compound. The complete quenching of the fluorescence of the porphyrin fragment of the P–Q compound was noted (the fluorescence quantum yield was $\Phi < 10^{-3}$). The experimental results were explained by the high efficiency of the electron transfer from the singlet-excited prophyrin fragment to the quinone.

Subsequently the hypothesis that the quenching of the fluorescence of P–Q compounds is caused by electron transfer was used frequently to account for the non-exponential character of the decay of the fluorescence and the dependence of the fluorescence quenching efficiency on the length of the bridge connecting P and Q, the presence of the metal in the P–Q compound, and the nature of the solvent.[39,80,81]

In principle, four mechanisms of the quenching of the fluorescence of the donor D by the acceptor A are possible: (1) energy transfer from *D to A; (2) the mixing of the electronic states of D and A leading to an increase in the non-radiative transition of *D to the ground state; (3) the spin–orbital coupling of the $^1(\pi,\pi^*)$,$^3(\pi,\pi^*)$, and S_0 states of the donor by virtue of the addition of the acceptor; (4) electron transfer from *D to A.

We shall consider each of these quenching mechanisms for a covalently bound P–Q compound. The energy transfer from porphyrin in the S_1 state ($E_{S_1} \simeq 1.8$ eV) to the quinone is unlikely because the lowest excited state of the quinone is fairly high (2.6 eV for benzoquinone in solution[82]). This energy difference is also sufficient to rule out the hypothesis of the mixing of the electronic states of P and Q. The spin–orbital coupling of states also appears unlikely because the efficiency of the quenching of the fluorescence of porphyrins by quinones is determined mainly by their oxidation-reduction properties[83,84] and not by the capacity for spin–orbital coupling.[85] The hypothesis that the electron transfer from *P to Q responsible for the appreciable decrease in the efficiency of the luminescence of the porphyrin in P–Q compounds therefore appears reasonable. Measurements of the redox potentials of the P–Q compounds have shown that the singlet excitation energy of the porphyrin is indeed sufficient in many cases for the formation of the P^+–Q^- pair.[86]

The first study in which the formation of a radical-ion pair on irradiation of P–Q compound was demonstrated was that of Ho et al.[87] By a procedure similar to that used by Kong and Loach,[28,29] it was found that a much lower fluorescence intensity (~10%) is observed for compound (Ib) in methanol at room temperature than for a porphyrin without a quinone residue. At low temperatures, it is possible to detect the EPR signal of the photolysis products in vitreous methanol. Comparison of the EPR spectrum obtained with the individual EPR spectra of P^+ and Q^- enabled the authors[87] to interpret the light-induced EPR signal as a superposition of the EPR spectra of P^+ and Q^-. The efficiency of the formation of radical-ions for a P–Q compound was many times greater than the efficiency of the generation of P^+ and Q^- in a homogeneous solution of the porphyrin and the quinone at the same concentrations of the reactants, not bound to one another, as in the P–Q compound. The subsequent generation of the EPR signals on irradiation of compounds (Ia–c) and their zinc analogues has also been demonstrated in another study.[80]

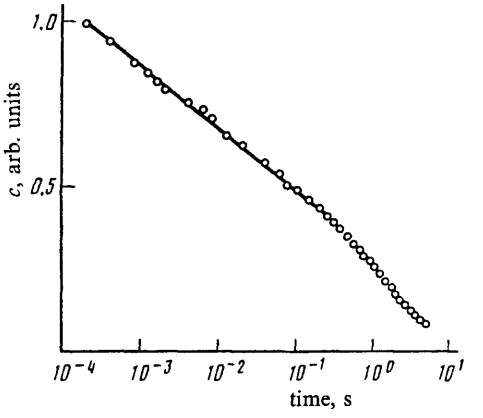


Figure 2. Kinetics of the destruction of the radical-ion pairs P^+–Q^- at T = 160 K in a 98 : 2 vitreous methanol–chloroform structure; c = concentration.[87]

At T = 160 K, the formation of the P^+–Q^- radical-ion pair is followed by the intramolecular recombination of charges, whose kinetics at low temperatures are described by a linear dependence of the number of P^+–Q^- pairs on the logarithm of the observation time (Fig. 2).[87] A similar relation had been observed earlier for the low-temperature recombination of charges in the reaction centres of the photosystems (I) of subchloroplasts.[88] On the grounds that the efficiency of the P^+–Q^- recombination depends strongly on temperature, the logarithmic character of the recombination of charges in compound (I) was explained[87] by the difference between

the activation energies for the recombination of different P^{+}–Q^{-} pairs. The difference may be caused by the presence of several conformations of the carbon chain linking the porphyrin and the quinone. However, it has been noted[88] that other causes of the logarithmic character of the kinetics of the recombination of charges in structures analogous to P–Q are also possible. These may be a difference between the distances over which an electron is transferred from Q^{-} to P^{+} (if the electron transfer does not proceed via the bridge but directly from Q^{-} to P^{+}), a difference between the mutual orientations of P^{+} and Q^{-}, or a difference between the values of some other parameter on which the efficiency of charge recombination depends exponentially.

At room temperature, the quantum yield in the separation of charges in compound (Ib) reaches 0.5%. The addition of tetrabutylammonium perchlorate lowers the rate of charge recombination in P^{+}–Q^{-}.[80] The observed[80] dependence of the fluorescence quenching efficiency on the solvent polarity (the increase in efficiency with increase in polarity) can be explained naturally within the framework of modern models of electron transfer in the condensed phase by the dependence of the charge separation energetics on the parameters of the medium.

Subsequently the light-induced charge separation in the model systems (IIIa–c) was observed by the EPR method. The high resistance of the diamide bridge to hydrolysis enabled the authors[89] to carry out optical, EPR, and luminescence studies on the separation of charges in P–Q compounds. It was observed that spin–exchange and dipole–dipole intramolecular interactions of the P^{+} and Q^{-} radical-ions are manifested in the EPR spectra of vitreous P–Q solutions irradiated with light. The degree of the dipole–dipole interaction ($D \simeq 2.0\ mT$) made it possible to estimate the average distance between the unpaired electrons of P^{+} and Q^{-}, amounting to 10–12 Å for compound (IIIa). Molecular models have shown that this distance corresponds to the conformation of the P–Q compound in which the quinone interacts with the nearest phenyl residue.

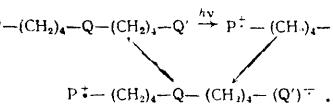
The quantum yield in the formation of the $P^{+}Q^{-}$ radical-ion pair, measured by EPR, depends on temperature and increases markedly, to $\Phi \simeq 0.02$, when the temperature is reduced by $\sim$20 K below the melting point of the solvent. On further reduction of temperature, Φ also falls. It has been suggested that charge separation quantum yield in P–Q compounds is determined by the microviscosity of the solvent. The increase in the temperature of the frozen matrix then increases the mobility of the P–Q fragments relative to one another promoting thereby the attainment of conformations favourable for electron transfer. In the temperature range near the melting point of the solvent, the recombination of charges becomes effective and, having reached a maximum, the charge separation quantum yield again diminishes.

The existence of different conformations of compounds (IIIa–c) has been established.[90] The most effective quenching of the fluorescence has been observed for the derivative (IIIb). These data agree with the results of EPR studies.[89]

The charge separation on pulsed irradiation of the derivative (IV) with light has been described.[32] The dependence of the efficiency of electron transfer from the porphyrin to the quinone on the refractive index n of the solvent was found: with increase in n, k_e increased from $1.4 \times 10^{7}\ s^{-1}$ for $n = 1.352$ (diethyl ether) to $7.7 \times 10^{8}\ s^{-1}$ for $n = 1.633$ (1-chloronaphthalene). The results of the above study show that for P–Q compounds the solvent can exert an appreciable influence on the process energetics even when the length of the bridge connecting P and Q is small.

The dependence of the rate of electron transfer from the electronically excited porphyrin fragment to Q and of the rate of the reverse process on the length of the bridge for the derivatives (Xa–c) has been described.[39,42,43] It was established that the reciprocal of the P–Q fluorescence decay time is $10^{9}\ s^{-1}$, $10^{10}\ s^{-1}$, and $10^{11}\ s^{-1}$ for $n = 6$, 4, and 2 respectively. A similar dependence has been observed also for the efficiency of the reverse electron transfer from Q^{-} to P^{+}. The pronounced dependence of the rates of the forward and reverse electron transfers on the length of the bridge connecting P and Q shows that the electron transfer takes place via the tunnel mechanism.[43]

The two-step electron transfer from the porphyrin to trichlorobenzoquinone in the molecule of compound (XV) [P–$(CH_2)_4$–Q–$(CH_2)_4$–Q′] has been investigated.[42,43] The charge separation takes place with participation of the intermediate state P^{+}–$(CH_2)_4$–Q^{-}–$(CH_2)_4$–Q′:



The two-step electron transfer mechanism ensures rapid ($\tau < 10^{-11}$ s) charge separation. This time is much shorter than the time of the single-step charge separation in the molecule of compound (Xc) with a shorter bridge ($\tau > 5 \times 10^{-10}$ s). The greater length of the bridge in the molecule of compound (XV) ensures a comparatively long charge recombination lifetime $\tau = (3\text{–}4) \times 10^{-10}$ s. The present authors' data[42,43] confirm the results[91,107] showing that the multistep electron transfer along the redox potential gradient of the acceptor groups ensures a higher efficiency of charge separation than the single-step process.

2. Porphyrin–quinone compounds with a rigid bridge

The appreciable conformational mobility of the P–Q compounds with a flexible chain precludes the elucidation of the detailed mechanism of the intramolecular electron transfer. One of the ways of solving this problem has been the synthesis of "capped" P–Q structures.

Thus the parallel disposition of the fragments in compound (LXXXIV) ensured an appreciable (greater than 30%) P^{+}–Q^{-} quantum yield for its zinc complex.[92] For the metal-free derivative (LXXXIV), the intramolecular electron transfer was not observed. The appearance of additional luminescence quenching channel reduced the quantum yield and resulted in a two-component character of the P–Q fluorescence decay curve. The electron transfer rate constants, estimated from the biexponential curve, are $k_1 = 3 \times 10^{8}\ s^{-1}$ and $k_2 = 1.5 \times 10^{3}\ s^{-1}$. The electron transfer to the quinone is observed also with participation of the excited triplet state of the porphyrin fragment.

The diquinone compound (LXXX) has been investigated.[79] The small distance between the planes of the porphyrin and the quinone is apparently the cause of the almost complete absence of the luminescence of this derivative compared with its non-quinonoid analogue. A similar effect has been observed also for the monoquinone analogue of compound (LXXX).[69] The quenching of the fluorescence of compounds (LXXX) and (LXXXI) can be explained by electron transfer from the singlet-excited porphyrin fragment to the quinone.

Compounds with a linear structure and a rigid bridge [compounds (XLVI)–(LII) and (LXI)–(LXIII)] provide considerable possibilities for the elucidation of the factors determining the efficiency of the electron phototransfer in P–Q systems.[59,60,62,93] The absence from

the absorption spectra of any manifestations of the interaction of the porphyrin and quinone fragments, typical for systems with a flexible bridge, is characteristic of these compounds. A rigid structure prevents the interactions of the fragments in the ground state. Another characteristic feature of systems with a rigid bridge is the monoexponential character of the fluorescence decay curve, indicating the existence of only one P–Q conformation, in which an effective electron transfer takes place.

It has been observed for compounds (LXI)–(LXIII) that the fluoresence quantum yield of the porphyrin fragment of the P–Q compound is lower than for the individual porphyrin.[62] A correlation was then observed between the free energy of the electron transfer from the donor to the acceptor ($-\Delta G^0$) and the quenching efficiency (see Table 1). The free energy $-\Delta G^0$ was calculated from the formula

$$-\Delta G^0 = E(S_1) - E(P/P^+) + E(Q/Q^-),$$

where $E(S_1)$ is the excitation energy of the singlet state S_1 of the porphyrin fragment, $E(P/P^+)$ the oxidation potential of the porphyrin, and $E(Q/Q^-)$ the reduction potential of the quinone.

Table 1. The free energies $-\Delta G^0$ of the electron transfer from P to Q and the fluorescence quantum yields (Φ) for the P–Q compounds in CH_2Cl_2.[62]

Compound	Φ	$-\Delta G^0$, eV
Tetraphenylporphyrin (TPP)	0.14	—
(LXIIIa)	0.119	0.02
(LXIIa)	0.001	0.29
(LXIa)	<0.001	0.47
Zn complex of TPP	0.023	—
(LXIIIb)	0.002	0.43
(LXIIb)	<0.001	0.70
(LXIb)	<0.001	0.88

A similar correlation has been found for two other solvents: toluene and butyronitrile. The increase in $-\Delta G^0$ with decrease in the dielectric constant of the solvent led to an increase in the luminescence quenching efficiency. This character of the dependence of the luminescence quantum yield on the free energy change shows that the quenching of the luminescence is due to electron transfer from $^*P$ to Q.[91,94–97] This hypothesis is supported also by picosecond absorption spectroscopic data. Wasielewski and Niemczyk[62] were able to record the characteristic absorption bands of P^+ and Q^- in the absorption spectrum of a solution of the zinc complex (LXIIb) in toluene irradiated by a light pulse. The time of the intramolecular charge recombination $P^+-Q^- \rightarrow P-Q$ in this compound is 3.7×10^{-10} s.

The electron transfer rate constant for this process decreases with increase in $-\Delta G^0$.[93] This fact can also be explained within the framework of the modern theories of electron transfer. Indeed, the quantities $-\Delta G^0$ for charge recombination in compounds (LXI)–(LXIII) investigated by Wasielewski and Niemczyk[93] exceed 1 eV. The decrease in k_e with the increase in $-\Delta G^0$ is apparently caused by the fact that the quantity $-\Delta G^0$ exceeds the reorganisation energy (λ is a parameter determining, together with $-\Delta G^0$, the nuclear multiplier k_{nu} in the expression for the electron transfer rate constant):

$$k_{nu} = \exp\left(-\frac{(\lambda + \Delta G^0)^2}{4\lambda RT}\right). \quad (1)$$

Eqn. (1) shows that the increase in $-\Delta G^0$ leads under these conditions to a decrease in the nuclear multiplier and hence in the electron transfer rate constant.

We may note that, in contrast to the "capped" P–Q compounds considered above, the effective electron transfer between the P and Q fragments observed by Wasielewski and Niemczyk[62] takes place over a considerable distance in the conformation hindering the overlap of the π orbitals of the reactants.

A dependence of the efficiency of the transfer from $^*P$ to Q on the dielectric constant and the refractive index of the solvent employed has been observed for the model systems (XLVI)–(LII).[59,60] The electron transfer rate constants reaches its maximum value for an intermediate and (and not the maximum) polarity of the solvent and varies from $k_e = 3.3 \times 10^7$ s^{-1} in propionitrile ($\varepsilon = 27.2$, $n = 1.3659$) to $k_e = 1.6 \times 10^6$ s^{-1} in 2-methyltetrahydrofuran (MTHF) ($\varepsilon = 7.6$, $n = 1.4060$) and falls almost to zero in dibutyl ether ($\varepsilon = 3.04$, $n = 1.3992$) and acetonitrile ($\varepsilon = 37.5$, $n = 1.3441$). Such variation is associated with the fact that the solvation energy of the P^+-Q^- state, which determines the energetics of the charge separation process, depends both on dielectric constants of the solvent and (to a greater extent) on its refractive index.[98] For solvents having similar structures, it is possible to obtain a quantitative correspondence between the quantities k_e, ε, and n.[60]

For the quantitative determination of the tunnelling parameters, the P–Q compounds (XLVIII) and (L) have been investigated.[99] The rate constant for electron transfer from $^*P$ to Q was estimated from the decrease in the luminescence decay time. Typical P–Q fluorescence decay curves are illustrated in Fig. 3. It is seen that the transition from the structure (LI) to compound (XLIX) results in a sharp decrease of the fluorescence decay time. The quantity k_e then increased from $k_e^2 \lesssim 10^7$ s^{-1} to $k_e^1 = 10^{10}$ s^{-1}. Using the maximum value of k_e for the derivative (LI), it is easy to obtain $a_e \leqslant 1.4$ Å and $\nu_e \geqslant 10^{19}$ s^{-1} from the exponential dependence of k_e on the distance R between the donor and acceptor: $k_e = \nu_e \exp(-2R/a_e)$.[97] If the minimum distance between P and Q is used instead of the intercentre distance, then ν_e may be estimated as $\nu_e \geqslant 10^{16}$ s^{-1}.

At $T = 77$ K, the kinetics of the quenching of the fluorescence of compound (XLIX) in vitreous MTHF are non-exponential. This effect is due to the existence in the frozen solution of several rotational conformations of the molecule. The monoexponential character of the decay curve at 298 K shows that at this temperature the rate of rotation exceeds k_e. The decay time of the principal component of the kinetic curve $\tau = 1.1 \times 10^{-10}$ s is almost identical with the value of τ at 298 K. Thus the rate of electron transfer from $^*P$ to Q in the structure (XLIX) is almost independent of temperature.

3. Model systems having a rigorous spatial orientation without a covalent bond between the porphyrin and the quinone

Together with the covalent bonding between the porphyrin and the quinone, a fixed distance between P and Q can be ensured, in principle, also in a number of other ways. Thus the synthesis of a porphyrin bound covalently to β-cyclodextrin (PC) has been described.[100] In a solution containing electron-accepting additives, cyclodextrin coordinates the acceptor molecules in its interior. On

irradiation with light at $\lambda > 550$ nm of a vitreous solution of PC containing added benzoquinone at 77 K, paramagnetic charge separation products are detected, their amount exceeding by a factor of 3–4 that in the control (P + Q solution). The efficiency of the charge separation depends on the oxidation-reduction potential of the electron acceptor. For an oxidation-reduction potential below –0.3 eV relative to the normal hydrogen electrode, a sharp decrease, greater than by an order of magnitude, in the intensity of the EPR signal of the charge separation products was observed when the oxidation-reduction potential changed from –0.3 to –0.6 eV. Such a decrease in the charge separation efficiency is caused, according to Gonzalez et al.,[100] by the rapid reverse charge recombination.

Yet another interesting example of a structure permitting the study of electron transfer between the porphyrin and the quinone, separated by a fixed distance, is provided by planar molecular assemblies obtained by the Langmuir–Blodget method. [101–103] The planar molecular assemblies constitute multilayer structures in which the acceptor layer is separated from the donor layer as a rule by a monolayer made up of saturated aliphatic acid molecules. The thickness of the monolayer and hence the distance between the donor and acceptor can be varied by increasing the number of CH_2 fragments in the acid molecule.

The electron phototransfer from chlorophyll to a quinone in a multilayer structure, where a layer of chloranil, bromanil, or *NN*-distearoyl-1,4-diaminoanthraquinone was deposited on a layer of chlorophyll *a* molecules, has been investigated.[104,105] The structural organisation was such that the phytol fragments of the chlorophyll molecules were turned towards the layer of quinone molecules. Thus the insulating layer consisted of the phytol fragments of the chlorophyll molecules. It was observed that irradiation of such a structure with light leads to electron transfer from chlorophyll to the quinone and the formation of the corresponding radical-ions. The charge separation took place via a two-quantum mechanism. The reason for the inefficiency of the one-quantum reaction channel is apparently the short lifetime of the excited state of chlorophyll *a* and the appreciable distance between the donor fragment of the chlorophyll molecule and the quinone. After the light had been switched off, charge recombination was observed. Its duration ($\tau_{1/2}$) amounted to 6×10^{-4} s and was almost independent of temperature in the range 100–300 K.

The introduction of ubiquinone, plastoquinone, or squalene (whose molecules have an unsaturated chain) into the system led to a tenfold increase in the charge separation efficiency for the given light intensity. The electron transfer became a one-quantum process and occurred with participation of the first excited triplet state of chlorophyll *a*. The observed effect was explained by a change in the form of the barrier to the tunnelling of the electron caused by the insertion of molecules or molecular fragments with a polyisoprene chain in the insulating layer. The use of molecules with a saturated chain in control experiments did not accelerate the electron phototransfer process. The results of the above studies[104,105] demonstrate the fruitfulness of the use of planar molecular assemblies for the investigation of the electron tunnelling mechanisms in porphyrin–quinone systems. However, the uncertainty in the interpretation of the results of experiments with molecular layers due to the non-rigid character of the linkage between the reacting species makes covalently bound P–Q compounds a preferable object for the modelling of photosynthesis and for the study of the mechanisms of electron phototransfer from the porphyrin to the quinone.

4. Covalently bound triads

As already mentioned above, the next step in the modelling of the charge separation process in photosynthesis involved the study of trifunctional molecules (D–P–Q) containing a porphyrin, a quinone, and a donor fragment.[72,73,75,106]

By analogy with photosynthesis, one might have expected that a fairly considerable increase in the lifetime of the separated charges compared with the bifunctional P–Q molecules would be achieved in the trifunctional compounds as a result of the two-step charge separation mechanism. Thus the excitation of the triads (LXXXVI)

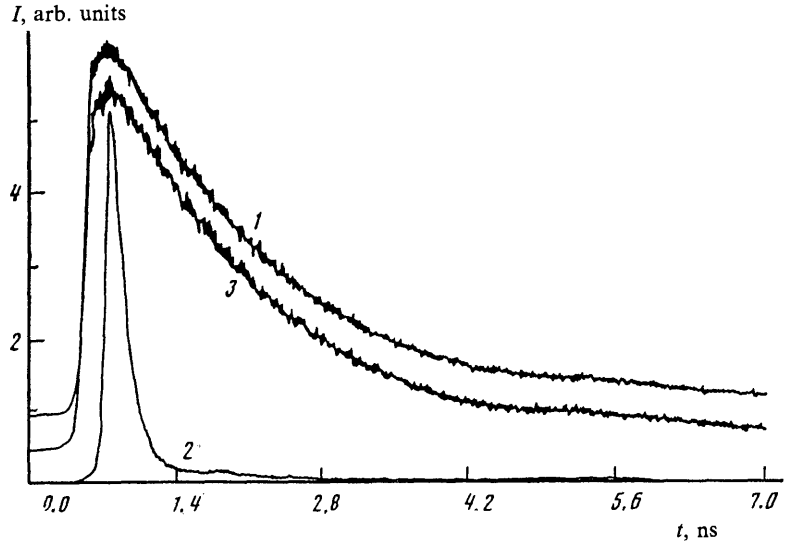


Figure 3. Kinetics of the decay of the fluorescence of compound (XLIX) (curve *1*), compound (LI) (curve *2*), and zinc 2,3,7,8,12,13,17,18-octamethyl-5-phenylporphyrinate (curve *3*); T = 298 K; I = intensity.[99]

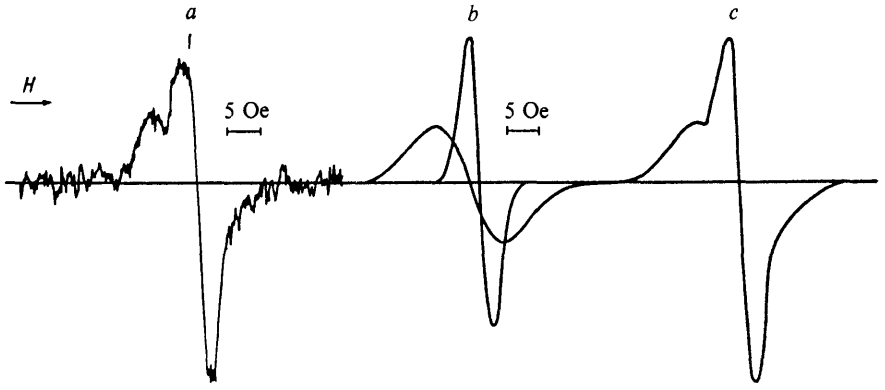
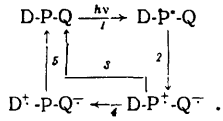


Figure 4. *a*, the EPR spectrum of a vitreous solution of compound (XXIIIa) (10^{-3} M) in triethylamine irradiated with the light from a DKSSh 1000 lamp (KS 10 filter); irradiation time 600 s; power of the light flux 2×10^{-3} W cm^{-2}; T = 77 K; the vertical line indicates the position of the EPR line of polycrystalline αα′-diphenyl-β-picrylhydrazyl;[108,109] *b*, EPR spectra of the radical-anion $P^{\cdot-}$ obtained by photoreduction in triethylamine and the radical-anion $Q^{\cdot-}$ obtained by reduction on a Na mirror; *c*, the calculated EPR spectrum representing a superposition of the EPR spectra of the radical-anions $P^{\cdot-}$–Q and $P–Q^{\cdot-}$; $P^{\cdot-}–Q : P–Q^{\cdot-} = 3:1$.

by a light pulse leads to the rapid (over a period less than 10^{-10} s) formation of $D^{+}–P–Q^{\cdot-}$:[72,73,106]



Charge separation is achieved via electron transfer from the excited singlet porphyrin to the quinone with formation of $D^{+}–P–Q^{\cdot-}$ [reaction (2)]. The formation of $D^{+}–P–Q^{\cdot-}$ [reaction (4)] competes with the charge recombination process [reaction (3)]. The quantum yield in the generation of $D^{+}–P–Q^{\cdot-}$ reaches 0.25. An amount of energy equal to 1 eV is then stored. The charge recombination time in $D^{+}–P–Q^{\cdot-}$ [reaction (5)] is several microseconds. This exceeds by a factor of 10^{6} the charge recombination time for the analogue without a donor fragment.

As in the covalently bound triad considered above, the formation of $D^{+}–P–Q^{\cdot-}$ in compound (XCII) is achieved over a period $< 10^{-10}$ s.[75] However, the charge separation quantum yield and the energy stored were greater than $\Phi = 0.7$ and $\Delta G = 1.4$ eV. The charge recombination time [reaction (5)] was 2.45×10^{-6} s.

Thus the two-step mechanism of electron transfer from the donor to the acceptor ensures a rapid charge separation and makes it possible to attain high quantum yields and lifetimes of the separated charges. The results of studies described in the literature[72,73,75,106] constitute evidence in support of theoretical models of electron transport in photosynthesis,[91,107] according to which the stepwise character of the process actually ensures a high efficiency of the charge separation at the photosynthetic reaction centres.

VII. Modelling of the intermediate stage of the primary charge separation in photosynthesis with the aid of porphyrin–quinone compounds

A simple system for the modelling of the concluding stage of the primary charge separation has been proposed and investigated.[108,109] Electron phototransfer and dark transfer reactions in frozen vitreous matrices comprising solutions of covalently bound P–Q compounds (XXIII)–(XXVI) in an electron-donating solvent were investigated in the above studies. The solvent was triethylamine. The presence of the bridging heteroatom served as an additional lever for controlling the efficiency of the intramolecular electron transfer processes. It was observed that irradiation with light at 77 K of P–Q solutions in the region of the long-wavelength absorption bands of P leads to the formation of the radical-ions $P^{\cdot-}$ and $Q^{\cdot-}$, detected from their characteristic EPR spectra. Fig. 4 presents as an example the experimental EPR spectra of the light-irradiated solutions of compound (XXIIIa) (Fig. 4*a*), the EPR spectra of the individual radical-anions $P^{\cdot-}$ and $Q^{\cdot-}$ (Fig. 4*b*), and the EPR spectrum representing the superposition of the $P^{\cdot-}$ and $Q^{\cdot-}$ signals (Fig. 4*c*). The radical-anions $P^{\cdot-}$ and $Q^{\cdot-}$ were generated by irradiating the pigment in triethylamine with light at 77 K ($P^{\cdot-}$) or by reduction on a sodium mirror ($Q^{\cdot-}$). Fig. 4 shows that the calculated EPR spectrum describes satisfactorily the experimentally observed signal of the light-irradiated solution.

The analysis in the above studies of the possible mechanisms of the formation of the radical-anions $P^{\cdot-}$ and $Q^{\cdot-}$ showed that these species are formed in accordance with the following scheme:

$$P\text{-}Q \xrightleftharpoons[\leftarrow]{h\nu^{1},\,(C_2H_5)_3N} (C_2H_5)_3N^{+} + P^{\cdot-}\text{-}Q \xrightarrow{h\nu^{2},\,(P\text{-}Q)_y}$$
$$\rightarrow (C_2H_5)_3N^{+} + P\text{-}Q + (P^{\cdot-}\text{-}Q)_y \rightarrow (P\text{-}Q^{\cdot-})_y \ .$$

After the absorption of the first light quantum, the P–Q compound is reduced by the nearest solvent molecule $[(C_2H_5)_3N]$. The radical-anions $P^{\cdot-}$–Q formed are unstable and, together with charge recombination, there is a possibility of electron transfer from $P^{\cdot-}$ to Q. After the absorption of the second light quantum by the radical-anion $P^{\cdot-}$–Q, an electron is transferred to remote $(P–Q)_r$ species. The electron is then localised initially at the porphyrin fragment of the P–Q molecule. This is followed by the dark intramolecular electron transfer from the porphyrin fragment of the molecule to the quinone fragment. The kinetics of this process for compound (XXIIIa) are illustrated in Fig. 5. Evidently the intramolecular electron transfer $P^{\cdot-}–Q \rightarrow P–Q^{\cdot-}$ is described by a nearly linear relation between the concentration of the $P^{\cdot-}$–Q species and the logarithm of the observation time. This indicates a difference between the probabilities of the electron transfer from $P^{\cdot-}$ to Q for different P–Q molecules. The causes of this difference are so far obscure. They may involve, for example, different P–Q conformations in the frozen solution, which leads to a difference in the electron transfer distances and (or) different mutual orientations of the molecular fragments relative to one another.

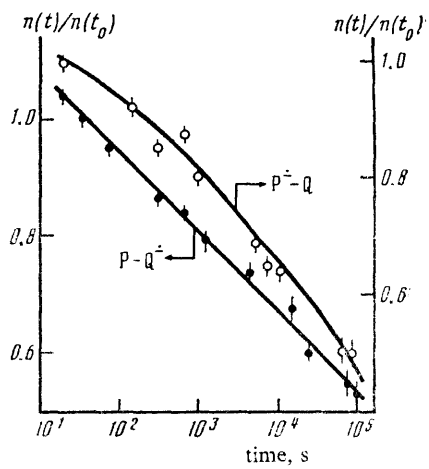


Figure 5. Kinetics of the dark destruction of $P^{\cdot-}$–Q and P–$Q^{\cdot-}$ in an irradiated vitreous solution of compound (XXIIIa) in triethylamine; the time is reckoned from the instant when irradiation ceases; T = 77 K;[108,109] $n(t)$ and $n(t_0)$ are the radical concentrations at times t and t_0.

The use of the quinone fragments of the P–Q molecules, differing in the electron-donating properties, and variation of the heteroatom in the bridge connecting P and Q make it possible to regulate the efficiency of the intramolecular electron transfer from $P^{\cdot-}$ to Q. It has been found that an increase in the oxidation-reduction potential of the quinone fragment of the P–Q molecule lowers the efficiency of the reduction of Q. This result can be explained if it is assumed that in the systems investigated the reorganisation energy is lower than the quantity $-\Delta G^0$ for the process[97] [see also Eqn. (1)].

The results of studies by Strekova and co-workers[108,109] demonstrate the possibility, in principle, of using solutions of P–Q compounds in electron-donating solvents for the modelling of one of the "elementary" stages of the charge separation process in photosynthesis—the stage involving electron transfer from phaeophytin to the primary acceptor. It is known that the electron transfer in photosynthesis from the electronically excited photosensitiser to the primary acceptor does not take place directly and occurs with participation of intermediate acceptors, one of which is phaeophytin.[110]

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We shall now formulate briefly the principal results of experimental studies on the intramolecular electron phototransfer in P–Q compounds, which are convenient models of the reaction centres in photosynthesis.

The possibility of the synthesis of such compounds with a fixed distance between the donor and acceptor and a definite mutual orientation makes it possible, as shown above, to investigate the influence of various factors on the efficiency of electron transport. As in photosynthesis, the transfer of an electron in the P–Q compounds takes place mainly with participation of excited singlet states of the pigments over distances reaching 15–20 Å. The electron transfer is manifested by the efficient quenching of the fluorescence of the porphyrin fragment and is recorded from the appearance of the characteristic EPR signals of the corresponding radical-ions and the appearance of new absorption bands in the optical spectra of the light-irradiated solutions. In conformity with the existing models of electron tunnelling, the probability of the process decreases exponentially with increase in chain length, depends on the mutual orientation of the porphyrin and the quinone, and is determined by the free energy of the reaction. The variation of the length and nature of the bridge and of the mutual orientation of the porphyrin and the quinone by specific synthesis makes it possible to control the electron transport process in the P–Q compounds. The ineffectiveness of the charge separation via the reaction channel involving the participation of the excited triplet state of the porphyrin is apparently caused by the lower energy of the triplet states compared with the singlet states. For $-\Delta G^0 < 1$–2 eV, this should entail, according to theoretical ideas about the mechanisms of electron transfer reactions, smaller rate constants for processes with participation of excited triplet states of the porphyrin. We may note in this connection studies[110–112] in which intramolecular electron transfer and the charge separation processes were investigated in covalently bound porphyrin–viologen and porphyrin–trinitroaryl compounds. According to preliminary data, the charge separation in these compounds takes place mainly with participation of the triplet states of porphyrins. Further investigation of the dependence of the electron transfer efficiency on the spin state of the pigment is of considerable interest for the theory of oxidation-reduction electron transfer reactions.

The solvent apparently plays an important role in the charge transfer in the P–Q compounds. The data obtained hitherto suggest that the medium influences only the process energetics. However, one must expect the involvement of the medium also in the dissipation of the energy of the resonance defect. This hypothesis is supported by the results of a study[113] of the influence of the isotope composition of the medium on the efficiency of the charge separation process in photosynthesis. The covalently bound P–Q compounds are convenient objects for the study of this interesting phenomenon, which is important for the theory of electron transfer and for the understanding of the mechanisms of charge separation in photosynthesis.

An appreciable increase in the lifetime of the separated charges is attained on passing from P–Q compounds to covalently bound triads. The stepwise character of the charge separation in these molecules ensures a high rate of charge separation and a low rate of their dark recombination.

Appreciable progress has now been achieved in the study of charge transfer processes in P–Q compounds. The results of these investigations promote a correct interpretation of data on the kinetics of electron transfer in photosynthesis. The synthesis and investigation of covalently bound triads with different donor fragments and bridging chains and other model structures containing P–Q fragments permit a deeper understanding of the mechanisms of electron transport in biological structures and will assist in progress towards the development of artificial molecular photocatalytic systems for the utilisation of solar energy.

References

1. U Govindjee (Editor) *Photosynthesis* (Translated into Russian from English), Izd. Mir, Moscow, 1987, Vol. 1, 728 pp
2. U Govindjee (Editor) *Photosynthesis* (Translated into Russian from English), Izd. Mir, Moscow, 1987, Vol. 2, 470 pp
3. R K Clayton *Photosynthesis: IUPAB Biophysics Series, Vol. 4, Physical Mechanisms and Chemical Patterns* (Translated into Russian from English), Izd. Mir, Moscow, 1984, 350 pp
4. D O Hall, K K Rao *Photosynthesis* (Translated into Russian from English), Izd. Mir, Moscow, 1983, 134 pp
5. V S Pshezhetskii, T S Lebedeva, A A Yaroslavov, et al. *Biofizika*, 1985, **30**
6. Y Nosaka, A Kuwabar, H Miyama *J. Phys. Chem.*, 1986, **90** 1465
7. K Mandal, M Z Hoffman *J. Phys. Chem.*, 1984, **88** 5632
8. T Sakata *J. Synth. Org. Chem. Jpn.*, 1981, **39** 909
9. D Dolphin, J Hiom, J B Paine *Heterocycles*, 1981, **16** 417
10. T Matsuo *J. Photochem.*, 1985, **25** 41
11. J H Fendler *J. Phys. Chem.*, 1985, **89** 2730
12. D Holten, M Gouterman, W W Parson, et al. *Photochem. Photobiol.*, 1976, **23**
13. D Huppert, P M Rentzepis, G Tollin *Biochim. Biophys. Acta*, 1976, **440** 356
14. A Harriman, G Porter, N Searle *J. Chem. Soc., Faraday Trans. 2*, 1979, **75** 1514
15. I N Ivanitskaya, I I Dilung *Biofizika*, 1974, **19** 647
16. D R Kemp, G Porter *Proc. R. Soc. London, A*, 1971, **326** 117
17. G Tollin, G Green *Biochim. Biophys. Acta*, 1962, **60** 524
18. G Tollin *J. Phys. Chem.*, 1976, **80** 2274
19. L V Natarajan, L R Humphreys, R Chang *Spectrosc. Lett.*, 1985, **18** 219
20. A Harriman, G Porter, A Wilowska *J. Chem. Soc., Faraday Trans. 2*, 1983, **79**
21. N Mataga, A Karen, T Okada, et al. *Phys. Chem.*, 1984, **88** 4650
22. K Maruyama, H Furuta *Chem. Lett.*, 1986, 473
23. Y Degani, I Willner *J. Phys. Chem.*, 1985, **89** 5685
24. S M B Costa, M R Aires de Barros, J P Conde *J. Photochem.*, 1985, **28** 153
25. N B Joshi, J R Lopez, H T Tien, et al. *J. Photochem.*, 1982, **20** 139
26. I Tabushi, M Kinnaird, S-I Kugimiya *J. Photochem.*, 1985, **29** 217
27. M C Gonzalez, A C Weedon *Can. J. Chem.*, 1985, **63** 602
28. J L Y Kong, P A Loach *Frontiers of Biological Energetics: From Electrons to Tissues*, 1978, Vol. 1, p. 73
29. J L Y Kong, P A Loach *J. Heterocycl. Chem.*, 1980, **17** 737
30. J A Anton, J L Y Kong, P A Loach *J. Heterocycl. Chem.*, 1976, **13** 717
31. T-F Ho, A R McIntosh, A C Weedon *Can. J. Chem.*, 1984, **62** 967
32. J A Schmidt, A Siemiarczuk, A C Weedon, J R Bolton *J. Am. Chem. Soc.*, 1985, **107** 6112
33. I Tabushi, N Koga, M Yanagita *Tetrahedron Lett.*, 1979, **20** 257
34. J P Collman, R R Gagne, C A Reed, et al. *J. Am. Chem. Soc.*, 1975, **97** 7185
35. G M Sanders, M van Dijk, G P Koning, et al. *Recl. Trav. Chim. Pays-Bas*, 1985, **104** 243
36. G M Sanders, M van Dijk, A van Veldhuizen, H C van der Plas *J. Chem. Soc., Chem. Commun.*, 1986, 1311
37. K Maruyama, H Puruta, A Osuka *Chem. Lett.*, 1986, 475
38. A Osuka, S Morikawa, K Maruyama, et al. *J. Chem. Soc., Chem. Commun.*, 1987
39. S Nishitani, N Kurata, Y Sakata, et al. *Tetrahedron Lett.*, 1981, **22** 2099
40. D Arnold, A W Johnson, M Winter *J. Chem. Soc., Perkin Trans. 1*, 1977, 1643
41. D P Arnold, R Gaete-Holmes, A W Johnson, et al. *J. Chem. Soc., Perkin Trans.* 1, 1978, 1660
42. S Nishitani, N Kurata, Y Sakata, et al. *J. Am. Chem. Soc.*, 1983, **105** 7771
43. N Mataga, A Karen, T Okada, et al. *J. Phys. Chem.*, 1984, **88** 5138
44. R P Evstigneeva, V V Borovkov, E I Filippovich, S I Sviridov *Dokl. Akad. Nauk SSSR*, 1987, **293** 1130
45. V V Borovkov, E I Filippovich, R P Evstigneeva *Khim. Geterotsikl. Soedin.*, 1988(5), 608
46. C E D Chidsey, S G Boxer *Biophys. J.*, 1981, **33** 172a
47. J Deisenhofer, O Epp, K Miki, et al. *J. Mol. Biol.*, 1984, **180** 385
48. I Tabushi, N Koga, A Yazaki *Kukusokan Kagaku Toronkai Koen Yoshishu XII*, 1979, p. 246
49. M R Wasielewski, W A Svec, B T Cope *J. Am. Chem. Soc.*, 1978, **100** 1961
50. R R Bucks, S G Boxer *J. Am. Chem. Soc.*, 1982, **104** 340
51. C K Chang, I Abdalmuhdi *J. Org. Chem.*, 1983, **48** 5388
52. J A Cowan, J K M Sanders *J. Chem. Soc., Chem. Commun.*, 1985, 1214
53. Y Sakata, S Nishitani, N Nishimizu, et al. *Tetrahedron Lett.*, 1985, **26** 5207
54. J P Collman, A O Chong, G B Jameson, et al. *J. Amer. Chem. Soc.*, 1981, **103**
55. J E Guillet, Y Takahashi, A R McIntosh, J R Bolton *Macromolecules*, 1985, **18**
56. J Dalton, L R Milgrom *J. Chem. Soc., Chem. Commun.*, 1979, 609
57. A C Chan, J Dalton, L R Milgrom *J. Chem. Soc., Perkin Trans. 2*, 1982, 707
58. L R Milgrom *J. Chem. Soc., Perkin Trans. 1*, 1984, 1483
59. A D Joran, B A Leland, G G Geller, et al. *J. Am. Chem. Soc.*, 1984, **106** 6080
60. J R Bolton, T-F Ho, S Liauw, et al. *J. Chem. Soc., Chem. Commun.*, 1985, 559

61. N Kobayashi, Y Nishiyama, T Ohya, M Sato *J. Chem. Soc., Chem. Commun.*, 1987, 390
62. M R Wasielewski, M P Niemczyk *J. Am. Chem. Soc.*, 1984, **106** 5043
63. K N Ganesh, J K M Sanders *J. Chem. Soc., Chem. Commun.*, 1980, 1129
64. K N Ganesh, J K M Sanders *J. Chem. Soc., Perkin Trans. 1*, 1982, 1611
65. H P Isenring, E Zass, K Smith, et al. *Helv. Chim. Acta*, 1975, **58** 2357
66. A Osuka, H Furuta, K Maruyama *Chem. Lett.*, 1986, 479
67. B Morgan, D Dolphin *Angew. Chem., Int. Ed. Engl.*, 1985, **24** 1003
68. J Weiser, H A Staab *Angew. Chem., Int. Ed. Engl.*, 1984, **23** 623
69. J Weiser, H A Staab *Tetrahedron Lett.*, 1985, **49** 6059
70. J S Lindsey, D C Mauzerall *J. Am. Chem. Soc.*, 1982, **104** 4498
71. J Lindsey *J. Org. Chem.*, 1980, **45** 5215
72. T A Moore, D Gust, P Mathis, et al. *Nature*, 1984, **307** 630
73. D Gust, T A Moore, P A Liddell, et al. *J. Am. Chem. Soc.*, 1987, **109** 846
74. P A Liddell, D Barrett, L R Makings, et al. *J. Am. Chem. Soc.*, 1986, **108** 5350
75. M R Wasielewski, M P Niemczyk, W A Svec, E B Pewitt *J. Am. Chem. Soc.*, 1985, **107**
76. K N Ganesh, J K M Sanders, J C Waterton *J. Chem. Soc., Perkin Trans. 1*, 1982
77. P Leighton, J K M Sanders *J. Chem. Soc., Chem. Commun.*, 1985, 24
78. J E Baldwin, M J Crossley, J E Debernadis, et al. *Tetrahedron*, 1981, **37**
79. C Krieger, J Weiser, H A Staab *Tetrahedron Lett.*, 1985, **26** 6055
80. J L Y Kong, K G Spears, P A Loach *Photochem. Photobiol.*, 1982, **35** 545
81. M Migita, T Okada, N Mataga, et al. *Chem. Phys. Lett.*, 1981, **84** 263
82. G I Gleicher *The Chemistry of the Quinoid Compounds*, Wiley, New York, 1974, Part 1, p. 24
83. K P Quinlan *J. Phys. Chem.*, 1968, **72** 1797
84. P A Shakhverdov *Dokl. Akad. Nauk SSSR*, 1967, **174** 1141
85. M A Bergkamp, J Dalton, T L Netzel *J. Am. Chem. Soc.*, 1982, **104** 253
86. J H Wilford, M D Archer, J R Bolton, et al. *J. Phys. Chem.*, 1985, **89** 5395
87. T-F Ho, A R McIntosh, J R Bolton *Nature*, 1980, **286** 254
88. B Ke, S Demeter, K I Zamaraev, R F Khairutdinov *Biochim. Biophys. Acta*, 1979, **545** 264
89. A R McIntosh, A Siemiarczuk, J R Bolton, et al. *J. Am. Chem. Soc.*, 1983, **105**
90. A Siemiarczuk, A R McIntosh, T-F Ho, et al. *J. Am. Chem. Soc.*, 1983, **105** 7224
91. J Jortner *J. Am. Chem. Soc.*, 1980, **102** 6676
92. J S Lindsey, D C Mauzerall, H Linschitz *J. Am. Chem. Soc.*, 1983, **105** 6528
93. M R Wasielewski, M P Niemczyk, W A Svec, E B Pewitt *J. Am. Chem. Soc.*, 1985, **107**
94. J R Miller, J A Peeples, M J Schmitt, G L Closs *J. Am. Chem. Soc.*, 1982, **104** 6488
95. R A Marcus *J. Chem. Phys.*, 1956, **24** 966
96. B S Brunschwig, J Logan, M D Newton, N Sutin *J. Am. Chem. Soc.*, 1980, **102** 5798
97. K I Zamaraev, R F Khairutdinov, V P Zhdanov *Tunnelirovanie Elektrona v Khimii. Khimicheskie Reaktsii na Bol'shikh Rasstoyaniyakh* (Electron Tunnelling in Chemistry. Chemical Reactions over Long Distances), Izd. Nauka, Novosbirsk, 1985
98. N Mataga, M Ottolenghi *Molecular Associations* (Edited by R Foster), Acad. Press, London, 1979, p. 40
99. B A Leland, A D Joran, P M Felker, et al. *J. Phys. Chem.*, 1985, **89** 5571
100. M C Gonzalez, A R McIntosh, J R Bolton, A C Weedon *J. Chem. Soc., Chem. Commun.*, 1984, 1138
101. D Mobins *Ber. Bunsenges Phys. Chem.*, 1978, **82** 848
102. H Kuhn *Pure Appl. Chem.*, 1979, **51** 341
103. H Kuhn *Thin Solid Films*, 1983, **99** 1
104. A F Janzen, J R Bolton, M J Stillman *J. Am. Chem. Soc.*, 1979, **101** 6337
105. A F Janzen, J R Bolton *J. Am. Chem. Soc.*, 1979, **101** 6342
106. D Gust, T A Moore *J. Photochem.*, 1985, **29** 173
107. M A Vorotinzev, E M Itskovich *J. Theor. Biol.*, 1980, **86** 223
108. L N Strekova, et al. *Dokl. Akad. Nauk SSSR*, 1988, **298** 487
109. R F Khairutdinov, L N Strekova, V V Borovkov, et al. *Khim. Vys. Energ.*, 1988, **22** 520
110. A Harriman, G Porter, A Wilowska *J. Chem. Soc., Faraday Trans. 2*, 1984, **80**
111. G Blondcel, et al. *Chem. Phys. Lett.*, 1985, **118** 77
112. H Nakamura, A Motonaga, T Ogata, et al. *Chem. Lett.*, 1986, 1615
113. L N Strekova, et al. *Biofizika*, 1988, **33** 495

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Quantum-chemical studies of the structure and reactivity of carbenes

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ABSTRACT. The results of quantum-chemical studies on the electronic and geometrical structures and of the singlet–triplet splitting of carbenes (methylene and its derivatives, including unsaturated and cyclic carbenes) are examined and surveyed. The factors regulating the geometrical characteristics and the multiplicity of the electronic ground state of carbenes are discussed. The features of the reaction pathways leading to the addition of electrophilic and nucleophilic carbenes to single and double bonds and the structures of the transition states are analysed.

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I. Introduction

The improvement of the methods of modern quantum chemistry and especially the colossal progress in the development of high speed computers have created during the last decade a new situation in chemical science. In many fields, theory has become an equal partner of experiment not only in the formulation of general rules and the development of a conceptual language but also in direct quantitative estimation of particular physical and structural characteristics as well as reactivity. The important role of quantum-chemical analysis, which has assumed a parallel or even a leading position, is manifested particularly strikingly in the study of kinetically unstable intermediate compounds whose experimental detection frequently requires the overcoming of considerable difficulties. Carbenes and their analogues are precisely compounds of this kind. An enormous number of original and review communications have been devoted to the theoretical study of carbenes. The fact that carbenes are non-classical organic structures—derivatives of divalent carbon (more precisely dicoordinate carbon), characterised by a very narrow energy gap between the lowest electronic states with different multiplicities—is of special interest for theory. This leads to unique features in the structure and reactions of carbenes which do not fit within the framework of standard classical ideas.

The main task of this review is to demonstrate the role and possibilities of quantum-chemical research in individual principal aspects of the chemistry of carbenes. We shall consider initially a key carbene–methylene. This is a polyatomic molecule which has been subjected to what has probably been the most detailed theoretical study. The structural and energetic parameters of methylene have been calculated in recent years with unprecedented accuracy. The data obtained constitute the basis of the analysis of the geometrical and electronic structures of substituted carbenes and their analogues. Equal attention will be devoted to both quantitative calculations and to qualitative theories which make it possible to treat in general terms the available results and to predict new ones. The description of reactivity will be limited to the consideration of two most representative types of carbene reactions—addition (insertion) to σ and π-bonds.

Although the review deals almost exclusively with studies of the last decade only, it by no means represents an exhaustive treatment even of this period. Nevertheless we hope that the data presented will make it possible to deduce the leading trends in theoretical research into carbenes—the field of chemical knowledge in which the interaction of theory and experiment is especially effective.

II. Methylene

Although the rigorous spectroscopic identification of methylene, obtained in the flash photolysis of gaseous diazomethane, was not achieved until the beginning of the 1960's,[1,2] this simplest divalent carbon compound has been at the centre of attention of chemists—both experimenters and theoreticians—for almost a century since Nef's first "general theory of methylene" (see the relevant reviews[3–5]). The explanation is, firstly, that methylene is the prototype of all carbenes and without due understanding of the nature of its electronic states, structural features, and reactivity, it is impossible to proceed to the formulation of general ideas about the corresponding characteristics of more complex carbenes and their analogues. Secondly, the study of methylene has created a situation, rare as regards its fruitfulness, of a true partnership and mutual enrichment between theory and experiment in chemical science.

In view of the small size of the methylene molecule, in the 1970's it already became possible to calculate all its characteristics using the most powerful arsenal of non-empirical (*ab initio*) quantum-chemical methods, which are comparable to or even superior to modern experimental methods as regards accuracy. Even in the qualitative aspect, the rigorous theoretical conclusions proved to be more accurate than the conclusions drawn from earlier or current experiments. Thus theoretical predictions have stimulated the formulation of more refined experiments and promoted their more accurate interpretation. The need to test and improve quantum-chemical methods, induced by the observed incomplete agreement between the theoretical predictions and experimental data, stimulated in its turn the development of a methodology for the selection of computational models adequate for the problem formulated. The triumphal history, as regards quantum chemistry, of the establishment of the existing views of the electronic and steric structures and

Table 1. The electronic structure, geometry, and energy characteristics of the angular structure of methylene in different electronic states.

Electronic state	Electron shell	Designation adopted*1	HCH angle, deg		R_{CH}, nm		Relative energy, kJ mol^{-1}*3	
			calc*2	expt.	calc.*2	expt.	calc.	expt.
$^3B_1$	$(1a_1)^2(1b_2)^2(2a_1)^1(1b_1)^1$	$^3(\sigma p)$	134±2	133.84±0.05	0.1088	0.108	0	0
			[16]	[17]	[16]	[17]		
1^1A_1	$(1a_1)^2(1b_2)^2[(2a_1)^2-\lambda_1(1b_1)^2]$	$^1(\sigma^2)$	102.4	102.4	0.112	0.11	41.00*4	37.75±0.058
	$(0<\lambda_1<1)$		[18]	[19]	[18]	[19]		[20]
$^1B_1$	$(1a_1)^2(1b_2)^2(2a_1)^1(1b_1)^1$	$^1(\sigma p)$	141.2	140	0.1065	0.106	139.7	—
			[21]	[19]	[21]	[19]	[22]	
2^1A_1	$(1a_1)^2(1b_2)^2[\lambda(2a_1)^2+(1b_1)^2]$	$^1(p^2)$	180	—	0.107	—	279.8	—
	$(0<\lambda<1)$		[23]		[23]		[23]	

*1According to the σ,p designations, introduced by Hoffmann et al.,[24] the $2a_1$ MO belong to the σ type and the $1b_1$ MO belong to the p type; only the principal components of the two-determinant function are indicated for the 1^1A_1 and 2^1A_1 electronic states.[25] *2The basis set $(5s3p1d/3s1p)$ was used by McLaughlin et al.[16] and 617 configurations were examined taking into account the configuration interaction (CI); the DZP basis set was used by Bauschlicher and Shavitt[18] and in the calculation for the $^1A_1$ state, account was taken of all the singly and doubly excited configurations constructed both relative to the $(2a_1)^2$ configuration and relative to the $(1b_1)^2$ configuration (2R-CI, see Table 2); Meadows and Schaefer[21] used the $(9s6p3d/4s2p)$ basis set; Bauschlicher and Yarkony[23] used the Dunning–Husinaga basis set, supplemented by d and p functions, and the MC SCF method; in the calculation for the 2^1A_1 state, they took into account all the singly and doubly excited configurations (SD-CI, see Table 2). *3A detailed compilation of the singlet-triplet ($^3B_1$–$^1A_1$) CH_2 splittings is given in Table 2. *4The estimate is based on the calculated ($^1B_1$–$^3B_1$) energy difference[22] and the experimental ($^1B_1$–$^1A_1$) difference equal to 98.74 kJ mol^{-1}.[26]
Note. Here and henceforth the numerals in square brackets denote references (Editor of Translation).

energetics of the electronic state of methylene has been described in detail in numerous reviews[5–10] and here we shall trace only concisely the principal stages in the solution of the problems involved, emphasising the final results.

1. Electronic configuration

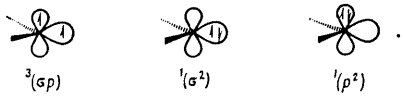
Methylene belongs to the class of molecules with a triplet electronic ground state, which has been unambiguously demonstrated by the observation of the EPR spectrum of CH_2 in a xenon matrix at 4.2 K.[11,12] The results of almost all sufficiently rigorous computations, both semiempirical (INDO,[13] MINDO,[3,14] MNDO[15]) and non-empirical, agree with the idea that the triplet electronic state of CH_2 is energetically preferred, and this conclusion remains valid for all the geometrical forms of methylene possible in principle: linear ($D_{\infty h}$) and angular (C_{2v}) (Table 1). Fig. 1 presents Walsh's diagram illustrating the dependence of the positions of the energy levels of the valence MO of methylene on the HCH valence angle.

For the electronic valence shell $(1\sigma_g)^2(1\sigma_u)^2(1\pi_u)^2$, the electronic states of the linear molecule are arranged in the following energy sequence:

$$^3\Sigma_g^- < {}^1\Delta_g < {}^1\Sigma_g^+.$$

The angular deformation of the linear structure of methylene induces the splitting of the $^1\Delta_g$ state into the $^1A_1$ and $^1B_1$ states.

The structure of the electronic shells of different electronic states of the angular (C_{2v}) form of methylene is characteristic of biradical systems having virtually degenerate highest partly occupied MO.[7] Table 1 illustrates the types of occupation of the MO of methylene and the corresponding electronic states and also presents data obtained by the most rigorous non-empirical calculations in which account has been taken of the electronic correlation and the experimental data for the geometrical characteristics of these states. On the other hand, the $^3(\sigma p)$ and $^1(\sigma p)$ states are described satisfactorily by the usual one-determinant functions:



The states $^1(\sigma^2)$ and $^1(p^2)$, having the same symmetry, require the application of two-determinant functions taking into account the contributions of doubly excited configurations.

2. The geometry of the electronic ground state

The first non-empirical calculation, carried out in 1960[27] using a minimal basis set of Slater type orbitals with allowance for the introduction of a fairly large number (at that time) of electronic configurations (128), already led to the conclusion that the angular structure of the triplet state $^3B_1$ with a HCH angle of 129° is preferred. However, this conclusion was regarded as one not meriting particular confidence, because the interpretation of the electronic spectrum of methylene, current at the time, although not excluding its assignment to a bent structure,[2,19,28] nevertheless favoured the alternative linear $D_{\infty h}$ form.

The conclusion drawn from subsequent quantum-chemical calculations for the methylene molecule (see Schaefer's detailed review[29]) that the triplet state has a linear structure was regarded as "being in excellent agreement with the observed electronic states of CH_2",[28] whereas predictions of the angular structure were regarded

as a consequence of an unsuccessful selection of the computational method.

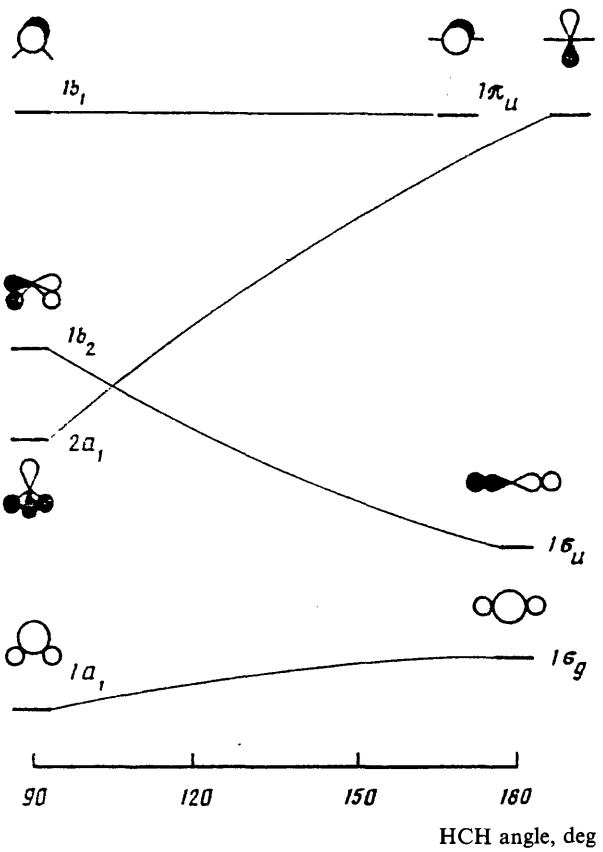


Figure 1. The correlation diagram for the lowest valence MO of the linear and angular structures of methylene illustrating the dependence of the energy levels of the orbitals on the HCH angle.

The situation changed radically after non-empirical calculations,[30] performed with an extremely high degree of accuracy (basis set of Gaussian orbitals of the *DZ* type, allowance for 408 configurations including all single and double excitations) and predicting a HCH angle of 135.1° for the angular C_{2v} form of the ground state of methylene. This value proved to be in good agreement with the value 135 ± 8° obtained soon afterwards from the analysis of the EPR spectrum of triplet methylene,[11] which induced a return to the interpretation of the spectroscopic parameters of CH_2 on the basis of the bent structure.[31] According to the best experimental estimate, it is currently believed that the HCH angle for methylene in the $^3B_1$ state is 133.84 ± 0.05° [17] (Table 1). The energy barrier to the planar inversion of the triplet ($^3B_1$) methylene, i.e.

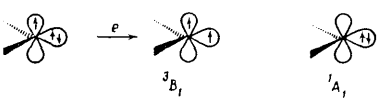


is only 22.32 ± 0.96 kJ mol^{-1} [17] and only two vibrational levels lie below the barrier. This means that the methylene molecule in the ground state should be regarded as essentially quasi-linear, like BaX_2 (X = Cl, Br).[32]

3. Singlet–triplet splitting

The most exact energy difference (ΔE_{S-T}) between the ground triplet ($^3B_1$) and first excited singlet ($^1A_1$) states is 37–38 kJ mol^{-1}. Before proceeding to the discussion of the experimental and calculated data, we may note the difference between the values of ΔE_{S-T} determined experimentally and obtained as a result of the primary quantum-chemical calculation. In the former case, ΔE_{S-T} corresponds to the energy difference between the ground vibrational states (which were designated by T_0) and in the second to the difference (T_e) between the energies of the minima on the potential energy surfaces for the electronic states $^3B_1$ and $^1A_1$. Since in the ground electronic state $^3B_1$ the C–H bonds are shorter and stronger than in the state $^1A_1$ (see Table 1; the experimental energies of the C–H bonds and the theoretical values close to them are 441 kJ mol^{-1} for $^3B_1$ and 410 kJ mol^{-1} for $^1A_1$ [33]), the extension of these bonds in the state $^3B_1$ requires more energy. As a result, the energy of the zero-point vibrations is greater for the triplet state than for the excited singlet state. According to Petek et al.[34] and Bunker and Jensen,[35] $T_e - T_0$ = 0.12 ± 0.71 kJ mol^{-1}. Although allowance for the relativistic correction (about 0.17 kJ mol^{-1} [5,36]) increases this difference to 0.3 kJ mol^{-1}, it is clear that the effects considered are comparatively small.

Up to the middle of the 1970's, ΔE_{S-T} = 33 ± 4 kJ mol^{-1} was adopted as an experimental estimate based on different indirect determinations,[29,37,38] which was in acceptable agreement with the results of most accurate non-empirical quantum-chemical calculations.[6,29,39] However, a direct determination of ΔE_{S-T} in the laser photoionisation of the CH_2^- anion was reported in 1976. This yielded 81.6 ± 2.9 kJ mol^{-1}.[40]



The subsequent series of calculations, in which an increasingly higher accuracy was employed (see the relevant reviews[9,10]) did not bring the theoretical value ΔE_{S-T} and that found by Zittel et al.[40] closer together. This induced theoreticians to reinterpret the experimental data.[41] According to Zittel et al.[40] and Engelking et al.,[41] the beam of CH_2^- anions contains no vibrationally excited ions which could lead to the appearance of additional "hot bands" in the photoelectron spectrum. However, calculation of the energy of the vibrational levels using wave functions obtained with the aid of the generalised valence bond method showed that the fourth vibrational level of CH_2^- lies above the ground vibrational level of the triplet $^3B_1$ state of CH_2,[42] which means that three "hot" bands might have been observed in the photoelectron spectrum of CH_2^- and this band assignment would in fact lead to T_0 = 37.6 kJ mol^{-1} [43,44] in agreement with previous theoretical and experimental data. Modification of the photoionisation experimental method in order to exclude the appearance of "hot bands" made it possible to obtain experimentally T_0 = 37.6 kJ mol^{-1}.[45] Very similar values of T_0 (35.6 ± 2.9 kJ mol^{-1} [46] and 37.86 ± 0.025 kJ mol^{-1} [47]) were found almost simultaneously in other studies whose aim was a direct experimental determination of the energy of the singlet–triplet

splitting in methylene (see also a detailed compilation in other reviews[5,8,9]). At the present time the most accurate experimental estimate of ΔE_{S-T} is believed to be $T_0 = 37.75 \pm 0.058$ kJ mol^{-1}.[20] When account is taken of the corrections for the relativistic effects and the zero-point vibration energy, $T_e = 38.03 \pm 0.84$ kJ mol^{-1} (the diagonal correction to the Born–Oppenheimer approximation is 0.46 kJ mol^{-1} [48]).

4. Methylene as a test structure in quantum chemistry

The theoretical results examined above have generally been achieved with methods giving the highest degrees of accuracy whose employment in the study of more complex carbenes involves considerable computational difficulties. The questions to what extent particular properties of methylene are described by simpler methods, including semiempirical ones and also whether qualitative theoretical ideas adopted in chemistry are applicable to the description of the properties of methylene have therefore acquired extremely great importance. Although the answers to these questions do not guarantee an unambiguous selection of an adequate method for the calculation of the characteristics of more complex carbenes, nevertheless they could be regarded as a very important basis for such a selection and for the estimation of the reliability of a particular calculation.

We shall deal initially with non-empirical calculations (Table 2). The refinement of the results is achieved here both by expanding the set of basis functions and by improving the allowance for electron correlation. In order to obtain geometrical characteristics of methylene in the $^3B_1$ and $^1A_1$ states close to experimental values, it is sufficient to use even the minimal basis set (STO-3G) or the simplest split basis set (3-21G) of the orbitals and the transition from the approximation of the restricted Hartree–Fock method to the unrestricted method and allowance for the energy of electron correlation do not exert a significant influence on the results of the calculation of the CH bond length and the HCH angle.[58,59] On the other hand, Table 2 shows that the selection of the basis set and allowance for the correlation corrections are very important for the estimation of ΔE_{S-T}. When polarisation functions are included in the basis set, the state $^1A_1$ is stabilised to a greater extent because the description of the polarisation orbital of the unshared electron pair $2a_1$ is then improved more than that of the non-polar p orbital $^1b_1$ (Fig. 1). An especially significant improvement is attained when the two-determinant function (TCSCF) is resorted to for the state $^1A_1$. If account is taken of all the single and double excitations relative to both configurations used for the description of this state (2R-CI), it is possible to obtain $\Delta E_{S-T} = 41.0$ kJ mol^{-1}. According to the best estimate of ΔE_{S-T} obtained at the present time by the non-empirical calculation, this quantity is 37.78 kJ mol^{-1},[52] which virtually agrees with the experimental value.

In contrast to the non-empirical computational methods, for which there exists a definite hierarchy ensuring a gradual improvement of the results on going over to higher degrees of accuracy, the semiempirical methods have been parametrised in order to reproduce specific properties (see, for example, Minkin et al.[60]). As a result of this, not only individual properties of a compound but also the properties of all classes of compounds are described better by one of the methods than by others. Comparison of the results of calculations for methylene and its derivatives by the most widely used semiempirical CNDO, INDO,[61] MINDO/2,[62] MINDO/3,[63] and MNDO[15] methods shows quite definitely that preference should be given to the MINDO/3 method. The calculation by this method for the $^3B_1$ state yields the following values: HCH angle 134.1°, $R_{CH} = 0.1078$ nm, and $\Delta E_{S-T} = 36.4$ kJ mol^{-1},[14]† which agrees well with the most accurate experimental data (Table 1).

Table 2. The results of non-empirical calculations of the energy of the singlet–triplet splitting ΔE_{S-T} for methylene (in kJ mol^{-1}).

Basis set	Computational scheme*1					
	SCF	TCSCF	SD-CI	SD(Q)-CI	2R-CI	GVB-RCI
Minimal (2*s*1*p*) for C, (1*s*) for H	167.7 [49]	133.9 [50]				
DZ (4*s*2*p*/2*s*)	135.5 [18, 51]	95.4 [18, 51]	99.2 [18]	92.0 [18]	92.8 [18]	
DZP (4*s*2*p*1*d*/2*s*1*p*)	109.6 [18]	53.5 [18]	61.1 [18]	51.9 [18]	51.0*2 [18]	48.1 [52]
Extended basis set with polarisation functions (6*s*4*p*2*d*/3*s*2*p*)	104.6 [18]	46.4 [18]	55.2 [18]	45.6*3 [18]	44.3*4 [18]	
Very large basis sets [from (8*s*5*p*3*d*/4*s*1*p*) to (9*s*7*p*2*d*1*f*/5*s*2*p*)]	103.7 [18]	44.8 [53]	54.8 [54]	45.2 [54]	41.0 [53]	37.8 [52]

Note. Data presented in two reviews,[5,8] supplemented by the results of subsequent studies, were adopted as a basis; the experimental energy difference is $\Delta E_{S-T} = 37.75 \pm 0.058$ kJ mol^{-1}.[20]

*1For the readers convenience, the notation adopted in the original English language publications has been retained: TCSCF—two-configuration wave function for the state $^1A_1$ (see Table 1); SD-CI—configuration interactions (CI) with allowance for all the singly and doubly excited configurations; SD(Q)-CI—as for SD-CI but account is taken of the correction for fourfold excitations;[55] 2R-CI—allowance for single and double excitations both in the configuration $(2a_1)^2$ and in the configuration $(1b_1)^2$ for the state $^1A_1$; GVB-RCI—calculation by the generalised valence bond method taking into account the restricted CI.

*2With more complete allowance for the CI, $\Delta E_{S-T} = 50.1$ kJ mol^{-1} was obtained.[56]

*3Calculation in terms of the 6-31G basis set.

**Allowance for the electronic configuration in terms of the Meller–Plesset theory (MP4SDTQ) yields $\Delta E_{S-T} = 54.8$ kJ mol^{-1}; expansion of the basis set and extrapolation make it possible to obtain $\Delta E_{S-T} = 34.3$ kJ mol^{-1}.[33]

*4Calculation in terms of the (6*s* 4*p*2*d*; 4*s* 2*p*) basis set yields $\Delta E_{S-T} = 45.6$ kJ mol^{-1}.[57]

The question arises to what extent qualitative theories make it possible to account for the electronic and geometrical structure of methylene. The conclusion that the lowest singlet state of methylene $^1A_1$ or $^1(\sigma)^2$ has a bent structure follows quite definitely from simple orbital ideas and Walsh diagrams. This structure is preferred because of the significant decrease in the energy of the doubly

† However, one should note that the solution obtained by the MINDO/3 method for the state $^1A_1$ is triplet-unstable.[66] This means that the unrestricted Hartree–Fock (UHF) approximation must be resorted to, which makes it possible to obtain for the given state a solution with a lower energy (see, for example, Refs. 67–69). As a consequence of this, ΔE_{S-T} is reduced.

occupied $2a_1$ MO as the valence angle is reduced[64] (Fig. 1). When hybrid orbital ideas are used, i.e. on going over from canonical to localised orbitals, the valence state of the carbon atom of the angular form $^1(\sigma)^2$ of methylene can be described as $(sp^3)^2(sp)^2$, i.e. $s^{3/2}p^{5/2}$,[65] or as $(sp^2)^4$, i.e. $s^{4/3}p^{8/3}$,[8] whereas the valence state of carbon in the linear form is $(sp)^2(p)(p)$, i.e. sp^3. If the valence state of the carbon atom in methylene remained the same as in the ground state of the carbon atom $(1s)^2(2s)^2(2p)^2$, i.e. s^2p^2, singlet methylene would have an angular structure with a valence angle of 90°. In this structure, there is no need for energy expenditure on the $s \rightarrow p$ promotion of a whole electron, as in the transition to the linear form ($s^2p^2 \rightarrow sp^3$) or of "part" of an electron, as in the transition to forms with C–H sp^3-bonds (109.5°) or C–H sp^2-bonds (120°). However, with increase in the valence angle, the repulsion between the electron pairs of these bonds diminishes. The balance between the expenditure on the promotion of an electron from the s to the p orbital, which increases with increase in the valence angle, and the gain attained under these conditions in the repulsion energy of the electrons of the C–H bonds with a simultaneous increase in the strength of the latter as a result of the hybridisation of their constituent carbon orbitals determines the geometry of the singlet methylene.[6,65]

On the other hand, analysis of the Walsh diagram (Fig. 1) for the triplet state $^3B_1$ or $^3(\sigma p)$ does not make it possible to settle reliably on the angular structure. Indeed, the stabilisation attained with decrease in the valence angle of the singly occupied $2a_1$ MO is accompanied by an increase in the energy of the doubly occupied $1b_2$ MO and also by a slight destabilisation of the singly occupied $1b_1$ MO. In particular, Walsh himself was inclined towards the conclusion that the triplet state of methylene has a linear geometrical structure.[64] According to Dewar,[65] the angular structure of the triplet state of methylene can be accounted for within the framework of the idea of σ-conjugation if allowance is made for the fact that the transition, not requiring an energy expenditure on the promotion of s electrons, from the valence state $(sp)^2(p)(p)$, corresponding to the linear structure, to the state $(sp^2)^3(p)$ ensures additional stabilisation of the angular structure as a consequence of the σ-conjugation between the three-hybrid sp^2 orbitals.

III. Derivatives and isoelectronic analogues of methylene

When the hydrogen atoms in the methylene molecule are replaced by the usual substituents (X, Y), the frontier character of the $^3(\sigma p)$ and $^1(\sigma^2)$ states is retained on passing to silylene and other isoelectronic analogues. However, the replacement of the hydrogen atom in CH_2 can induce changes in the XCY valence angle and in the singlet–triplet splitting extending to the stabilisation of the linear form and the reversal of the multiplicity of the ground electronic state. The latter effect is well known. For example, halogenomethylenes as well as silylene SiH_2 and germylene GeH_2 have singlet $^1(\sigma^2)$ ground electronic states.[5,25,70]

The question which substituents promote the stabilisation of the singlet or triplet electronic states is especially interesting, since the reactivity of the carbene depends significantly on the character of the electronic state. The triplet state is preferred if the energy difference between the frontier orbitals is less than the Coulombic repulsion integral J_{12} between the electrons in these orbitals, i.e. $\Delta\varepsilon_{12}-J_{12} < 0$. As a rule, this condition is fulfilled when the splitting of the level of the frontier orbitals $\Delta\varepsilon_{12} \leqslant 1.5$ eV (145 kJ mol^{-1}). With increase in the above energy gap, the ground state of the carbene corresponds to the singlet electronic configuration.[24] Thus the energy gap between the frontier orbitals a_1 and b_1 of methylene is 113 kJ mol^{-1} according to the extremely accurate MP4SDTQ/6-31G** calculations,[71] while for silylene the corresponding value is as much as 217 kJ mol^{-1}.

Hoffmann and co-workers[24,72] formulated qualitatively the general principles of the selection of substituents at the carbene centres which ensures an increase in the energy gap $\Delta\varepsilon_{12}$ and an increased stabilisation of the singlet (compared with the triplet) electronic state of the carbene.[24,72] The substituents must meet the following requirements: (1) they must tend to decrease the XCY valence angle, which leads, as can be seen from Fig. 1, to an appreciable increase in the distance between the σ and p levels; (2) it must have low-lying unoccupied π^* orbitals in one or both substituents; (3) it must have high-lying occupied π or n orbitals in these substituents. The orbital interaction diagrams illustrated in Fig. 2 explain the nature of the stabilisation of the states with closed electron shells.

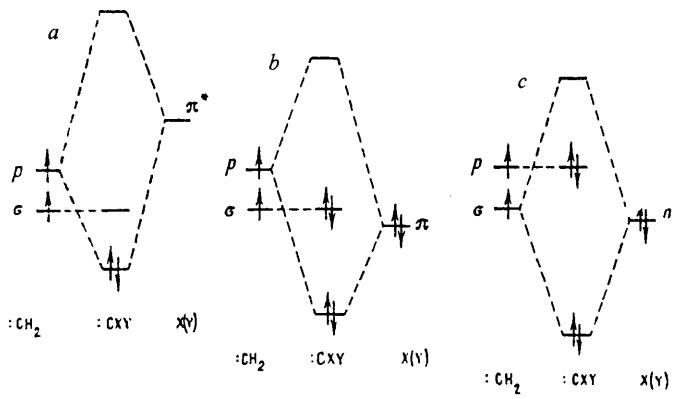


Figure 2. The interactions between the frontier orbitals of methylene (see Fig. 1) and the orbitals of the substituents X and Y in the carbene: CXY; *a*, acceptor substituents with a low-lying unoccupied π^* orbital; *b*, and *c*, donor substituents with high-lying occupied π and n (orbital of the unshared electron pair) orbitals.

Table 3. The singlet–triplet splitting energies ΔE_{S-T} for certain carbenes and their analogues obtained with the aid of non-empirical calculations taking into account the electronic correlation.

Molecule	ΔE_{S-T}, kJ mol^{-1}*1	Method of calculation*2	Refs.
CH_2	37.8 (37.75 [20])	See Table 2	[52]
CHF	−55.2 (~−63 [74]) [−94±28]	A	[74]
CHCl	−22.6 [−70±34]	A	[74]
CHBr	−17.2	A	[74]
CF_2	−240.5 (−236.8 [75])	B	[76]
CCl_2	−108.3 [−130±45]	B	[76]
CHLi	145.2	C	[77]
CLi_2	200.4	D	[78]
CHBeH	156.1	C	[77]
$CHBH_2$	−18.0	C	[77]
$CHNH_2$	−13.0	E	[79]
CHOH	−97.5	C	[77]
$C(OH)_2$	−110.0	F	[73]
FCCN	117.6	F	[73]
$HCCH_3$	69.4	E	[79]
$C(CH_3)_2$	58±8	E	[79]
HCCN	80.3	E	[79]
$C(CN)_2$	75±8	E	[79]
HCCOOH	31.8	G	[80]
$C(Bu\text{-}t)_2$	104.6	H	[81]
$C{=}CH_2$	−207.5	C	[77]
C=O	−682.8	C	[77]
SiH_2	−74.0 (~−58 [87])	I	[82]
	−77.8	K	[21]
	−68.6	C	[71]
	−73.6*3	L	[83]
SiHLi	40.6*4	C	[77]
$SiLi_2$	43.1	L	[83]
SiF_2	−309.6 (−314.6 [84])	L	[83]
GeH_2	−79.5	M	[85]
GeF_2	−309.6	M	[85]
NH_2^+	121.5	N	[86]
$NHLi^+$	175.7	D	[78]
NLi_2^+	166.1	D	[78]
	−25.9	E	[79]
	−298	E	[79]

Note. Compilations of data on the geometries of a number of substituted methylenes have been published.[7,73]

*1The experimental values are given in round brackets and the thermochemical estimates are given in square brackets.[74]

*2Here and below the designations indicated in Table 2 are used.

A) TCSCF, allowance for Davidson's correction;[55] basis set: (5*s*4*p*2*d*) for C, (5*s*4*p*2*d*) for F, (3*s*2*p*) for H, (7*s*6*p*2*d*) for Cl, and (10*s*8*p*4*d*) for Br.[74]

B) Generalised valence bond method (GVB); allowance for CI.

C) MP4SDTQ/6-31G*—calculation in terms of the 6-31G* basis set taking into account the electronic correlation on the basis of the Meller–Plesset perturbation theory (see the footnotes to Table 2).

D) (9*s*5*p*/8*s*) basis set for CLi_2 and the (9*s*5*p*/4*s*/8*s*), 2R-CI basis set for CHLi.

E) STO-3G basis set for the triplet states; caculations in terms of the UHF approximation.

F) Basis set of the STO-3G type; CI 2 × 2 for the singlet state.

G) DZ basis set; SD-CI.

H) STO-3G basis set.

I) 6-31G** basis set; MCSCF.

K) (9*s*6*p*3*d*) basis set for silicon and (4*s*2*p*) basis set for hydrogen.

L) 6-31G* basis set; SD-CI.

M) DZ + P basis set; CI with allowance for not only single and double excitations but also triple excitations.

N) (9*s*6*p*3*d*) basis set for nitrogen and (4*s*2*p*) basis set for hydrogen; TCSCF.

*3When account is taken of the full CI, the quantity ΔE_{S-T} varies from −77 to −73 kJ mol^{-1} depending on the basis set.[88]

*4In calculations in terms of the DZ + P basis set, allowance for the CI (SD-CI) made it possible to observe two minima on the PES for HSiLi corresponding to different structures of the triplet state $^3A''$; ΔE_{S-T} = 29.3 kJ mol^{-1}.[89]

Table 3 presents a compilation of calculated data, which are currently most accurate, for the singlet–triplet splittings in certain simple derivatives and analogues of methylene (in conformity with the requirements imposed on the computational scheme which were discussed in the previous Section).

The results presented agree well with the predictions of the orbital model. In the presence of *n*,π-donor substituents (halogens, amino- and hydroxy-groups) as well as π-acceptor substituents with low-lying unoccupied π^* orbitals (BH_2, O=), the singlet electronic state of the carbene is highly stabilised. The decrease in the electronegativity of the central atom leads to the same result in the series of isoelectronic analogues of methylene: NH_2^+, CH_2, PH_2^+, SiH_2, GeH_2.

A convenient heuristic model, permitting an extremely reliable prediction of the trend towards the stabilisation or destabilisation of the singlet (triplet) state in carbenes and their analogues $AX_2(AXY)$ from the relation between the electronegativity of the central atom A and the substituents X, has been proposed.[78,90]

The increase in the electronegativity of the substituents X(Y) and in the electropositive character of the central atom A led ultimately to the ionic structure $X^-A^{2+}X^-$, in which A^{2+} has a valence electron shell similar to the shell of the beryllium atom with its singlet electronic state ^1S. Consequently, the above factors tend to stabilise the singlet forms of the carbenes and their analogues, as has been observed, for example, for dihalogenocarbenes, silylene, etc. On the other hand, a decrease in the electronegativity of the substituents X and an increase in the electronegativity of the central atom create conditions for the appearance of the limiting ionic structure $X^+A^{2-}X^+$, in which A^{2-} has the electron shell of the oxygen atom. It has a triplet (^3P) ground electronic term. Hence it follows that such substitutions should stabilise the triplet form of carbene and its analogues. This is confirmed by the preference for the triplet states of the cation $^+NH_2$ and the carbenes CHLi and CHBeH (Table 3).

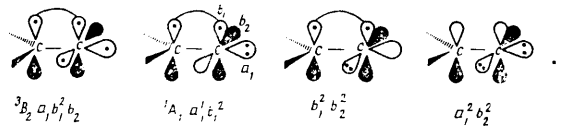
When substituents with a low electronegativity of the central atom, such as those of the Group I–III elements, are introduced at the carbon atom, an interesting stereoelectronic effect appears—the stabilisation of the linear $D_{\infty h}$ structure of the singlet state of the carbene CX_2. The linear form of these carbenes has been predicted qualitatively both within the framework of the delocalised three-centre two-electron bond model[91] and within the framework of the ideas of Pauling's resonance theory.[92] The Li, Be, and B atoms contain unoccupied *p* MO capable of forming common MO with the σ orbital of the singlet carbene, the best overlap conditions and hence the highest stabilisation being attained for the linear and not the angular configuration. The results of non-empirical calculations[59,71,77,78,93] (see also Table 3) agree with this model.

IV. Unsaturated and cyclic carbenes

The multiplicity and electronic structure of unsaturated and cyclic carbenes in their ground states and the reactivity associated with these features are determined by the following three factors: (1) the character of the hybridisation of the σ orbital of the carbene centre, which depends on its valence angle, (2) the aromaticity or anti-aromaticity of the π system which includes the π orbital of the carbene centre, and (3) the effects induced by the involvement of the σ orbital of the carbene centre in the formation of the cyclic σ-conjugation system. The importance of the first two factors was already noted in early theoretical investigations of the electronic structure of carbenes,[24,72,79] while the role of the σ-conjugation began to become clear comparatively recently.[65,94,95] We shall

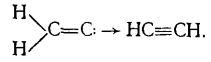
examine the manifestation of the above effects in relation to the most representative carbenes.

Vinylidene. Vinylidene is the prototype of unsaturated alkylidenecarbenes $R^1R^2C=(C)_n=C$: detected as intermediates in many reactions.[96] It can be regarded formally also as a cyclic carbene whose ring has contracted to the maximum extent, i.e. with the minimum (0°) valence angle at the carbene centre. As a result of this, the non-bonding σ orbital a_1 of the vinylidene has the greatest amount of *s* character[97] and therefore has a lower energy level than the σ orbital in methylene. As a result, the presence of the electron pair in the σ orbital (with the configurations $a_1^2b_1^2$ and $a_1^2b_2^2$) proves to be energetically more favourable than the occupation of the $a_1b_1^2b_2$ orbital corresponding to the triplet state. The largest additional contribution to the wave function of the ground singlet state $^1A_1$ of vinylidene also comes from the $b_1^2b_2^2$ valence configuration:[97]



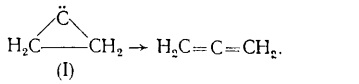
The results of numerous semiempirical[62,72,98] and non-empirical[97,99–101] calculations agree with experimental data[102] showing that the singlet electronic state of vinylidene is preferable. The calculated values of ΔE_{S-T} are as follows (in kJ mol^{-1}): –85.8 (MINDO/2 [62]), –192.0 [*ab initio*, generalised valence bond method, (4*s*2*p*1*d*, 4*s*2*p*1*d*/2*s*) basis set[99]], and –213.8 (*ab initio*, the same basis set, allowance for electron correlation on the basis of the many-particle perturbation theory[97]).

Structurally vinylidene is the prototropic tautomer of the thermodynamically more stable acetylene and the possibility of the experimental detection of vinylidene therefore depends on the energy barrier to the 1,2-shift of hydrogen:



According to the results of non-empirical calculations, the height of this barrier is (taking into account the zero-point vibration energies) 19.2 kJ mol^{-1} [103] or even 3.8 kJ mol^{-1} [104] and it has therefore been suggested that the structure of vinylidene corresponds to a very shallow minimum on the potential energy surface of C_2H_2 or in fact represents the transition state in a degenerate rearrangement of acetylene.[104] Calculations[105] have shown that the energy barrier to the 1,2-shift of hydrogen persists even when a very expanded basis set is used. The barrier has been estimated as 8–17 kJ mol^{-1} (the corresponding lifetimes range from 0.24×10^{-12} to 4.6×10^{-12} s). Experimental studies on the photoionisation of $H_2C=C^-$ have led to the conclusion that the vinylidene does indeed exist and has a lifetime of at least 10^{-14} s.[102] There exist fairly detailed reviews of the theoretical calculations of the 1,2-shift of hydrogen and other migrants in vinylidene and its derivatives.[104,106,107]

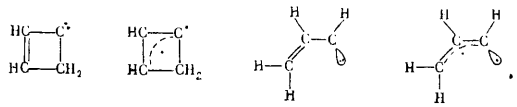
Cyclopropylidene (I). There are no experimental data for the multiplicity of the ground electronic state of cyclopropylidene, but, in view of the smallness of the valence angle at the carbene centre, one may expect in this instance the stability of the singlet electronic configuration $^1(\sigma^2)$. The σ-conjugation effect stabilising this configuration should also be manifested. Indeed, although the results of early non-empirical calculations using the orbital basis sets STO-3G [108] and 4-31G [109] indicated a triplet ground state, allowance for electron correlation and the inclusion in the basis set of polarisation functions led to a revision of this conclusion.[79,110,111] The calculated values of ΔE_{S-T} proved to be –52 kJ mol^{-1} [DZP basis set, SD(Q)-CI allowance for configuration interactions[110]] and –39 kJ mol^{-1} (MP3/6-31G** [111]). It is striking that the CH_2CCH_2 valence angle for the singlet state $^1A_1$ is smaller by 6–7° than for the triplet state. This creates an additional strain in the structure of the ground state of cyclopropylidene, which leads to a low-barrier valence isomerisation (of the "bond extension" type) to the more stable allene:



(I)

According to MP3/6-31G** calculations,[111] the barrier to this reaction is 48 kJ mol^{-1} (see also Klett and Johnson[112]).

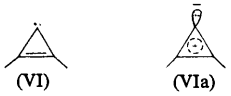
Cyclobutenylidene (II). The role of the effect due to the fusion of the *p* orbital of the carbene centre with the π system of the remaining fragment of the molecule is clearly manifested in the case of cyclobutenylidene, although the CH_2CCH angle in this species is much smaller than the HCH angle in methylene. However, both semiempirical (MINDO/3 [113]) and non-empirical (STO-3G, 2 × 2 CI [79]) calculations make it necessary to give preference to the triplet ground state. The quantity ΔE_{S-T} has been estimated as 25 ± 8 kJ mol^{-1}.[79] The evident explanation is that the triplet cyclobutenylidene is in essence a stabilised σ,π-biradical of the allyl type (III):



(II) (III) (IV) (V)

The structure of the species (III) represents the cyclic analogue of the vinylmethylene (IV), which has been studied both experimentally[114] and theoretically[110,115] and for which a planar structure with a triplet ground electronic state of type (V) has been shown to be preferable.

Cyclopropenylidene (VI). When the *p* orbital of the carbene centre is included in the overall π system of the three-membered ring, the latter contains two π electrons, which means that the singlet $^1(\sigma^2)$ configuration is more favourable than the $^3(p\sigma)$ configuration. An important factor promoting the appearance of the $^1(\sigma^2)$ configuration is also the decrease in the energy of the σ orbital of the carbene atom as a consequence of the increased amount of *s* character as a result of the smaller bond angle as compared with methylene.[116,117] Thus the singlet state 1^1A_1 of the zwitter-ionic[25] π-aromatic type (VIa) is stabilised:

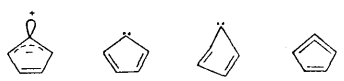


(VI) (VIa)

The stability of the singlet state of cyclopropenylidene has been predicted by both semiempirical[72,118–120] and non-empirical[79,93,121–124] calculations. According to the most accurate estimates, ΔE_{S-T} is –217 kJ mol^{-1} [MK SSP (MCSCF), (4*s*2*p*-C/2*s*-H) basis set[123]] and –294 kJ mol^{-1} (TCSCF, DZ + P basis set[124]). The calculated dipole moment (3.4 D)[124] is extremely high for a hydrocarbon, which agrees well with the prediction that cyclopropenylidene has the structure of the onium anion (VIa).

Cyclopropenylidene has been identified in the matrix isolation of the products of the flash pyrolysis of a quadricyclane derivative[125] and the absence of the EPR signal confirmed the singlet character of its electronic state. Probably by virtue of its π-aromatic character, the species (VI) is distinguished by a fairly high stability towards isomerisation reactions. It is not fortuitous that cyclopropenylidene is one of the components of the molecular clouds in interstellar space.[126]

Cyclopentadienylidene (VII). The singlet π-aromatic six-electron configuration of cyclopentadienylidene arises under the conditions of the double occupation of the $^1(p^2)$ *p*-orbital of the carbene centre, so that the σ orbital remains unoccupied.[25] However, the 6π-electron structure (VIIa) with a carbanion–cation electron distribution (see, for example, the results of calculations by the MINDO/3 and MNDO methods[119,120]) is less stable according to non-empirical MCSCF calculations[127] than the π-antiaromatic 4π-electron structure of the type $^1(\sigma^2)$ (VIIb):

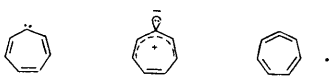


(VIIa) (VIIb) (VIII) (IX)

This unexpected result can be simply explained qualitatively within the framework of the idea of σ-aromaticity and σ-antiaromaticity.[94] In contrast to cyclopropenylidene, whose molecule is both π-aromatic and σ-aromatic, the simultaneous attainment of both π- and σ-aromaticity is impossible for cyclopentadienylidene. The structure (VIIa) is σ-antiaromatic, while the structure (VIIb) is π-antiaromatic. As a result, their energies may prove to be higher than the energy of the triplet state $^3B_1$. Accordingly the zwitterionic singlet state 2^1A_1 ($p^2\sigma^2$) and the singlet state $^1B_1$ of the biradical type ($p^1\sigma^1$) have similar energies for (VIIa), whereas the states 1^1A_1 ($p^0\sigma^2$) and $^1B_1(p^1\sigma^1)$ have similar energies for (VIIb). Consequently the "lumomeric"[128] forms (VIIa) and (VIIb) should be subject to a second-order Jahn–Teller effect and are unstable relative to the b_1-distortion ($a_1 \times b_1 = b_1$) with formation of the structure (VIII) having the C_s symmetry. As a result, the multiplicity of the ground electronic state is determined by the extent to which this distortion stabilises the singlet electronic configuration relative to the structure of the triplet state.

Indeed, according to semiempirical[94,120,129] and non-empirical[130] calculations, the planar structures (VIIa) and (VIIb) do not correspond to minima on the potential energy surface (PES) of the singlet state‡ in contrast to the C_s structure, which has a lower energy. According to the experimental data (see, for example, Wasserman et al.[132] and Baird et al.[133]), calculations by the MINDO/3,[94,120,129] MNDO,[120] and *ab initio*[94,130] methods indicate that cyclopentadienylidene has the $^3B_1$ triplet ground state.

Cycloheptadienylidene (X). With increase in ring size, the effects of σ-aromaticity and σ-antiaromaticity rapidly decay[65] and their role becomes insignificant. The degree of π-aromaticity [the tendency to form the 6π-electron onium anion (Xa)] proved insufficient for the stabilisation of the singlet $^1(\sigma^2)$ state as happens in the case of cyclopropenylidene:



(X) (Xa) (XI)

Indeed the EPR spectrum indicates the triplet character of cycloheptatrienylidene (X),[134,135] which agrees with the results of semiempirical calculations by the MINDO/3[120] and MNDO[120,136] methods. However, the results of non-empirical calculations[137,138] conflict with this conclusion. According to recent calculations (TCSCF, DZ + P basis set[138]), cycloheptatrienylidene nevertheless has a singlet ground state [the planar structure (X) with C_{2v} symmetry, ΔE_{S-T} = –18.8 kJ mol^{-1}]. At the same time, for the equilibrium geometry of the triplet state, the structure of the singlet state has an energy higher by 28.0 kJ mol^{-1}. This can be used to explain the experimental data[134,135] if it is assumed that the rate of the triplet–singlet transition is low and that the carbene (X), generated in the triplet form on photolysis of diazocycloheptatriene, does not have time to relax to the more stable singlet form during the measurement of the spectrum.

It has been shown by semiempirical[120,136,139] and non-empirical[139] calculations that the most stable valence-isomeric form of the carbene (X) is the less symmetrical chiral C_s structure of the singlet cycloheptatetraene (XI), whose energy is lower by 61–96 kJ mol^{-1} than that of the singlet cycloheptatrienylidene. The reactions and rearrangements of cycloheptatetraene (XI) then differ from the reactions of the carbene (X) and different pathways lead to their formation.[140,141]

The energy balance between the carbene and allene forms of cyclic carbenes is determined by the relative contributions of two opposed tendencies: the endeavour to retain the aromaticity in the carbene form and to undergo a transition to a structure with a tetravalent carbon atom. This balance depends primarily on the ring size. Thus, whereas the allene isomer of cyclopentadienylidene (VII) is too strained and does not correspond to a minimum on the PES for C_5H_4,[120] for both cyclononatetraenylidene C_9H_8 and the species (X), the stable cyclic isomer is cyclononapentaene.[120]

V. Reactions of carbenes

The experimental data concerning the influence of the multiplicity of the carbene on its reactivity enabled Skell and co-workers[4,142,143] to formulate definite rules. Firstly, carbenes react at much higher rates in the singlet electronic state than in the triplet state and the absolute rates of typical reactions involving addition to multiple bonds and insertion in C–H bonds normally exceed the rate of intersystem crossing. Secondly, single-stage stereospecific addition to double bonds is characteristic of singlet carbenes, while triplet carbenes react non-stereospecifically, forming initially an intermediate biradical on addition to one of the atoms of the double

‡ *Ab initio* calculations (3-21G basis set) have shown that the planar 6π-electron structures of aza-substituted (2,3-diaza- and 2,3,4- and 2,3,5-triaza) cyclopentadienylidenes also do not correspond to minima on the corresponding potential energy surfaces.[131]

bond. The formation of the trimethylene radical on addition of triplet methylene ($^3B_1$) to ethylene has been confirmed by semi-empirical[62,144] and non-empirical[145,146] quantum-chemical calculations.

Such specificity of the reactivity of carbenes as well as the fact that the majority of the experimentally investigated carbenes have a singlet state have been responsible for the special interest in the reactions of singlet carbenes. The vast majority of theoretical studies have been devoted to their analysis. We shall consider only the reactions involving addition to a carbon–carbon double bond and to single bonds in the study of which the conceptual basis of the theoretical chemistry of carbenes and their analogues has been created.

1. Addition to a C = C bond

From the electronic configuration $^1(\sigma^2)$ of singlet carbenes, one would expect that they should manifest both electrophilic (unoccupied p orbitals) and nucleophilic (the electron pair of the σ orbital) properties. In reactions involving addition to alkenes and other compounds with multiple bonds, the "philicity" of the carbene is determined by the energy gap (ε_{LUMO}–ε_{HOMO}) between the frontier orbitals of the reacting molecules. The stabilising two-electron interaction between these orbitals is greater the smaller the gap and the greater the overlap integral between the frontier orbitals in the region of the transition state of the reaction. The relative disposition of the frontier orbitals of the reactants most typical for carbenes is illustrated in Fig. 3*a*. It corresponds to the predominance of the electrophilic properties of the carbene. Fig. 3*b* illustrates the destabilisation of the p orbital of the carbene after the introduction of strong π-donor substituents X and Y, which has been predicted by non-empirical calculations[147] and which leads to the manifestation of nucleophilic properties ($\sigma \rightarrow \pi^*$ interaction). Finally there is a possibility of the approximate equality of the $\sigma \rightarrow \pi^*$ and $\pi \rightarrow p$ interactions (Fig. 3*c*), which makes it possible to introduce the concept of ambiphilic carbenes.

The "philicity" of the carbene is directly related to the structure of the transition state of the addition reaction. It is well known that the orbital symmetry conservation rules forbid the symmetrical minimum movement pathway (C_{2v}).[144] For electrophilic carbenes with the predominant $\pi \rightarrow p$ interaction, the so called π-approach is preferable (Fig. 3). In the case of nucleophilic carbenes, the best conditions for the overlap of the σ_{CXY} and π^* orbitals are created by the asymmetric σ-approach (Fig. 3*b*). Using certain assumptions, the overlap integrals S between the corresponding frontier orbitals of the carbene and the alkene have been calculated[147,148] in terms of the versions based on the π- and σ-approaches and the energies of the above orbitals have been evaluated, which made it possible to find the stabilisation energies for the two types of interaction of the frontier orbitals:

$$\Delta E \simeq S^2_{HOMO\text{-}LUMO}/(\varepsilon_{LUMO} - \varepsilon_{HOMO} - Q),$$

where $Q \simeq 5$ eV is the correction for the change in the values of ε for the reactants when they approach one another.

The ratio of the stabilisation energies in the nucleophilic (σ) and the electrophilic (π) approaches the theoretical value of the "philicity" $PI_{CXY} = \Delta E_n/\Delta E_e$, which is less than unity for electrophilic carbenes, more than unity for nucleophilic carbenes, and approximately unity for ambiphilic carbenes.

The values obtained are well correlated with the experimental quantities. The following experimentally known carbenes have been assigned to the electrophilic class: BrCCOOEt, MeCCl, CBr_2, PhCBr, PhCCl, PhCF, CCl_2, CFCl, and CF_2 (the electrophilicity diminishes from left to right); MeOCCl and MeOCF are ambiphilic and $(MeO)_2C$ and $MeOCNMe_2$ are nucleophilic. The "philicity" of the carbene can depend even on its conformation. Thus, according to a theoretical estimate,[149] the *cis*-conformer of methoxyphenylcarbene has nucleophilic properties, while its *trans*-conformer is ambiphilic. A review[148] presents calculated data also for the

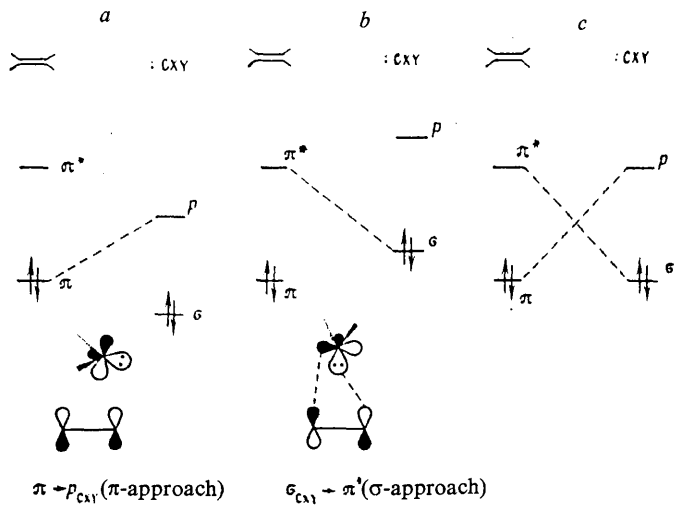


Figure 3. The principal versions of the relative positions of the energy levels of substituted carbenes: CXY and ethylene as a function of the substituents X and Y: *a*, electrophilic carbenes; *b*, nucleophilic carbenes; *c*, ambiphilic carbenes. The order of the energy levels for $:CCl_2$ (*a*) and $:C(NH_2)_2$ (*b*) is maintained.

differences between the orbital energies as a function of the nature of the substituents in the alkene (with the carbene unchanged). Electrophilic carbenes add more readily to alkenes with an electron excess, i.e. after the introduction of π-donors, while nucleophilic carbenes exhibit an increased reactivity following the weakening of the π-bond of the alkene, i.e. after the introduction of acceptor substituents.

Naturally, the "philicity" determined by the method indicated is associated with a specific alkene and on passing from one alkene to another the "philicity" series can be inverted.[148] The causes of this can be understood from Fig. 3: the stabilisation or destabilisation of the π,π^* levels of the alkene induced by the substituents can alter the relative contributions of the π–p and σ–π^* interactions. In practical correlations, the estimates of their extents are frequently restricted to the differences between the energies of the frontier orbitals and the calculation of the quantities ΔE is not resorted to. Thus the relative rate constants for the addition of dichlorocarbene to substituted styrenes are well correlated with the energy difference between the HOMO of styrene and the LUMO of the carbene.[150]

Direct calculations of the reaction pathway leading to the addition of carbenes to alkenes make it possible to discover important details of the internal reaction mechanism. At the level of non-empirical calculations, the reaction of singlet methylene with ethylene has been studied in greatest detail.[151] Like the addition of silylene,[152] this reaction proceeds without a barrier as the attacking species approaches under the plane of the alkene ("internal" approach). The "external" approach of methylene and other carbenes is energetically less favourable[153] and leads to their insertion in a C–H bond.[154] Calculations of reaction pathways of substituted carbenes with the location and identification of the structures of transition states are of greater theoretical interest. The "internal" pathway in the mutual approach of the reactants is a hybrid of the π- and σ-approaches and the transition states of all the reactions investigated have a common structure. In these states $r_1 \neq r_2$. The results of some of the calculations are presented in Table 4.

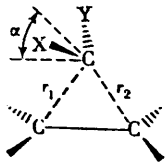


Table 4. Principal geometrical parameters of the structures of the transition states of the reactions involving the addition of carbenes to ethylene according to the results of non-empirical calculations.

Carbene CXY	r_1, nm	r_2, nm	α	Orbital basis set	Refs.
CCl_2	0.195	0.228	19.0	3-21G	[155]
CF_2	0.174	0.216	30.0	3-21G	[155]
FCOH	0.178	0.235	27.6	STO-3G	[147]
$C(OH)_2$	0.178	0.224	49.2	STO-3G	[156]
$C(NH_2)_2$	0.180	0.231	61.2	STO-3G	[156]

A characteristic of the transition states of the reaction involving addition to an alkene, which is especially sensitive to the "philicity" of the carbene, is the angle of inclination of the carbene plane relative to the plane of the double bond. According to Moss and co-workers,[147,148] one can assume that carbenes for which the angle α is less than 45° in the transition states of the reaction involving addition to alkenes are electrophilic. The angles $\alpha > 50°$ correspond to nucleophilic carbenes. The range $45° < \alpha < 50°$ corresponds to ambiphilic carbenes. Non-empirical[147,155,156] and semiempirical (MNDO)[157] calculations of the reaction pathways leading to the addition of various carbenes to ethylene confirmed this rule.

Calculations of the energy barriers and heats of the addition reaction showed that the selectivity of carbenes (at normal temperatures) is linearly related to their stability.[147] This conclusion, reached in the spirit of the usual activity–selectivity relation, does not, however, explain the experimental data about the entropic control of the addition of dichlorocarbene to alkenes,[158] the temperature dependence of the selectivity of dihalogenocarbenes,[159,160] and the zero and even negative activation energies for many cycloaddition reactions of carbenes.[161,162]

The last effect has come to be usually attributed to the presence on the reaction coordinate of an intermediate complex stable relative to the reactants. Such complexes, corresponding to the very early stages of the π-approach, do indeed appear in non-empirical calculations (basis sets up to the 6-21G level), but, when account is taken of the effects of electron correlation (MP 2/3-21G), they no longer correspond to minima on the PES and cannot therefore exist as kinetically isolatable species.[155,163] The vibration frequencies and entropies of the carbene–alkene reaction system have been calculated[155] at all its stages and the following hypothesis has been put forward. Since the entropy decreases monotonically as the reaction proceeds along the reaction coordinate and these changes are almost independent of the nature of the alkene and the carbene, when the enthalpy is rapidly reduced for reactive carbenes the quantity ΔG is controlled by the entropy term ($-T\Delta S$). Since ΔG reaches a maximum as a result of the increase in this term (with decrease of ΔH along the reaction coordinate), negative activation energies, characteristic of the reactions of the most electrophilic carbenes with electron-enriched alkenes, can also appear. Model potentials have been proposed[155] for the description of ΔH and $-T\Delta S$, which ensure a satisfactory reproduction of the experimental data for the reaction energetics without the inclusion of a stage involving the formation of intermediate complexes.

2. Insertion in single bonds

The reactions involving the addition of carbenes to single bonds, accompanied by the dissociation of the latter, have come to be designated as insertion in the bond. These reactions are extremely characteristic of carbenes and numerous theoretical studies have been devoted to them.[164–170] The calculations have established that the insertion in the H–H, C–H, halogen–halogen, and C–C bonds does not require the overcoming of an energy barrier and proceeds as a concerted reaction which does not follow the path of minimum motion. Two phases can be distinguished in the process involving insertion in a σ-bond: (1) electrophilic attack in which the unoccupied p orbital of the carbene interacts with the bonding orbital of the σ-bond attacked to form a three-centre bond; (2) the subsequent nucleophilic phase determined by the two-electron interaction of the σ orbital of the carbene with the antibonding σ^* orbital. In the second stage, the σ-bond is stretched and dissociates.

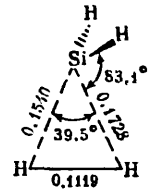
Insertion in the H–H bond. It followed from the early semiempirical (EHM) calculations[164] that the linear configuration >C...H–H, characteristic of a mechanism of the abstraction-recombination type, should occur in the reaction involving the insertion of methylene in the H_2 molecule up to the formation of the transition state. However, more rigorous non-empirical calculations[166,167] led to the observation of the extremely rapid formation of three-centre bonds in the initial stage of the reaction. In contrast to the singlet state, methylene in the ground triplet ($^3B_1$) state is inserted in the H–H bond, overcoming the activation barrier predicted by non-empirical calculations[171] (Table 5). The transition state has a linear configuration and the H–H...CH_2 distance is 0.140 nm. Triplet carbenes also tend to undergo hydrogen abstraction reactions ($^3CH_2 + H_2 \rightarrow CH_3 + H$) and the energy barriers in this and similar reactions are about 100 kJ mol^{-1}.[172]

Table 5. Results of non-empirical calculations of the activation barriers in reactions involving the insertion of carbenes and silylenes in σ-bonds.

Carbene (silylene)	σ-Bond	Reaction product	Method of calculation	Activation barriers*, kJ mol^{-1}	Refs.
$CH_2(^1A_1)$	H—H	—	DZ, CI	0	[167]
$CH_2(^3B_1)$	H—H	CH_4	DZ, CI	45.2	[171]
SiH_2	H—H	SiH_4	DZ+P, CI	26.3	[173]
CHF	H—H	CH_3F	MP4/6-31G*	64.0 (2.7)	[174]
CF_2	H—H	CH_3F_2	MP4/6-31G*	197.0	[174]
SiHF	H—H	SiH_3F	MP4/6-31G*	130.0	[174]
SiF_2	H—H	SiH_2F_2	MP4/6-31G*	273.0	[174]
	H—H		DZ, CEPA	171.2	[168]
$CH_2(^1A_1)$	H—CH_3	C_2H_6	MP3/6-31G*	0	[175]
$CH_2(^1A_1)$	H—CH_2CH_3	CH_3—CH_2—CH_3	MP3/6-31G	0.9	[169]
SiH_2	H—CH_3	SiH_3CH_3	MP3/6-31G*	115.1	[175]
$CH_2(^1A_1)$	H—SiH_3	SiH_3CH_3	MP3/6-31G*	0	[175]
SiH_2	H—SiH_3	Si_2H_6	MP3/6-31G*	0	[175]
$CH_2(^1A_1)$	CH_3—CH_3	$CH_3CH_2CH_3$	MP3/6-31G	192.5	[169]
$CH_2(^1A_1)$			MP3/6-31G	9.2	[169]
$CH_2(^1A_1)$	H—NH_2	CH_3NH_2	MP4/6-31G*	52.3 (118.0)	[176]
SiH_2	H—NH_2	SiH_3NH_2	MP4/6-31G*	159.1 (104.6)	[177]
SiH_2	H—PH_2	SiH_3PH_2	MP4/6-31G*	83.7 (75.3)	[177]
$CH_2(^1A_1)$	H—OH	CH_3OH	MP4/6-31G*	0	[176]
SiH_2	H—OH	H_3OH	MP4/6-31G*	92.1 (54.4)	[177]
SiH_2	H—SH	SiH_3SH	MP4/6-31G*	58.6 (37.7)	[177]
$CH_2(^1A_1)$	H—F	CH_3F	MP4/6-31G*	0	[176]
SiH_2	H—F	SiH_3F	MP4/6-31G*	41.8 (29.3)	[177]
SiH_2	H—Cl	SiH_3Cl	MP4/6-31G*	33.5 (8.4)	[177]

*The stabilisation energy (E_{st}) of the intermolecular complex relative to the separated reactants is indicated in brackets. The activation barrier differs in such cases from the energy of the complex. For $E_{st} > E_a$, the reaction proceeds without a barrier.

Experimental data for the insertion of silylene in the H_2 molecule are still not available, but according to estimates[178] the lower limit of the activation barrier is 23 kJ mol^{-1}. Theoretical estimates[173,179] (Table 5) agree with this value. Analysis of the structural changes during the reaction $^1SiH_2 + H_2 \rightarrow SiH_4$ led to the conclusion that they are almost identical with those found for the reaction of methylene with hydrogen. The main cause of the appearance of the activation barrier is the different order of the singlet and triplet states of silylene and the appreciable S–T splitting.[180,181] The structure of the transition state in the reaction involving the insertion of silylene in the H_2 molecule is shown below [the distances are expressed in nanometers and the calculation was carried out by the MCSCF (4,4)/6-31G* method]:[178]



The influence of the substitution of the hydrogen atoms in silylene on the exothermicity and activation barrier of the reaction involving insertion in H–H bonds has been investigated in relation to its fluoro- and difluoro-derivatives.[174] The activation barrier increases by ~80 kJ mol^{-1} when one fluorine atom is introduced and by 130 kJ mol^{-1} when two fluorine atoms are introduced. This result is almost independent of the size of the basis set and the allowance for the correlation energy. Analysis of the structures of the transition states made it possible to conclude that they become of a "later" type and that there is a simultaneous decrease in the exothermicity of the insertion reaction, in agreement with Hammond's postulates.

A very high activation barier (171 kJ mol^{-1}) has been predicted in non-empirical calculations[168] for the insertion of the cyclic carbene cyclopropenylidene in the H–H bond. This is apparently caused by the marked destabilisation of the "electrophilic" π^* orbital of the carbene and the associated difficulties in the initial stage of the reaction.

Insertion in C–H and Si–H bonds. The insertion of singlet methylene in a C–H bond proceeds without a barrier or with very low activation barriers (0.9 kJ mol^{-1} for ethane) according to experimental[182] and theoretical[169,175,183] data, while an appreciable barrier (115 kJ mol^{-1}) has been predicted for silylene, which agrees with the experimental observations (70–80 kJ mol^{-1} [184,185]). The transition states of the reactions have angular structures with three-centre bonds.

The insertion of methylene and silylene in a Si–H bond does not require the overcoming of an activation barrier. This experimental conclusion has been reproduced theoretically only after careful allowance for correlation corrections.[175]

Insertion in a C–C bond. According to non-empirical calculations taking into account the correlation energy and using an extended basis set of the type 6-31G,[169] the energy profile of the reaction involving the insertion of methylene in a C–C single bond is mainly determined by steric factors. Thus the activation barrier to the insertion in a C–C bond is very high (192.5 kJ mol^{-1}). On the other hand, the similar reaction with cyclopropane should proceed without activation (the barrier is only 9.2 kJ mol^{-1}). After insertion in a C–C bond of a strained ring, whose electron density has a maximum outside the bond axis, strong electronic interactions become possible over longer internuclear distances and the insertion in strained C–C bonds should therefore proceed without an activation barrier according to Gordon et al.[169] Table 5 presents calculated data also for reactions involving the insertion of carbenes in other bonds of the type X–H.

Naturally, the carbene cycloaddition and insertion reactions examined by no means exhaust the entire wide variety of their reactivity. On the other hand, it is these reactions that determine the fundamental stages in the main types of intramolecular rearrangements of carbenes, including the 1,2-shift, ring expansion, and other reactions.[186–188]

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During the preparation of the review for the press, a number of studies on the electronic structure and reactivity of carbenes were published. In particular, semiempirical (MNDO) and non-empirical (3-21G basis set, TCSCF, SD-CI) calculations for low-energy electronic states of cyclopropenylidene (VI) and cyclopentadienylidene (VII) were carried out.[189,190] The lowest biradical type singlet state $^1A_2$ (structure with the C_{2v} symmetry) of cyclopentadienylidene has a lower energy than the singlet states $1^1A_1(p^0\sigma^2)$ (VIIb) and $^1B_1$. The structure (VIIa) of the state $2^1A_1(p^2\sigma^0)$ does not correspond to a minimum on the PES. Non-empirical calculations[190] did not confirm the existence of the allene-type structure (IX), detected in calculations by the MNDO method.[120]

In order to explain the experimentally observed findings concerning the influence of electron-donating solvents on the reactivity of carbenes, non-empirical calculations (3-21G basis set) were carried out[191] for the addition of methylene to ethylene in the presence of a single water molecule. A complex between water and methylene molecules, whose formation makes it possible to account for the decrease in the electrophilicity of methylene, has been found on the PES.

References

1. G Herzberg, J Shoosmith *Nature (London)*, 1959, **183** 1801
2. G Herzberg *Proc. R. Soc. A*, 1961, **262** 291
3. W Kirmse *Carbene Chemistry* (Translated into Russian), Izd. Mir, Moscow, 1966, 324 pp
4. P S Skell *Tetrahedron*, 1985, **41** 1427
5. E R Davidson *Diradicals* (Edited by W T Borden), Wiley, New York, 1982, p. 73
6. J F Harrison *Acc. Chem. Res.*, 1974, **47** 378
7. W T Borden, E R Davidson *Annu. Rep. Phys. Chem.*, 1979, **30** 125
8. I Shavitt *Tetrahedron*, 1985, **41** 1531
9. P R Bunker *Comparison of ab initio Quantum Chemistry with Experiment for Small Molecules. The State of Art* (Edited by R J Bartlett), D Reidel Publ., Dordrecht, 1985, p. 141
10. H F Schaefer *Science*, 1986, **231** 1100
11. E Wasserman, V J Kuck, R S Hutton, W A Yager *J. Am. Chem. Soc.*, 1970, **92** 7491
12. R A Bernheim, H W Bernard, P S Wang, et al. *J. Chem. Phys.*, 1970, **53** 1280
13. M S Gordon, J A Pople *J. Chem. Phys.*, 1968, **49** 4643
14. M J S Dewar, R C Haddon, W-K Li, et al. *J. Am. Chem. Soc.*, 1975, **97** 4540
15. M J S Dewar, H S Rzepa *J. Am. Chem. Soc.*, 1978, **100** 784
16. D R McLaughlin, C F Bender, H F Schaefer *Theoret. Chim. Acta*, 1972, **25** 352
17. P R Bunker, P Jensen *J. Chem. Phys.*, 1983, **79** 1224
18. C W Bauschlicher, I Shavitt *J. Am. Chem. Soc.*, 1978, **100** 739
19. G Herzberg *Spectra and Structure of Simple Free Radicals* (Translated into Russian), Izd. Mir, Moscow, 1974, 208 pp
20. P R Bunker, P Jensen, W P Kraemer *J. Chem. Phys.*, 1986, **85** 3724
21. J H Meadows, H F Schaefer *J. Am. Chem. Soc.*, 1976, **98** 4383
22. C W Bauschlicher *Chem. Phys. Lett.*, 1980, **74** 273
23. C W Bauschlicher, D R Yarkony *J. Chem. Phys.*, 1978, **69** 3875
24. R Hoffmann, G D Zeiss, G W Van Dine *J. Am. Chem. Soc.*, 1968, **90** 1485
25. L Salem *Electrons in Chemical Reactions* (Translated into Russian), Izd. Mir, Moscow, 1985, 285 pp
26. G Duxbury *J. Chem. Soc., Faraday Trans. 2*, 1982, **78** 1433
27. J M Foster, S F Boys *Rev. Mod. Phys.*, 1960, **32** 305
28. G Herzberg *Molecular Spectra and Molecular Structure, Vol. 2, Infrared and Raman Spectra of Polyatomic Molecules* (Translated into Russian), Izd. Mir, Moscow, 1969, 772 pp
29. H F Schaefer *The Electronic Structure of Atoms and Molecules*, Addison-Wesley Publ., Massachusetts, 1972, 309 pp
30. C F Bender, H F Schaefer *J. Am. Chem. Soc.*, 1970, **92** 4984
31. G Herzberg, J W C Johns *J. Chem. Phys.*, 1971, **54** 2276
32. O P Charkin *Stabil'nost' i Struktura Gazoobraznykh Neorganicheskikh Molekul, Radikalov i Ionov* (The Stability and Structures of Gaseous Inorganic Molecules, Radicals, and Ions), Izd. Nauka, Moscow, 1980, 278 pp
33. J A Pople, M J Frisch, B T Luke, J S Binkley *Int. J. Quantum Chem., Symp.*, 1983, **17** 307
34. H Petek, D J Nesbitt, P R Ogilby, C B Moore *J. Phys. Chem.*, 1983, **87** 5367
35. P R Bunker, P Jensen *J. Chem. Phys.*, 1983, **79** 1224
36. C P Wood, N C Pyper *Chem. Phys. Lett.*, 1980, **71** 368
37. J W Simons, R Curry *Chem. Phys. Lett.*, 1976, **38** 171
38. F Lahfani *J. Phys. Chem.*, 1976, **80** 2623
39. W A Goddard *Science*, 1985, **227** 917
40. P F Zittel, G B Ellison, S V O'Neil, et al. *J. Am. Chem. Soc.*, 1976, **98** 3731
41. P C Engelking, R R Corderman, J J Wendoloski, et al. *J. Chem. Phys.*, 1981, **74** 5460
42. L B Harding, W A Goddard *Chem. Phys. Lett.*, 1978, **55** 217
43. T J Sears, P R Bunker, A R W McKellar *J. Chem. Phys.*, 1982, **77** 5363
44. T J Sears, P R Bunker *J. Chem. Phys.*, 1983, **79** 5265
45. D G Leopold, K K Murray, W C Lineberger *J. Chem. Phys.*, 1984, **81** 1048
46. C C Hayden, D M Neumark, K Shobatake, et al. *J. Chem. Phys.*, 1982, **76** 3607
47. A R W McKellar, P R Bunker, T J Sears, et al. *J. Chem. Phys.*, 1983, **79** 5251
48. N C Handy, Y Yamaguchi, H F Schaefer *J. Chem. Phys.*, 1986, **84** 4481
49. W A Lathan, W J Hehre, et al. *J. Am. Chem. Soc.*, 1971, **93** 6377
50. J F Harrison, L C Allen *J. Am. Chem. Soc.*, 1969, **91** 807
51. S V O'Neil, H F Schaefer, C F Bender *J. Chem. Phys.*, 1971, **55** 162
52. E A Carter, W A Goddard *J. Chem. Phys.*, 1987, **86** 862
53. H J Werner, E A Reinsch *J. Chem. Phys.*, 1982, **76** 3144
54. P Saxe, H F Schaefer, N C Handy *J. Phys. Chem.*, 1981, **85** 745
55. S R Langhoff, E R Davidson *Int. J. Quantum Chem.*, 1974, **8** 61
56. C W Bauschlicher, P R Taylor *J. Chem. Phys.*, 1986, **85** 5936
57. B O Roos, P M Siegbahn *J. Am. Chem. Soc.*, 1977, **99** 7716
58. L Fornell, J A Pople, L Radom *J. Phys. Chem.*, 1983, **87** 79

59. W J Hehre, L Radom, P V R Schleyer, J A Pople *Ab initio Molecular Orbital Theory*, Wiley-Intersci., New York, 1986, 548 pp
60. V I Minkin, B Ya Simkin, R M Minyaev *Kvantovaya Khimiya Organicheskikh Soedinenii* (The Quantum Chemistry of Organic Compounds), Izd. Khimiya, Moscow, 1986, 246 pp
61. J A Pople, D L Beveridge *Approximate Molecular Orbital Theory*, McGraw-Hill, New York, 1970, 214 pp
62. N Bodor, M J S Dewar, J S Wasson *J. Am. Chem. Soc.*, 1972, **94** 9095
63. M J S Dewar *Further Perspectives in Organic Chemistry*, Elsevier, Amsterdam, 1978, pp.107–129
64. A D Walsh *J. Chem. Soc.*, 1953(8) 2260
65. M J S Dewar *J. Am. Chem. Soc.*, 1984, **106** 669
66. K Yamaguchi *Chem. Phys. Lett.*, 1975, **33** 330
67. M M Mestechkin *Nestabil'nost' Uravnenii Khartri-Foka i Ustoichivost' Molekul* (The Instability of the Hartree-Fock Equations and the Stability of Molecules), Izd. Naukova Dumka, Kiev, 1986, 175 pp
68. V I Pupyshev, A I Dement'ev, N F Stepanov, B Ya Simkin *Stroenie Molekul* (Molecular Structure), Izd. Mosk. Gos. Univ., Moscow, 1986, pp. 150–168
69. H Fukutome *Int. J. Quantum Chem.*, 1981, **20** 955
70. O M Nefedov, S P Kolesnikov, A I Ioffe *J. Organomet. Chem. Lib., Vol. 5, Organomet. Chem. Rev.*, 1977, 181
71. B T Luke, J A Pople, M-B Krogh-Jespersen, et al. *J. Am. Chem. Soc.*, 1986, **108** 260
72. R Gleiter, R Hoffmann *J. Am. Chem. Soc.*, 1968, **90** 5457
73. P H Mueller, N G Rondan, K N Houk, et al. *J. Am. Chem. Soc.*, 1981, **103** 5049
74. G E Scuseria, M Duran, R G A R Maclagan, H F Schaefer *J. Am. Chem. Soc.*, 1986, **108** 3248
75. S Koda *Chem. Phys.*, 1982, **66** 383
76. E A Carter, W A Goddard *J. Phys. Chem.*, 1987, **91** 4651
77. B T Luke, J A Pople, M-B Krogh-Jespersen, et al. *J. Am. Chem. Soc.*, 1986, **108** 270
78. J F Harrison, R C Liedtke, J F Liebman *J. Am. Chem. Soc.*, 1979, **101** 7162
79. N C Baird, K F Taylor *J. Am. Chem. Soc.*, 1978, **100** 1333
80. K S Kim, H F Schaefer *J. Am. Chem. Soc.*, 1980, **102** 5389
81. P H Mueller, N G Rondan, K N Houk, et al. *Tetrahedron Lett.*, 1983, **24** 485
82. M S Gordon *Chem. Phys. Lett.*, 1985, **114** 348
83. K Krogh-Jespersen *J. Am. Chem. Soc.*, 1985, **107** 537
84. D R Rao *J. Mol. Spectrosc.*, 1970, **34** 284
85. J C Barthelat, B S Poch, G Trinquier, J Satge *J. Am. Chem. Soc.*, 1980, **102** 4080
86. C F Bender, J H Meadows, H F Schaefer *Discuss. Faraday Soc.*, 1977, **62** 59
87. A Kasden, E Herbst, W C Lineberger *J. Chem. Phys.*, 1975, **62** 541
88. C W Bauschlicher, P R Talor *J. Chem. Phys.*, 1987, **86** 1420
89. M E Colvin, J Breulet, H F Schaefer *Tetrahedron*, 1985, **41** 1429
90. J F Harrison *J. Am. Chem. Soc.*, 1981, **103** 7406
91. W W Schoeller *J. Chem. Soc., Chem. Commun.*, 1980, 124
92. L Pauling *J. Chem. Soc., Chem. Commun.*, 1980, 688
93. R S Mulliken, W C Ermler *Polyatomic Molecules. Results of ab initio Calculations*, Acad. Press, New York, 1981, 431 pp
94. M N Glukhovtsev, B Ya Simkin, V I Minkin *Zh. Org. Khim.*, 1987, **23** 1129
95. V I Minkin, M N Glukhovtsev, B Ya Simkin *J. Mol. Struct. (THEOCHEM)*, 1988, **181** 93
96. P J Stang *Chem. Rev.*, 1978, **78** 383
97. J W Kenney, J Simons, G D Purvis, R J Bartlett *J. Am. Chem. Soc.*, 1978, **100** 6930
98. V L Lebedev, A A Bagatur'yants, I V Kalechits *Zh. Strukt. Khim.*, 1978, **19** 398
99. J H Davis, W A Goddard, L B Harding *J. Am. Chem. Soc.*, 1977, **99** 2919
100. M P Conrad, H F Schaefer *J. Am. Chem. Soc.*, 1978, **100** 7820
101. C E Dykstra, H F Schaefer *J. Am. Chem. Soc.*, 1978, **100** 1378
102. S M Burnett, A E Stevens, C S Feigerle, W C Lineberger *Chem. Phys. Lett.*, 1983, **100** 124
103. Y Osamura, H F Schaefer, S K Gray, W H Miller *J. Am. Chem. Soc.*, 1981, **103** 1904
104. J Pople *Pure Appl. Chem.*, 1983, **55** 343
105. T Carrington, L M Hubbard, H F Schaefer, W H Miller *J. Chem. Phys.*, 1984, **80** 4347
106. H F Schaefer *Acc. Chem. Res.*, 1979, **12** 288
107. J Goddard *J. Mol. Struct. (THEOCHEM)*, 1985, **133** 59
108. D J Pasto, M Haley, D M Chipman *J. Am. Chem. Soc.*, 1978, **100** 5272
109. T Minato, Y Osamura, S Yamabe, K Fukui *J. Am. Chem. Soc.*, 1980, **102** 581
110. N Honjou, J Pacansky, M Yoshimine *J. Am. Chem. Soc.*, 1985, **107** 5332
111. A Rauk, W J Bouma, L Radom *J. Am. Chem. Soc.*, 1985, **107** 3780
112. M W Klett, R P Johnson *J. Am. Chem. Soc.*, 1985, **107** 3963
113. H Nickels, H Dürr, F Toda *Chem. Ber.*, 1986, **119** 2249
114. R S Hutton, M L Manion, H O Roth, E Wasserman *J. Am. Chem. Soc.*, 1974, **96** 4680
115. N Honjou, J Pacansky, M Yoshimine *J. Am. Chem. Soc.*, 1984, **106** 5361
116. C F Bender, H F Schaefer, D R Franceschetti, L C Allen *J. Am. Chem. Soc.*, 1972, **94** 6888
117. J F Harrison, R C Liedtke, J F Liebman *J. Am. Chem. Soc.*, 1979, **101** 7162
118. H-T Tsang, W-K Li *J. Mol. Struct. (THEOCHEM)*, 1983, **104** 95
119. C Glidewell, D Lloyd *J. Chem. Soc. (S)*, 1983, 178
120. M L Kassaee, M R Nimlos, K E Downie, E E Waali *Tetrahedron*, 1985, **41** 1579
121. W H Lanthan, L Radom, P C Hariharan, et al. *Topics in Current Chemistry*, Springer, New York, 1973, Vol. 40, p.000
122. W J Hehre, J A Pople, W A Lathan, et al. *J. Am. Chem. Soc.*, 1976, **98** 4378
123. R Shepard, A Banerjee, J Simons *J. Am. Chem. Soc.*, 1979, **101** 6174
124. T J Lee, A Bunge, H F Schaefer *J. Am. Chem. Soc.*, 1985, **107** 137
125. H P Reisenauer, G Maier, A Riemann, R W Hoffman *Angew. Chem., Int. Ed. Engl.*, 1984, **23** 641
126. P Thaddeus, J M Vrtilek, C A Gottlieb *Astrophys. J.*, 1985, **299** L63
127. R Shepard, J Simons *Int. J. Quantum Chem., Symp.*, 1980, **14** 349
128. M J S Dewar, S Kirschner, H W Kollmar *J. Am. Chem. Soc.*, 1974, **96** 5240
129. R M Minyaev, V I Minkin, N S Zefirov, Yu A Zhdanov *Zh. Org. Khim.*, 1979, **15** 2009

130. V I Minkin, R M Minyaev, G V Orlova *J. Mol. Struct. (THEOCHEM), 1984,* **110** 241
131. D J Pasto, J P Freeman *J. Am. Chem. Soc.*, 1985, **107** 4090
132. E Wasserman, L Barash, A M Trozzolo, et al. *J. Am. Chem. Soc.*, 1964, **86** 2304
133. N C Baird, I R Dunkin, N Hacker, et al. *J. Am. Chem. Soc.*, 1981, **103** 5190
134. R J McMahon, O L Chapman *J. Am. Chem. Soc.*, 1986, **108** 1713
135. M Kuzaj, H Lüerssen, C Wentrup *Angew. Chem. Int. Ed. Engl.*, 1986, **25** 480
136. E E Waali *J. Am. Chem. Soc.*, 1981, **103** 3604
137. L Radom, H F Schaefer, M A Vincent *Nouv. J. Chim.*, 1980, **4** 411
138. C L Janssen, H F Schaefer *J. Am. Chem. Soc.*, 1987, **109** 5030
139. M J S Dewar, D Landman *J. Am. Chem. Soc.*, 1977, **99** 6179
140. J W Harris, W M Jones *J. Am. Chem. Soc.*, 1982, **104** 7329
141. R J McMahon, C J Abelt, O L Chapman, et al. *J. Am. Chem. Soc.*, 1987, **109** 2456
142. P S Skell, R C Woodworth *J. Am. Chem. Soc.*, 1956, **78** 4496
143. P S Skell, A Y Garner *J. Am. Chem. Soc.*, 1956, **78** 3409, 5430
144. R Hoffman *J. Am. Chem. Soc.*, 1968, **90** 1475
145. W A Goddard *J. Am. Chem. Soc.*, 1972, **94** 793
146. P J Hay, W J Hunt, W A Goddard *J. Am. Chem. Soc.*, 1972, **94** 638
147. N G Rondan, K N Houk, R A Moss *J. Am. Chem. Soc.*, 1980, **102** 1770
148. R A Moss *Acc. Chem. Res.*, 1980, **13** 58
149. R A Moss, S Shen, L H Hadel, et al. *J. Am. Chem. Soc.*, 1987, **109** 4341
150. R R Kostikov, E A Drygailova, E A Golovkina, et al. *Zh. Org. Khim.*, 1987, **23** 2170
151. B Zurawski, W Kutzelnigg *J. Am. Chem. Soc.*, 1978, **100** 2654
152. F Anwari, M S Gordon *Isr. J. Chem.*, 1983, **23** 129
153. Y Apeloig, M Karni, P J Stang, D P Fox *J. Am. Chem. Soc.*, 1983, **105** 4781
154. M Moreno, J M Lluch, A Oliva, J Bertran *J. Chem. Soc., Perkin Trans. 2*, 1985, 131
155. K N Houk, N G Rondan, J Mareda *Tetrahedron*, 1985, **41** 1555
156. M Moreno, J M Lluch, A Oliva, J Bertran *J. Chem. Soc., Perkin Trans. 2*, 1986, 183
157. W W Schoeller, N Aktekin *J. Chem. Soc., Chem. Commun.*, 1982, 20
158. P S Skell, M S Cholod *J. Am. Chem. Soc.*, 1969, **91** 7131
159. B Giese, J Meister *Angew. Chem., Int. Ed. Engl.*, 1978, **17** 595
160. B Giese, W-B Lee *Angew. Chem., Int. Ed. Eng.*, 1980, **19** 835
161. R A Moss, W Lawrynowicz, N J Turro, et al. *J. Am. Chem. Soc.*, 1986, **108** 7028
162. P C Wong, D Griller, J L Scaiano *Chem. Phys. Lett.*, 1981, **103** 2423
163. K N Houk, N G Rondan, J Mareda *J. Am. Chem. Soc.*, 1984, **106** 4291
164. R C Dobson, D M Hayes, R Hoffman *J. Am. Chem. Soc.*, 1971, **93** 6188
165. P Cremaschi, M Simonetta *J. Chem. Soc., Faraday Trans. 2*, **1974, 70** 1801
166. H Kollmar, V Staemmler *Theor. Chim. Acta*, 1979, **51** 207
167. C W Bauschlicher, K Haber, H F Schaefer, C F Bender *J. Am. Chem. Soc.*, 1977, **99** 3610
168. H Kollmar *J. Am. Chem. Soc.*, 1978, **100** 2660
169. M S Gordon, J A Boatz, D R Gano, M G Friederichs *J. Am. Chem. Soc.*, 1987, **109** 1323
170. D Jeziorek, B Zurawski *Int. J. Quantum Chem.*, 1979, **16** 277
171. C W Bauschlicher, C F Bender, H F Schaefer *J. Am. Chem. Soc.*, 1976, **98** 3072
172. M S Gordon *J. Am. Chem. Soc.*, 1984, **106** 4054
173. A Sax, G Olbrich *J. Am. Chem. Soc.*, 1985, **107** 4868
174. C Sasa, H B Schegel *J. Am. Chem. Soc.*, 1984, **106** 5847
175. M S Gordon, D R Gano *J. Am. Chem. Soc.*, 1984, **106** 5421
176. J A Pople, K Raghavachari, M J Frisch, J S Binkley, et al. *J. Am. Chem. Soc.*, 1983, **105** 6389
177. K Raghavachari, J Chandrasekhar, M S Gordon, K J Dykema *J. Am. Chem. Soc.*, 1984, **106** 5853
178. P John, J H Purnell *J. Chem. Soc., Faraday Trans. 2*, 1973, **69** 1455
179. M S Gordon, D R Gano, J S Binkley, M J Frisch *J. Am. Chem. Soc.*, 1986, **108** 2191
180. S S Shaik *J. Am. Chem. Soc.*, 1981, **103** 3692
181. A Pross, S S Shaik *Acc. Chem. Res.*, 1983, **16** 363
182. W Jones, R A Moss (Editors) *Carbenes*, Wiley, New York, 1972, Vol. 1; 1975, p. 2
183. A I Ioffe, O M Nefedov *IV Vsesoyuznaya Konferentsiya po Khimii Karbenov: Tezisy Dokladov* (The IV All-Union Conference on the Chemistry of Carbenes: Abstract of Reports), Izd. Nauka, Moscow, 1987, p. 130
184. B A Sawrey, H E O'Neal, M A Ring, D Coffey *Int. J. Chem. Kinet.*, 1984, **16** 31
185. I M T Davidson, F T Lawrence, N A Ostah *J. Chem. Soc., Chem. Commun.*, 1980, 659
186. W M Jones *Acc. Chem. Res.*, 1977, **10** 353
187. W M Jones *Rearrangements in Ground and Excited States* (Edited by P De Mayo), Acad. Press, New York, 1980, Vol. 1, p. 95
188. A K Mal'tsev, V A Korolev, O M Nefedov *Fizicheskaya Khimiya. Sovremennye Problemy* (Physical Chemistry. Modern Problems) (Edited by Ya M Kolotyrkin), Izd. Khimiya, Moscow, 1986, p. 144
189. J M Bofill, J Farras, S Olivella, et al. *J. Am. Chem. Soc.*, 1988, **110** 1694
190. J M Bofill, N Bru, J Farras, et al. *J. Am. Chem. Soc.*, 1988, **110** 3740
191. M Moreno, J M Lluch, A Oliva, J Bertran *Can. J. Chem.*, 1987, **65** 2774

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Spectroscopic study of carbenes in low-temperature matrices

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ABSTRACT. The review surveys and gives a systematic account of the literature data on the IR and UV spectroscopic studies on carbenes in low-temperature matrices. The methods of generation and isolation of carbenes in inert matrices at temperatures around 10 K are examined. The possibility of applying the data obtained to the study of the structure of carbenes and to the determination of the mechanisms of reactions involving them is demonstrated.

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I. Introduction

In connection with the wide-scale application of reactions involving carbenes in synthetic organic chemistry, there has been a sharp growth of interest during the last 15–20 years in the detailed investigation of these species by various physicochemical methods. Such studies not only make it possible to detect and identify carbenes but also provide information about their structure, which is important for the interpretation of the reaction mechanisms.

The principal difficulties in the direct spectroscopic detection of carbenes (as well as other unstable molecules) are associated with the high reactivity and the short lifetime of these species under normal conditions. There are two ways of overcoming these difficulties. The first is based on the use of pulse methods in order to create a high concentration of the unstable compounds during a short time interval (10^{-3} s and less). In this case the spectroscopic characteristics of the test species can be obtained with the aid of special high-speed devices. Another, more widely used method consists in the isolation of the unstable intermediates in low-temperature matrices, primarily in inert gas matrices at temperatures below 20 K (the matrix isolation method), which makes it possible to prevent secondary reactions and to increase almost indefinitely the lifetime of these species. The methods for the generation of carbenes in low-temperature matrices will be examined in greater detail below. The application of the matrix isolation method in combination with analytical procedures such as EPR, UV, and IR spectroscopy has proved extremely fruitful.

This review discusses the results of IR and UV spectroscopic studies on carbenes in low-temperature matrices obtained during the last 10 years. Earlier investigations have been surveyed in other publications.[1,2] Nor do we examine matrix studies using EPR, since they have been surveyed fairly completely in other reviews.[3–5]

II. Methods for the generation of carbenes in low-temperature matrices

Various methods are used to generate carbene in matrix studies. They can be obtained in the gas phase under the influence of a high temperature or a discharge (electrical, microwave, or radio-frequency) with subsequent freezing of the species formed in a low-temperature matrix. These methods have been examined in another review[6] and here we shall not deal with them in detail. We shall only note that the simplest triatomic carbenes can be isolated from the gas phase. More complex carbenes have sufficient time to undergo secondary reactions during their time of flight from the reactor to the cooled zone.

The most widely used method of synthesis of complex carbenes (i.e. carbenes consisting of more than three atoms) involves their generation by the UV photolysis of precursor molecules, mainly diazo-compounds and diazirines, isolated in inert matrices. The advantage of this method consists in the simplicity of the preparation of the matrix containing the stable initial compound, which is subsequently decomposed directly in the isolated state. The photodissociation of diazo-compounds and diazirines, yields, apart from the corresponding carbenes, also nitrogen molecules which are fairly inert and do not normally enter into recombination reactions with carbene molecules within the matrix cage. The majority of carbenes dealt with in the present review have been obtained by this method. Among other methods for the generation of carbenes in a low-temperature matrix, mention should be made of the reactions of stable molecules with free atoms, in particular with alkali metal atoms. The results of these investigations have been discussed in other reviews.[2,6]

III. IR and UV spectroscopic study of carbenes and their reactions

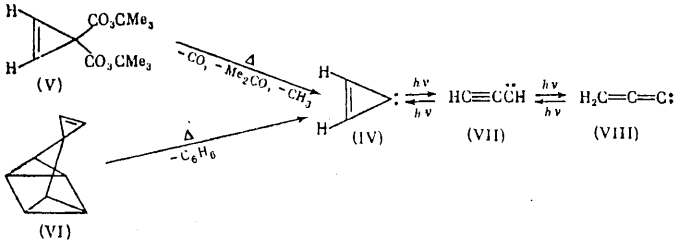
The comparatively small size of the simplest carbene (methylene) ensures that it has a definite mobility even in frozen inert matrices, which leads to the formation of dimerisation products under these conditions. It was not until 1981 that it became possible to detect[7] in the spectra of the diazomethane photolysis products bands at 1015 cm^{-1} (Ar matrix) and 1109 cm^{-1} (Xe matrix), which were attributed to the deformation vibration of methylene in its ground triplet state.

Dichlorocarbene (III) was formed on UV photolysis of dichloroketen (I), obtained by the thermal reaction of trichloroacetic acid chloride (II) with zinc and frozen in an Ar matrix at 12 K.[8]

The recombination of the carbene (III) with a CO molecule in the matrix cage was not observed:

$$\underset{\text{(II)}}{CCl_3\overset{O}{\overset{\|}{C}}Cl} \xrightarrow[-ZnCl_2]{\Delta,\,Zn} \underset{\text{(I)}}{Cl_2C{=}C{=}O} \xrightarrow[-CO]{h\nu(\lambda>200\text{ nm})} \underset{\text{(III)}}{Cl_2C:}\,.$$

Cyclopropenylidene (IV) has been obtained from two different sources — compounds (V) and (VI) — by their thermal decomposition in the gas phase.[9,10] The subsequent UV photolysis (λ = 313 and 254 nm) of this carbene in an Ar matrix led to its isomerisation to propargylene (VII) and further to vinylidenecarbene (VIII). The vibration frequencies of the carbene (VIII) were calculated from its matrix IR spectrum and it was shown that it has a singlet ground state. The results agree well with data obtained by the EPR method.[10]



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$$\underset{\text{(X)}}{N{\equiv}C\overset{N_2}{\overset{\|}{C}}H} \xrightarrow[-N_2]{h\nu} \underset{\text{(IX)}}{N{\equiv}C\ddot{C}H}.$$

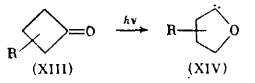
Taking into account the linear structure of the carbene (IX),[11] Dendramis and co-workers[12,13] carried out a full vibrational analysis of the spectra obtained and determined the force field of this species. Analysis of the numerical values of the valence force constants of the CC and CN bonds showed that their multiplicity in both cases is close to two. This as well as the high constant for the interaction of the CC and CN bonds indicate a high degree of delocalisation of electrons in the carbene (IX) and the similarity of its structure to the allene structure $\dot{N}{=}C{=}\dot{C}H$). The UV absorption spectrum of the cyanocarbene (IX) consists of a progression of bands in the range 240–340 nm. Estimation of the energy differences between the members of this progression makes it possible to assign it to the symmetrical stretching vibrations of the N=C=C group of the carbene in the electronically excited state.

The IR spectrum of dicyanocarbene has been obtained and its vibrational spectrum has been calculated.[13]

The IR spectrum of bis(trifluoromethyl)carbene (XI), generated by the UV photolysis (λ > 200 nm) of bis(trifluoromethyl)diazirine (XII), isolated in an Ar matrix at 12 K, has been published.[14,15] In contrast to the photodecomposition of the diazirine (XII), in the low-temperature matrix its gas-phase pyrolysis (300–500 °C) in the absence of the molecular collisions in the thermal reaction zone did not lead to the appearance of the carbene (XI) band in the matrix IR spectrum of the product. The only product of the thermal reaction was perfluoropropene—an isomer of the carbene (XI). The time taken for the rearrangement of the carbene (XI) in the excited singlet state to perfluoropropene has been estaimted[14,15] to be approximately 10^{-5} s:

$$\underset{\text{(XII)}}{(CF_3)_2C\overset{N}{\overset{\|}{\underset{N}{}}}} \xrightarrow[-N_2]{\Delta} \underset{\text{(XI)}}{[(CF_3)_2C:]^S} \rightarrow CF_3CF{=}CF_2.$$

Quantum-chemical calculations have shown that oxycarbenes have a singlet ground state,[16,17] which is stabilised by the interaction of the unshared electron pair of the oxygen atom with the unoccupied *p* orbital of the carbene centre. As a result of this, it is impossible to detect such species by EPR, which makes spectroscopic data obtained by other methods especially valuable. However, until recently the only successful example of this kind was a study[18] in which thermally unstable species with an absorption maximum in the electronic spectrum near 360 nm were detected on UV photolysis (λ > 300 nm) of a series of cyclobutanones (XIII) in organic glasses at 77 K. This absorption was attributed to tetrahydrofurylidene (XIV)—an oxycarbene formed from cyclobutanone as a result of photolytic rearrangement with ring expansion:

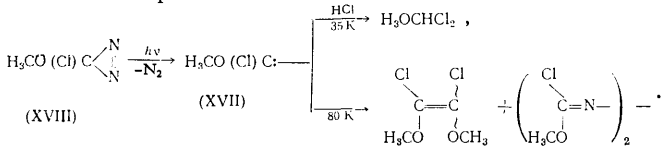


According to Quinkert et al.,[18] the carbenes (XIV) can be "captured" by alcohols, alkenes, or oxygen with formation of secondary products of the kind usual in such cases.

The attempt to measure the IR spectrum of the hydroxycarbene (XV) on UV photolysis (λ > 220 nm) of the formaldehyde (XVI) in an Ar matrix[19,20] was unsuccessful despite the fact that the structure of the final products of the reactions occurring suggest the intermediate participation of the carbene (XV) in the process. The carbene (XV) is probably sufficiently mobile even in a rigid matrix to be able to diffuse from the matrix cage and enter into the reaction:

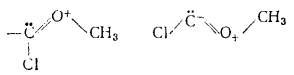
$$\underset{\text{(XVI)}}{H_2CO} \xrightarrow{h\nu} [H_2CO]^* \rightarrow \underset{\text{(XV)}}{[HO\ddot{C}H]} \xrightarrow{H_2CO} H_2C(OH)CHO.$$

Quite recently it has been possible[21,22] to record the IR and UV spectra of chloromethoxycarbene $H_3CO\ddot{C}Cl$ (XVII) and its isotope-substituted analogues $D_3CO\ddot{C}Cl$ and $H_3C^{18}O\ddot{C}Cl$, which were obtained by the UV photolysis (λ > 340 nm) of the corresponding diazirines (XVIII) isolated in matrices (Ar and N_2 12 K, 3-methylpentane, 45 K). At the same time the structure was confirmed by carrying out reactions with HCl and the initial diazirine as well as the dimerisation reaction, which occurs when the matrix is heated to the diffusion temperature:



According to Kasselmayer and Sheridan,[22] the unusually high stretching vibration frequency of the CO bond in the IR spectrum of chloromethoxycarbene (1300 cm^{-1}) is a consequence of an appreciable increase in the multiplicity of the carbon–oxygen bond as a result of the interaction of the unshared electron pairs of the oxygen atom with the unoccupied *p* orbital of the carbene centre.

The increased multiplicity of this bond suggests the possible existence of two isomeric forms of the carbene (XVII):

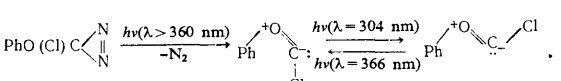


cis-(XVII) *trans*-(XVII).

Analysis of the IR spectra of the carbene (XVII) in different matrices as well as the results of experiments involving its prolonged irradiation with UV light at different wavelengths made it possible to discover the frequencies characteristic of each isomer. For example, the bands at 1310 and 1300 cm^{-1} were assigned to the antisymmetric stretching vibration of the CO bond in the *trans*- and *cis*-isomers respectively (the small frequency difference agrees with calculations of the vibrational spectra of hydroxycarbene[23]). The somewhat greater difference between the vibrational frequencies of the C–Cl bond in the *trans*- and *cis*-isomers of the carbene (XVII) (780 and 755 cm^{-1} respectively) is probably induced by the delocalisation of the unshared electron pair of the oxygen atom over the non-bonding σ orbital of the C–Cl bond.[24] The UV spectrum of the carbene (XVII) isolated in a N_2 matrix contains an absorption band in the region of 360 nm (the authors[22] were unable to differentiate the absorption bands due to different isomers). The extinction coefficient of the carbene was estimated approximately as 65 mol $litre^{-1}$ cm^{-1}.

Prolonged irradiation of the carbene (XVII) in a Ar matrix with UV light (λ > 270 nm) leads to its rearrangement to acetyl chloride, which partly decomposes with formation of keten and hydrogen chloride. The irradiation of compound (XVII) in a N_2 matrix induces the formation, apart from the products indicated, also of small amounts of methyl chloride and CO. The mechanisms of the reactions occurring have not been fully elucidated.

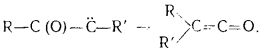
In the course of continuing studies on substituted oxycarbenes, the matrix IR and UV spectra of another representative of unstable species of this class—chloro(phenoxy)carbene (XIX)—were recorded.[25] Groups of bands due to the *cis*- and *trans*-isomers, which can be interconverted on irradiation with UV light at definite wavelengths, were differentiated in the IR spectra of both compound (XIX) and (XVII):



cis-(XIX) *trans*-(XIX)

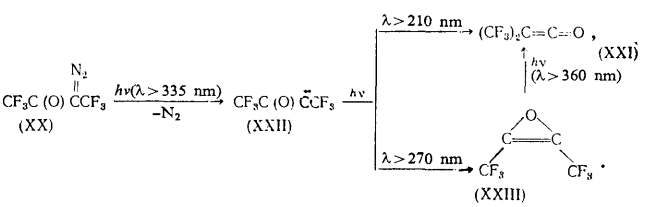
The higher frequency of the antisymmetric stretching vibrations of the CO bond in both isomers confirms, as in the previous case, its increased multiplicity. The bands at 850 cm^{-1} [*trans*-(XIX)] and 800 cm^{-1} [*cis*-(XIX)] have been assigned to the C–Cl bond stretching vibrations. The authors do not comment on the similar somewhat high C–Cl vibration frequency,[25] although by analogy with the carbene (XVII) one would be justified in expecting frequencies in the range 750–780 cm^{-1}. The UV spectrum of the carbene (XIX) has a broad absorption band with λ = 320 nm whose extinction coefficient has been estimated as 100 cm^{-1} mol^{-1}. Compound (XIX) behaves photochemically similarly to the carbene (XVII): the prolonged photolysis of the carbene (XIX) isolated in a N_2 matrix leads to the formation of benzoyl chloride, chlorobenzene, and CO.

For a long time, the spectroscopic data for carbonylcarbenes of the type R–C(O)–C̈–R′ were restricted to EPR spectra.[26–29] The attainment of higher concentrations of these carbenes, sufficient for their detection in matrices by IR and UV spectroscopy, is prevented by the ease with which they rearrange to the isomeric ketens[30,31] (the Wolff rearrangement):



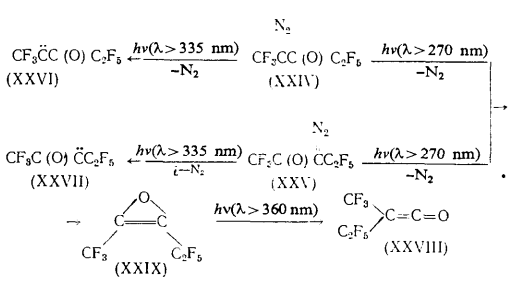
The rearrangement can be slowed down by stabilising the carbenes by introducing an electron-accepting substituent at the carbene centre and also by increasing the size of the migrating group. The first procedure is more effective, because an increase in the size of the substituent can lead to intramolecular secondary reactions in the carbene (for example, intramolecular insertion in the CH bond[32]).

Torres et al.[33] investigated the UV photolysis (λ > 335 nm) of hexafluoro-3-diazo-2-butanone (XX) in an Ar matrix. Together with bis(trifluoromethyl)keten (XXI), the carbene (XXII), which on subsequent irradiation (λ > 210 nm) was converted into the keten (XXI), was detected in the photolysis products by IR spectroscopy:



On the other hand, the irradiation of the carbene (XXII) by light at a longer wavelength (λ > 270 nm) leads to the appearance in the IR spectrum of bands due to a new unstable species, which is also converted into ketens on prolonged irradiation. The appearance of these new bands was explained by the formation of bis(trifluoromethyl)oxirene (XXIII) in the matrix. The intermediate formation of oxirenes has been postulated in a number of reactions,[34–36] but previously they could not be detected spectroscopically. Theoretical calculations have shown that oxirenes are thermodynamically less stable than the isomeric carbonylcarbenes.[37]

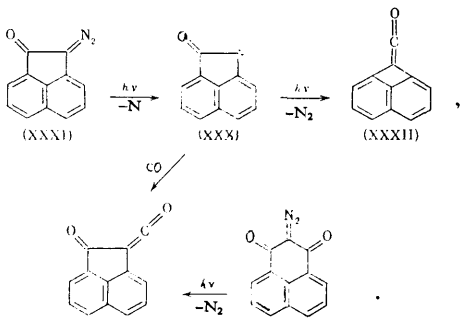
In order to confirm the conclusion that the oxirene (XXIII) is formed, a study was made[33] of the UV photolysis of two other perfluorodiazoketones—2-diazo-octafluoro-3-pentanone (XXIV) and 3-diazo-octafluoro-2-pentanone (XXV)—in an Ar matrix at 12 K:



Apart from the bands of the corresponding carbenes (XXVI) and (XXVII), the bands of only one unstable species were detected in the IR spectra of the products of the photolysis of compounds (XXIV) and (XXV) by UV light at λ > 270 nm. The conversion of this species into the keten (XXVIII) on further irradiation confirms its oxirene structure (XXIX).

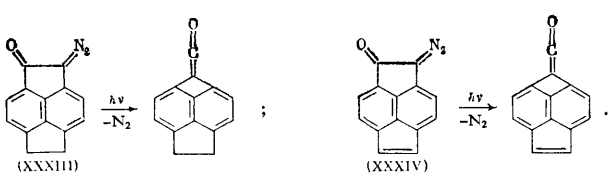
The IR and UV spectra of α-ketocarbene (XXX) were obtained on UV photolysis by light at λ = 365 ± 8 nm of the diazo-compound (XXXI) isolated in an Ar matrix at 10 K. The

formation of the carbene (XXX) was confirmed by the reactions with O_2 and CO:

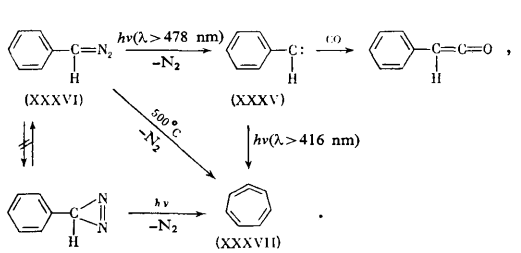


Further irradiation of the carbene (XXX) (λ = 625 ± 8 nm) leads to the Wolff rearrangement and the formation of the keten (XXXII).

In contrast to the example examined above, the attempts to generate ketocarbenes with similar structures by the matrix photolysis of the diazo-compounds (XXXIII) and (XXXIV) were unsuccessful: in both cases, the only detectable products of the photolytic reaction were the corresponding ketens obtained as a result of the Wolff rearrangement (XXXVIII).

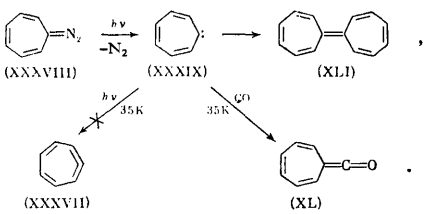


The IR and UV spectra of phenylcarbene (XXXV), formed on UV photolysis (λ > 478 nm) of phenyldiazomethane (XXXVI) in an Ar matrix, have been recorded.[39] Prolonged irradiation of the matrix-isolated carbene (XXXV) by UV light at a shorter wavelength (λ > 416 nm) leads to the disappearance from the IR spectrum of the absorption band characteristic of the aromatic ring and the methylidyne group and to the appearance of IR bands of an unknown compound. The same compound was detected among the products of the gas-phase pyrolysis of phenyldiazomethane (XXXVI) (500 °C), frozen in the matrix, and also on matrix photolysis of phenyldiazirine. The presence in its spectrum of bands at 1824 and 1816 cm^{-1}, close to the 1810 cm^{-1} band characteristic of the allene linkage of 1-azocyclohepta-1,3,4,6-tetraene,[40] indicates the formation of the cycloheptatetraene (XXXVII)—the product of the intramolecular reaction of the carbene (XXXV) with ring expansion. Analysis of the products of the matrix UV photolysis of various deuteriated phenylcarbenes has confirmed the proposed mechanism:



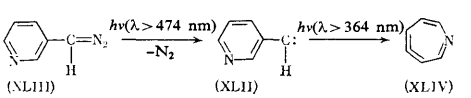
Systematic matrix studies of this rearrangement have shown that isomerisation with ring expansion and the formation of cycloheptatetraenes is a widely occurring reaction of many arylcarbenes.[41,42] The dimerisation reaction of the cycloheptatetraene (XXXVII) has also been investigated by matrix IR spectroscopy and it has been possible to discover alternative sources of this interesting cyclic compound.[42]

The IR and UV spectra of the triplet cycloheptatrienylidene (XXXIX) have been recorded quite recently[43] after the UV photolysis (λ > 574 nm) of diazocycloheptatriene (XXXVIII) in an Ar matrix. This carbene interacts with the CO added to the matrix, forming the keten (XL), and also dimerised with formation of heptafulvalene (XLI):

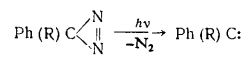


Experiments have shown that this cannot be converted into the cycloheptatriene (XXXVII) either thermally or photolytically. The presence in the electronic spectrum of compound (XXXIX) of an absorption maximum in the long-wavelength region at 530 nm suggests a planar structure of this carbene, which agrees well with EPR data.[43]

According to the results of Chapman and Sheridan,[44] pyridylcarbene (XLII), whose IR spectrum has been recorded on UV irradiation (λ > 474 nm) of 3-diazomethylpyridine (XLIII) in an Ar matrix, undergoes a photolytic rearrangement similar to that of phenylcarbene (XXXV). Thus its photolysis by UV light at λ > 364 nm leads to the formation of 1-azacyclohepta-1,3,4,6-tetraene (XLIV):



The IR and UV spectra of halogeno(phenyl)carbenes PhĊCl (XLVa), PhĊBr (XLVb), and PhĊF (XLVc), generated by the UV photolysis (λ > 300 nm) of the corresponding diazirenes (XLVI) in inert gas matrices at 10 K[42,45–47] or in a 3-methylpentane matrix at 77 K,[48] have been described in the literature. A correspondence was observed between the electronic spectra of the carbenes (XLVa)–(XLVc), formed in a 3-methylpentane matrix, and the spectra obtained on flash photolysis of the diazirines (XLVIa)–(XLVIc) in gaseous benzene or isooctane at 23 °C:[48]



(XLVI) (XLV)

R = Cl (a), Br (b), F (c), CF_3 (d).

Phenyltrifluoromethylcarbene (XLVd), whose IR spectrum has also been recorded, has been obtained similarly by the UV photolysis of phenyltrifluoromethyldiazirine (XLVId) and phenyltrifluoromethyldiazomethane, both frozen in an Ar matrix.[47]

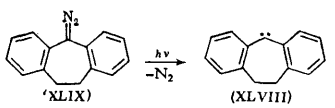
The electronic absorption and emission spectra of diphenylcarbenes (XLVII) have been obtained in the photolysis of diphenyldiazomethane isolated at 20–77 K in various crystals and vitreous organic matrices.[49–54] The spectrum of this carbene is characterised by the presence of two structureless broad bands with maxima at 301 nm (ε = 25000) and 465 nm (ε = 300) and possibly a third band at 240 nm.[51] The assignment of the observed bands to compound (XLVII) was based on their disappearance when the

matrix was heated and on the appearance of the absorption of benzophenone (in the presence of oxygen), on the parallel decrease in the intensities of the UV bands and the EPR signal due to the given carbene, and on the quantitative analogy with the electronic spectrum of the diphenylmethyl radical (absorption maxima at 336 and 515 nm). The absorption spectra of different 4-substituted diphenylcarbenes have a similar form with two main bands in the UV and visible regions. The electronic spectra of these carbenes have already been surveyed.[28]

Polarisation studies on the carbenes (XLVII), (XLVII)-d_{10}, and 4,4′-dichloro- and 4,4′-dibromo-diphenylcarbenes have made it possible to characterise the electronic configurations of the ground and first excited triplet states of these carbenes as $(p\pi)^1(p\sigma)^1$ and $(p\sigma)^1(\pi^*)^1$. Further investigations demonstrated the $(p\pi)^1(\pi^*)^1$ configuration of the second excited triplet state with an energy higher by 1000 cm^{-1} than that of the first excited triplet state.[52]

The IR spectrum of diphenylcarbene has been published.[55]

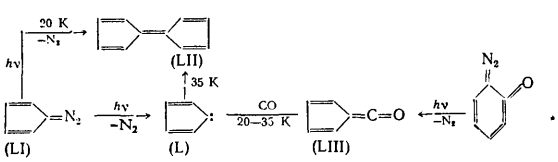
The electronic spectrum of 10,11-dihydrodibenzo[*a*,*d*]cycloheptenylidene (XLVIII) (λ_{max} = 510 nm) has been obtained in the photolysis of the corresponding diazo-compound (XLIX) frozen in various organic matrices at 77 K:[51]



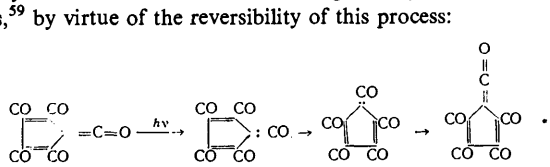
(XLIX) (XLVIII)

Later[56] the UV spectrum of this species was recorded in the flash photolysis of the diazo-compound (XLIX) in solutions in hydrocarbons at 20 °C.

After the first, partly unsuccessful (owing to the unsuccessful selection of experimental conditions) attempts to stabilise cyclopentadienylidene (L) in an inert matrix,[57,58] its IR and UV spectra were recorded.[59] The carbene (L) was obtained by the UV photolysis (λ > 300 nm) of diazocyclopentadiene (LI) isolated in low-temperature inert matrices. The reliability of the frequency assignments to compound (L) in the IR and UV spectra obtained was confirmed by the occurrence in the matrix at 20–35 K of the dimerisation of compound (L) to fulvalene (LII) and the formation of the keten (LIII) on interaction of compound (L) with the CO added to the N_2 matrix:

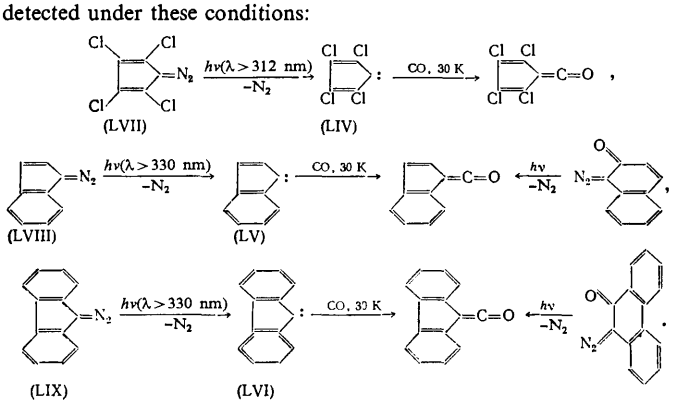


The carbene (L) is extremely reactive even at liquid helium temperature and, under the conditions of insufficient matrix dilution (less than 1000 : 1), it readily dimerises to compound (LII). Furthermore, even when the matrix dilution is raised to 100000 : 1, a certain amount of the dimer (LII) is formed. Such high reactivity in compound (L) may be associated with its ability to rotate within the matrix cage. Photolysis by polarised light of the keten (LIII), obtained by the interaction of compound (L) with a CO molecule in a CO matrix, leads to an appreciable reorientation of the initially randomly oriented keten molecules, most probably, according to the authors,[59] by virtue of the reversibility of this process:

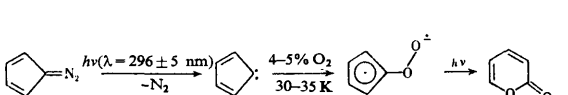


It has been possible to record[60] the IR and UV spectra of several derivatives of the carbene (L)—tetrachlorocyclopentadienylidene (LIV), indenylidene (LV), and fluorenylidene (LVI). They were all formed on UV photolysis of the corresponding diazo-precursors (LVII)–(LIX) in inert matrices and had a triplet ground state. The UV spectrum of compound (LVI), stabilised in a matrix, is close to the UV spectrum of the triplet (LVI) obtained by flash photolysis.[61] In contrast to compound (L), the dimerisation of the carbenes (LIV)–(LVI) was observed neither during their generation nor in the course of subsequent heating until the complete evaporation of the material of the matrix. According to Bell and Dunkin,[60] the possible causes of this are, firstly, the appreciably greater bulk of the carbenes considered compared with compound (L), which hinders their diffusion in the matrix and, secondly, the pronounced shielding of the carbene centres by the bulky substituents, which creates steric hindrance to dimerisation. For comparison, one should note that the formation of the dimer of the carbene (LVI) was observed only in the photolysis of diazofluorene (LVII) in solution.[62]

At 30 K in inert matrices with added CO, the carbenes (LIV)–(LVI) give rise to the corresponding ketens, although they exhibit under these conditions a lower reactivity than compound (L). Furthermore, the carbenes (LIV)–(LVI) were stabilised in a pure CO matrix at 12 K, whereas the free carbene (L) could not be detected under these conditions:



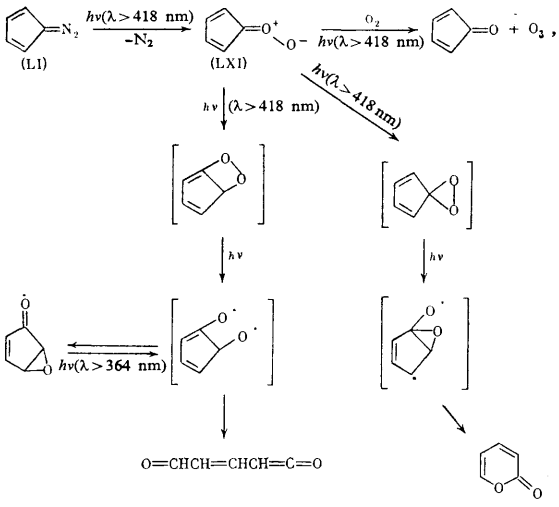
The different reactivities in relation to CO exhibited by compound (L) and its derivatives (LIV)–(LVI) may be associated, on the one hand, with the different degrees of shielding of the carbene centres and, on the other, with the different rates and hence different energies of the triplet–singlet transition of these carbenes, which necessarily precedes their reactions with singlet CO molecules.[60] The reactions of the carbenes (L) and (LIV)–(LVI) with oxygen have been investigated in a number of studies. Thus the carbene (L), generated on UV photolysis of diazocyclopentadiene (LI) in a N_2 matrix to which 4–5% of O_2 had been added, reacted with O_2 at 30–35 K, affording a new photolabile substance, which was converted on subsequent photolysis into α-pyrone:[63]



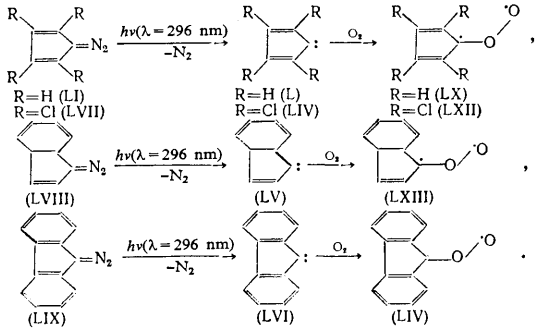
Careful analysis of the IR spectra of the compound obtained as well as examination of the isotope composition of the products formed in the presence of oxygen having the composition $^{18}O_2$ and $^{16}O^{18}O$ made it possible to attribute to this compound the structure of the oxide (LX).

Chapman and Hess,[64] who carried out the UV photolysis of compound (LI) under conditions close to those employed by Bell and Dunkin[63] (Ar matrix with addition of 25% of O_2, 10 K), also observed the formation of a photolabile product. However, the latter differed markedly from compound (LX) in terms of its set of frequencies in the IR, although the results of experiments involving the further irradiation of this compound do not conflict with the idea that it has an *O*-oxide structure [Chapman and Hess[64] postulated a zwitter-ionic structure of the carbonyl oxide (LXI) and not the radical form put forward by Bell and Dunkin[63]].

Later,[65] these discrepancies were accounted for by the fact that compound (LXI) could be formed as a result of the direct reaction of compound (LI) with O_2 without the participation of the carbene (L), especially since the usual photolytic decomposition of compound (LI) is observed on irradiation with light at a much shorter wavelength ($\lambda > 300$ nm). Furthermore, different isomers of the same carbonyl oxide may have been detected in the above studies:[63,64]

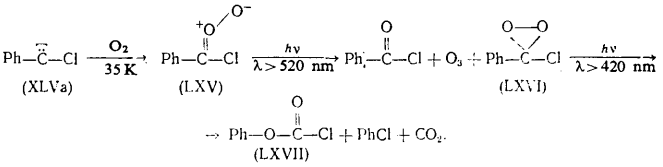


The reactions of O_2 with the carbenes (L) and (LIV)–(LVI), isolated in N_2 matrices at 10 K, were investigated by UV spectroscopy:[65]

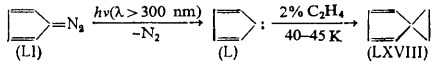


The carbonyl oxides (LX) and (LXII)–(LXIV) obtained were characterised by the presence in their electronic spectra of absorption maxima in the range 395–460 nm.

The reaction of chloro(phenyl)carbene (XLVa) with O_2 has been investigated.[45] When the Ar matrix containing 4% O_2 was heated together with the carbene (XLVa) stabilised in it from 10 to 35 K, the IR absorption of the carbene slowly weakened and new bands appeared in the spectrum, which the authors[45] assigned to the carbonyl oxide (LXV). Compound (LXV) proved to be so photolabile that it disappeared even on exposure to the IR emission from the spectrometer. The spectrum of this compound was recorded only by employing a silicon filter ($\lambda > 1100$ nm). Photolysis of compound (LXV) by light at $\lambda > 520$ nm led to its partial decomposition to benzoyl chloride and also to its rearrangement to the dioxiran (LXVI), which was converted into phenyl chloroformate (LXVII) on further irradiation. The UV spectra of compounds (LXV) and (LXVI) obtained agree well with the known spectra of the corresponding compounds of these classes:[63–65]



Finally matrix IR spectroscopy was used recently[66,67] for the direct observation and investigation of the principal reaction of carbenes—their [1 + 2]cycloaddition to alkenes—in the specific instance of the interaction of cyclopentadienylidene (L) with ethylene. UV photolysis ($\lambda > 300$ nm) of diazocyclopentadiene (LI) in an Ar matrix with added 2% C_2H_4 at 12 K resulted in the appearance in the IR spectrum of intense bands due to compound (L) together with weak bands due to its dimer (fulvalene) as well as spiro[2,4]hepta-4,6-diene (LXVIII) (734 and 560 cm^{-1}). The photolysis was continued until the complete disappearance of the bands of the initial compound (LI):



Subsequent heating of the matrix from 12 to 40–45 K resulted in a synchronous decrease in the intensity of the bands of the carbene (L) and the simultaneous intensification of the bands of the spiro-compound (LXVIII), which indicates the occurrence of the direct reaction of the carbene (L) with ethylene (Fig. 1). It must be emphasised that this is absolutely the first successful example of the direct spectroscopic investigation of the reactions of a carbene with organic acceptors.

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In conclusion we may note that the appearance in recent years of a large number of publications devoted to the direct spectroscopic study of carbenes and the examination of their reactions with trapping reagents and secondary reactions in low-temperature matrices indicates the growing importance of the matrix isolation method not only as a way of stabilising the carbenes and of

determining their analytical characteristics but also as an important instrument for the study of the mechanisms of processes in which they participate.

References

1. A K Mal'tsev *Materialy I Vsesoyuznogo Soveshchaniya po Khimii Krabenov i Ikh Analogov* (Proceedings of the I All-Union Conference on the Chemistry of Carbenes and their Analogues), Moscow, 1973, p. 10
2. A K Mal'tsev *Zh. Vses. Khim., im Ova D I Mendeleeva,* 1979, **24** 445
3. W Kirmse *Carbene Chemistry,* Acad. Press, New York, 1971
4. A M Trozzolo, E Wasserman *Carbenes* (Edited by R A Moss, M Jones), Wiley, New York, 1975, Vol. 2, p. 185
5. O P Strausz, H Murai, M Torres *J. Photochem.,* 1981, **17** 207
6. A K Mal'tsev, V A Korolev, O M Nefedov *Fizicheskaya Khimiya. Sovremennye Problemy* (Physical Chemistry. Modern Problems), Izd. Khimiya, Moscow, 1986, p. 144
7. Y P Lee, G C Pimentel *J. Chem. Phys.,* 1981, **75** 4241
8. V N Khabashesku, A K Mal'tsev, O M Nefedov *Dokl. Akad. Nauk SSSR,* 1987, **296** 403
9. H P Reisenauer, G Maier, A Riemann, R W Hoffmann *Angew. Chem., Int. Ed. Engl.,* 1984, **23** 641
10. G Maier, H P Reisenauer, W Schwab, et al. *J. Am. Chem. Soc.,* 1987, **109** 5183
11. R A Bernheim, R J Kempf, J V Grams, P S Skell *J. Chem. Phys.,* 1965, **43** 196
12. A Dendramis, G E Leroi *J. Chem. Phys.,* 1977, **66** 4334
13. A Dendramis, J F Harrison, G E Leroi *Ber. Bunsenges. Phys. Chem.,* 1978, **82** 7; W H Smith, G E Leroi *Spectrochim. Acta, Part A,* 1969, **25** 1917
14. A K Mal'tsev, P S Zuev, O M Nefedov *Izv. Akad. Nauk SSSR., Ser. Khim.,* 1985, 957
15. A K Mal'tsev, P S Zuev, O M Nefedov *Tezisy Dokladov V Vsesoyuznoi Konferentsii po Khimii Ftororganicheskikh Soedinenii* (Abstracts of Reports at the Vth All-Union Conference on the Chemistry of Organofluorine Compounds), Moscow, 1986, p. 139
16. N G Rondan, K N Houk, R A Moss *J. Am. Chem. Soc.,* 1980, **102** 1770
17. R R Lucchese, H F Schaefer *J. Am. Chem. Soc.,* 1978, **100** 298
18. G Quinkert, K H Kaiser, W D Stohrer *Angew. Chem. Int. Ed. Engl,* 1974, **13** 198
19. J R Sodeau, E K C Lee *Chem. Phys. Lett.,* 1978, **57** 71
20. E K C Lee, J R Sodeau, M Diem, K Shibuya *Proceedings of IIIrd Yamada Conference of Free Radicals,* 1978, p. 98
21. R S Sheridan, M A Kasselmayer *J. Am. Chem. Soc.,* 1984, **106** 436
22. M A Kasselmayer, R S Sheridan *J. Am. Chem. Soc.,* 1986, **108** 99
23. J D Goddard, Y Yamaguchi, H F Schaefer *J. Chem. Phys.,* 1981, **75** 3459
24. D C McKean *Chem. Soc. Rev.,* 1978, 7 399
25. M A Kasselmayer, R S Sheridan *J. Am. Chem. Soc.,* 1986, **108** 844

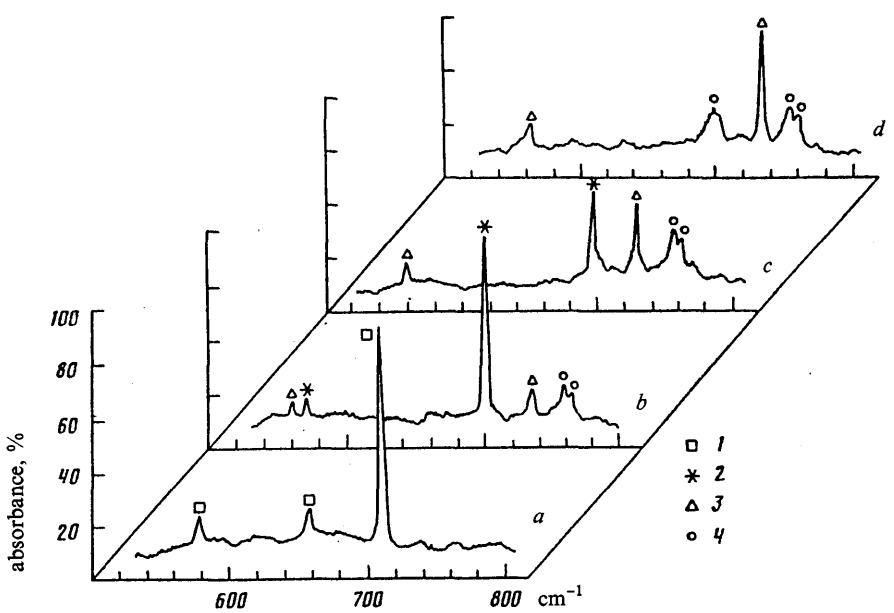


Figure 1. IR spectra of the products of the reaction of diazo-cyclopentadiene in an Ar matrix to which 2% C_2H_4 has been added: *a*, the spectrum of the initial compound before photolysis (12 K); *b*, after UV irradiation at 12 K ($\lambda > 300$ nm, 15 min); *c*, after heating the matrix from 12 to 40–45 K (10 min); *d*, ditto after intermediate recooling to 12 K; *1*, diazocyclopentadiene (LI); *2*, cyclopentadienylidene (L); *3*, spiro[2,4]hepta-4,6-diene (LXVIII); *4*, fulvalene.[66]

26. R S Hutton, M L Manion, H D Roth, E Wasserman *J. Am. Chem. Soc.*, 1974, **96** 4680
27. H Murai, J Ribo, M Torres, O P Strausz *J. Am. Chem. Soc.*, 1981, **103** 6422
28. A M Trozzolo *Acc. Chem. Res.*, 1968, **1** 329
29. H Murai, M Torres, O P Strausz *J. Am Chem. Soc.*, 1980, **102** 5104
30. A Krantz *J. Chem. Soc., Chem. Commun.*, 1973, **18** 670
31. G Maier, H P Reisenauer, T Sayrac *Chem. Ber.*, 1982, **115** 2192
32. I E Dolgii, E A Shapiro, G V Lun'kova, O M Nefedov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 1652
33. M Torres, J L Bourdelande, A Clement, O P Strausz *J. Am. Chem. Soc.*, 1983, **105** 1698
34. I L Csizmadia, J Front, O P Strausz *J. Am. Chem. Soc.*, 1968, **90** 7360
35. R A Cormier *Tetrahedron Lett.*, 1980, **21** 2021
36. M Torres, E M Loun, H E Gunning, O P Strausz *Pure Appl. Chem.*, 1980, **52** 1623
37. K Tanaka, M Yoshimine *J. Am. Chem. Soc.*, 1980, **102** 7655
38. R A Hayes, T C Hess, R J McMahon, O L Chapman *J. Am. Chem. Soc.*, 1983, **105** 7786
39. R P West, O L Chapman, J P Le Roux *J. Am. Chem. Soc.*, 1982, **104** 1779
40. O L Chapman, R S Sheridan, J P Le Roux *J. Am. Chem. Soc.*, 1978, **100** 6245
41. O L Chapman, R J McMahon, R P West *J. Am. Chem. Soc.*, 1984, **106** 7973
42. R J McMahon, Ch J Abelt, O L Chapman, et al. *J. Am. Chem. Soc.*, 1987, **109** 2456
43. R J McMahon, O L Chapman *J. Am. Chem. Soc.*, 1986, **108** 1713
44. O L Chapman, R S Sheridan *Prepr. Div. Pet. Chem. Am. Chem. Soc.*, 1979, **24** 130; Chem. Abs., Vol. 94, 74594
45. G A Ganzer, R S Sheridan, M T H Liu *J. Am. Chem. Soc.*, 1986 **108** 1517
46. A K Mal'tsev, P S Zuev, O M Nefedov *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1985, 2159
47. A K Mal'tsev, P S Zuev, O M Nefedov *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1987, 463
48. D P Cox, J R Gould, N P Hacker, et al. *Tetrahedron Lett.*, 1983, 5313
49. G Closs, C A Hutchison, B E Kohler *J. Chem. Phys.*, 1966, **44** 413
50. W A Gibbons, A M Trozzolo *J. Am. Chem. Soc.*, 1966, **88** 172
51. J Moritani, S I Murahashi, M Nishino, et al. *Tetrahedron Lett.*, 1966, 373
52. D J Grahan, T S Lin *Chem. Phys.*, 1982, **73** 411
53. Y Ono, W R Ware *J. Phys. Chem.*, 1983, **87** 4426
54. A M Trozzolo, W A Gibbons *J. Am. Chem. Soc.*, 1967, **89** 239
55. W Sander *Angew. Chem.*, 1986, **98** 255
56. I Moritani, S I Murahashi, H Ashitaka, et al. *J. Am. Chem. Soc.*, 1968, **90** 5918
57. W B De More, H O Pritchard, N Davidson *J. Am. Chem. Soc.*, 1959, **81** 5874
58. M S Baird, I R Dunkin, M Poliakoff *J. Chem. Soc., Chem. Commun.*, 1974, 904
59. M S Baird, I R Dunkin, N Hacker, et al., *J. Am. Chem. Soc.*, 1981, **103** 5190
60. G A Bell, J R Dunkin *J. Chem. Soc., Faraday Trans. II*, 1985, **81** 725
61. P B Grasse, B E Brauer, J J Zupanic, et al. *J. Am. Chem. Soc.*, 1983, **105** 6833
62. S Murashi, J Moritani, Y Nagai *Bull. Chem. Soc. Jpn.*, 1967, **40** 1655
63. G A Bell, I R Dunkin *J. Chem. Soc., Chem. Commun.*, 1983, 1213
64. O L Chapman, T C Hess *J. Am. Chem. Soc.*, 1984, **106** 1842
65. G A Bell, I R Dunkin, C J Shields *Spectrochim. Acta, Part A*, 1985, **41** 1221
66. A K Mal'tsev, P S Zuev, Yu V Tomilov, O M Nefedov *Izv Akad. Nauk SSSR, Ser. Khim.*, 1987, 2202
67. P S Zuev, A K Mal'tsev, O M Nefedov *Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Khimii Karbenov* (Abstracts of Reports at the IV All-Union Conference on the Chemistry of Carbenes), Moscow, 1987, p. 99

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Electrochemical methods for the generation of carbenes and their analogues

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ABSTRACT. The present review surveys and analyses the results of studies devoted to the use of electrochemical methods for the generation of carbenes, nitrenes, and also dichlorogermylene. The cathodic and anodic processes leading to the formation of these species are considered separately. Attention is concentrated on questions concerning the generation of dihalogenocarbenes in the cathodic reduction of polyhalogenomethanes and of dinitrocarbene in the anodic oxidation of dinitromethylides. In addition, data are presented concerning the possibility of the cathodic generation of carbene and nitrene radical-anions and the study of their properties. The examples of reactions involving electrochemically generated carbenes and their analogues examined in the review indicate that there are realistic prospects for the creation of highly selective processes leading to the electrochemical carbene synthesis.

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I. Introduction

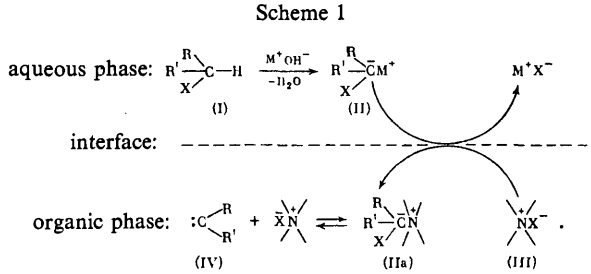
The various methods for the generation of carbenes are based on a fragmentation process initiated as a rule by the application of some kind of method involving a physical influence on a suitable organic substrate. Fragmentation results in the synchronous or successive dissociation of all the chemical bonds belonging to one reaction centre of the substrate molecule.

The aim of the present review is to show that, together with common methods for exerting a chemical influence such as, for example, thermolysis or photolysis, the electrochemical method can be used successfully for the generation of carbenes. In the last case, the fragmentation of the organic substrate leading to the formation of a carbene becomes possible because of the electrochemical activation of the substrate as a result of the transfer of one or several electrons. Such activation can be achieved as a result of the occurrence of both cathodic and anodic processes depending on the nature and structure of the substrate. Generally speaking, the method for the electrochemical generation of carbenes and their analogues has not yet come to be widely used and this review is perhaps the first attempt at a survey of the available experimental data. Nevertheless the many advantages of this method give rise to confidence that it has good prospects.

II. Reduction processes

One of the commonest methods of generating carbenes is the α-elimination of a substituent (usually a halide ion) from the carbanionic centre of a thermodynamically unstable anion. The conditions for the formation of such an anion exert a decisive influence on the efficiency of the generation of the carbene as a whole. Nowadays the greatest popularity has been gained by Makosha's method,[1] which is based on the following processes presented in Scheme 1:

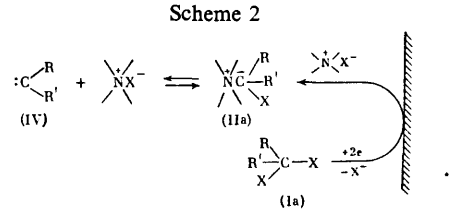
Scheme 1



The thermodynamically unstable carbanion (II) [zwitter-ion?] generated in the aqueous phase exchanges at the interface the metal cation for the tetraalkylammonium cation of the corresponding salt (III), catalytic amounts of which are added to the organic phase. The ion pair (IIa) formed migrates into the bulk of the organic phase where it dissociates with formation of the carbene (IV).

An alternative electrochemical method of generating the ion pair (IIa) does not require the presence of a base in the system and involves the reduction at the cathode of the C–X (X = halogen) bond of the precursor: †

Scheme 2



† In the light of the results of recent studies,[2] the following process occurs under certain conditions:

$$\rangle C{-}H + e \rightarrow \rangle C^{-} + {}^{1}/_{2}H_{2}.$$

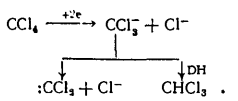
This is yet another possibility, in principle, of an effective electrochemical generation of a thermodynamically unstable carbanion and later a carbene. This possibility is being investigated at the present time.

Despite the fact that the process illustrated in Scheme 2 is evidently attractive, it would be premature to speak of its advantages over the thoroughly investigated process shown in Scheme 1. There is no doubt that the development of research into the electrochemical generation of carbenes (Scheme 2) has aroused interest both as regards the solution of specific synthetic problems and as a source of additional information about the mechanism of the process illustrated in Scheme 1.

1. Generation of carbenes

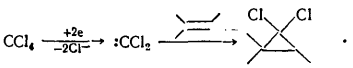
The possibility, in principle, of carrying out Scheme 2 was demonstrated as early as the beginning of the 1960's by Wawsonek and Duty,[3] who used the method of classical polarography to investigate the electrochemical reduction of various halogenomethanes in acetonitrile (AN) and dimethylformamide (DMF) and established that two electrons are transferred in the first stage [$E_{1/2}$ = –0.25 V (saturated calomel electrode)] of the reduction of CCl_4 at a Hg cathode in AN in the presence of Bu_4NBr as the supporting electrolyte. It is accompanied by the dissociation of the C–Cl bond and the formation of the carbanion CCl_3^-, which is partly protonated under the experimental conditions, affording $CHCl_3$, and undergoes partial fragmentation, which leads to the dichlorocarbene and Cl^-:

Scheme 3



The relative contributions of the above reactions depend on the proton-donating capacity of the medium. In the presence of proton donors (for example, H_2O), $CHCl_3$ is formed preferentially. The dichlorocarbene generated via Scheme 3 has been detected chemically by trapping it with an alkene (the yield of the adduct has not been indicated):[3]

Scheme 4



This process has been achieved at a Hg cathode in AN in the presence of Bu_4NBr as a supporting electrolyte at 20 °C and a current density of $(4-7) \times 10^{-3}$ A cm^{-2}. In view of the identity of the polarographic behaviour of CBr_4 and CCl_4, the same workers[3] concluded that dibromocarbene is probably formed on reduction of CBr_4. In addition, it has been suggested[3] that the reduction of CF_2Cl_2 and $PhCCl_3$ leads to difluoro- and phenylchloro-carbenes respectively. However, the formation of these carbenes has not been confirmed chemically.

Almost 20 years were needed before the conversion of alkenes into cyclopropanes in the electrochemical reduction of halogenomethanes was brought to the preparative level.[4–6] The successful solution of this problem was promoted by the rational selection of the electrode material and the solvent. Thus the current yield of cyclopropanes reaches 80% in the reduction of CCl_4 at a lead electrode in $CHCl_3$ in the presence of alkenes (Table 1, experiments 1–4).[4]

According to the authors,[4] the following processes can also lead to the formation of dichlorocarbene in the electrolysis of CCl_4 in $CHCl_3$ under these conditions:

Scheme 5

$$CHCl_3 + 2e \rightarrow CHCl_2^- + Cl^-,$$
$$CHCl_3 + CHCl_2^- \rightarrow CCl_3^- + CH_2Cl_2,$$
$$CCl_3^- \rightarrow :CCl_2 + Cl^-.$$

Table 1. The electrolysis conditions and the yields of the products of the conversion of alkenes into cyclopropanes by electrochemically generated dihalogenocarbenes.

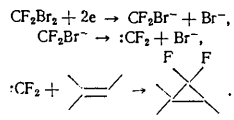
No. of expt.	Initial halogeno-methane	Carbene formed	T, °C	Solvent	Bu_4NBr concentration, M	Electrode	j, mA cm^{-2}	Alkene employed	Yield* of cyclopro-pane	Refs.
1	CCl_4	$:CCl_2$	—5÷—3	$CHCl_3$	0.35	Pb	2.5	2-methylbut-2-ene	80—82	[4]
2	CCl_4	$:CCl_2$	—5÷—3	$CHCl_3$	0.35	Pb	4.0	styrene	56—58	[4]
3	CCl_4	$:CCl_2$	—5÷—3	$CHCl_3$	0.35	Pb	2.5	2-phenylpropene	65—67	[4]
4	CCl_4	$:CCl_2$	—5÷—3	$CHCl_3$	0.35	Pb	4.0	2,3-dimethylbut-2-ene	77—82	[4]
5	CCl_4	$:CCl_2$	—5÷—3	CH_2Cl_2	0.25	Pb	4.0	2-methylbut-2-ene	62—63	[4]
6	CF_2Br_2	$:CF_2$	0÷18	CH_2Cl_2	0.35	Pt	1.0	2-methylbut-2-ene	54	[5]
7	CF_2Br_2	$:CF_2$	0÷18	CH_2Cl_2	0.35	Pt	1—2	2-phenylpropene	48—57	[5]
8	$CFBr_3$	$:CFBr$	<0	CH_2Cl_2	0.25—0.35	Pb	1—2	2-methylout-2-ene	~60	[6]
9	$CFBr_3$	$:CFBr$	<0	CH_2Cl_2	0.25—0.35	Pb	1—2	styrene	~60	[6]
10	$CFBr_3$	$:CFBr$	<0	CH_2Cl_2	0.25—0.35	Pb	1—2	cyclohexene	~60	[6]

* Calculated relative to the product isolated.

Indeed the electrolysis of $CHCl_3$ itself in the presence of 2-methylbut-2-ene afforded *gem*-dichlorocyclopropane in 22–25% yield.[4] Dichlorocarbene can be generated from CCl_4 also in CH_2Cl_2 whose acidity is insufficient for the protonation of CCl_3^-. The yield of cyclopropanes from alkenes proved to be fairly high also under these conditions (Table 1, experiment 5).

The reduction of CF_2Br_2 at a platinum cathode in CH_2Cl_2 leads to $:CF_2$, which interacts with 2-phenylpropene or 2-methylbut-2-ene to form difluorocyclopropane derivatives in good yields (Table 1, experiments 6 and 7):[5]

Scheme 6



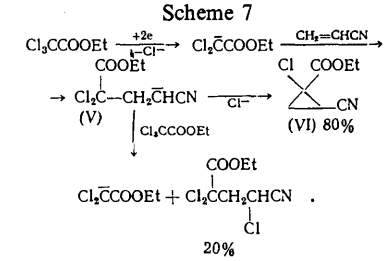
The reduction of $CFBr_3$ takes place similarly at a lead cathode. It leads to :CFBr, which forms bromofluorocyclopropane derivatives in the presence of alkenes (Table 1, experiments 8–10).[6]

We may note that the (IIa) → (IV) reaction stage presented in Schemes 1 and 2 provides an incomplete idea about the reactivity of the intermediate anion (IIa). In reality, this anion is capable of being partly protonated even in aprotic media of the type of AN, DMF, and propylene carbonate[5] (see Scheme 3). The polarisation curves for the reduction of CCl_4 then show a wave (the second wave) corresponding to the reduction of $CHCl_3$. It is of interest that the height of the second wave depends on the presence in the solution of an alkene, which functions as an acceptor of carbenes.[7] In certain cases, such data can serve as indirect confirmation of the formation of the carbene intermediate.[7]

The protonation of the anion (IIa) can influence greatly the efficiency of the generation of the carbene. For example, whereas the rapid proton exchange reactions between $CHCl_3$ and the electrochemically generated anion CCl_3^- do not lower the yield of dichlorocarbene on reduction of CCl_4 in chloroform because they lead to the same readily fragmented anion CCl_3^-,[4] the reduction of CF_2Br_2 in chloroform affords F_2CH_2. Owing to the high basicity of the intermediate anion CF_2Br^-, it is better to generate $:CF_2$ in the latter case in the less acid CH_2Cl_2.[5] In the generation of the highly basic anions (IIa) (see Scheme 2) in a medium containing the cations NR_4^+ (R = alkyl), account must be taken of the possibility of the Hofmann cleavage of the cations (for R ≠ Me) with formation of alkenes under the influence of compound (IIa) as a base.

In media with weak proton-donating properties, the carbene formed on fragmentation of the intermediate anion (IIa) interacts with alkenes, as shown in Schemes 4 and 6. However, when the double bond has been activated in relation to nucleophilic attack, the anion (IIa) can react rapidly with the alkene and the stage (IIa) → (IV) (see Scheme 2) is then excluded. This possibility has in fact been examined in detail by Baizer and Chruma[8] [including the process involving the anion CCl_3^- generated by the electrochemical reduction of CCl_4 at a mercury cathode in DMF in the presence of NEt_4Cl as the supporting electrolyte at an electrolysis potential of –0.85 V (w.r.t. sat. calomel electrode) and at a temperature of 25–45 °C]. It must be emphasised that, together with the products of the addition of the carbanion to the double bond, cyclopropane derivatives can also be formed in this case, as happens, for example, in the reduction of trichloroethyl acetate in the presence of acrylonitrile[8] (Scheme 7):

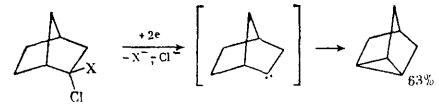
Scheme 7



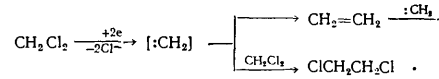
It is significant that cyclopropane (VI) is formed exclusively as a result of the intramolecular cyclisation of the adduct of the carbanion with the alkene (V).[8]

The data examined above are extremely important for the selection of optimal conditions for the synthesis of cyclopropanes with participation of electrochemically generated carbenes.

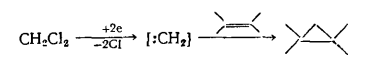
The electrochemical reduction of organohalogen compounds in accordance with Scheme 2 can be used to generate not only halogenocarbenes but also carbenes with a different structure. Thus, in the reduction of 2,2-dichloronorbornane [$E_{1/2}$ = –1.54 V (sat. c. e.)] or 2-bromo-2-chloronorbornane [$E_{1/2}$ = –0.83 V (sat. c. e.)] at a mercury cathode in DMF in the presence of NEt_4Br as the supporting electrolyte, the intermediate carbene is inserted in a C–H bond, which leads to a high yield of an intramolecular cyclisation product:[9]



According to Mottus and Ort,[10] the electrolysis of a CH_2Cl_2 solution containing $AlCl_3$ at an aluminium cathode leads to dichloroethane, ethylene, and cyclopropane (the yields have not been indicated), which are regarded as the methylene conversion products:

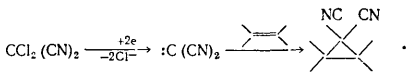


The reduction of different halogenomethanes by the electrochemically generated solvated electrons [aluminium cathode coated with lithium and magnesium in solution in hexamethylphosphoramide (HMP) containing LiCl and $MgCl_2$] leads to a mixture of gases (ethane, ethylene, cyclopropane, etc.), whose formation is explained by the participation of methylene.[11] In the presence of an alkene, the corresponding cyclopropanes were obtained:



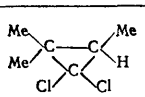
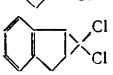
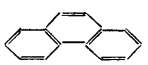
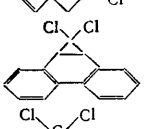
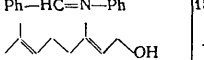
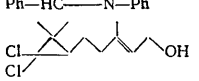
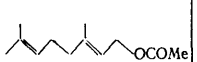
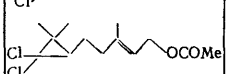
It has been shown by the polarographic method[12] that the carbene intermediate is formed also in the electrochemical reduction of 9,9-dichlorofluorene. Similarly, dicyanocarbene is formed as an intermediate in the reduction of dichloromalononitrile.[13] The results of polarographic studies and of electrolysis at a controlled potential [E = –0.47 V (rel. Ag/Ag^+), Hg cathode, AN, NBu_4Br,

0–5 °C] in the presence of tetramethylethylene made it possible to describe this process by the following scheme:



However, the yield of the cyclopropane proved to be less than 1%.

Table 2. The material and current yields of the products of the electrolysis of CCl_4 (c = 0.5 M) in $CHCl_3$ in the presence of various organic substrates.

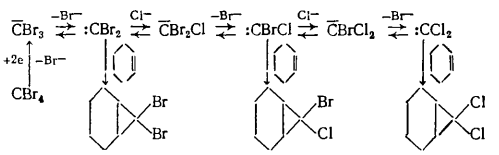
No. of expt.	Substrate	T, °C	Product	Yield, % w.r.t. material	Yield, % w.r.t. current	Refs.
1	$Me_2C{=}CHMe$	—5		—	66*	[14]
2		—5		90	45	[14]
3		0—5		75	32	[14]
4		25		90	12.5	[14]
5	Ph—HC=N—Ph	15—20	Ph—HC—N—Ph	80	19	[14]
6		—5		26	13	[15]
7		20		61	32	[15]
8	$PhCH_2OH$	27—28	$PhCH_2Cl$	83	36	[14]
9	Ph_2NH	20	Ph_2NCHO	95	58	[14]

Note. The electrochemical reduction was carried out at a lead cathode at j = 2–4 mA cm^{-2} in the presence of 0.35 M NR_4Br (R = alkyl) as the supporting electrolyte.
* According to Fritz and Kornrumpf,[4] the yield is 80%.

After the studies which confirmed the carbene mechanism of the processes considered above, it was important to assess the possibility of the synthetic application of the electrochemically generated carbenes. In particular, studies[14,15] on the electrolysis of CCl_4 at a lead cathode in $CHCl_3$ in the presence of organic substrates of different nature have shown that the dichlorocarbene generated in this way is capable of interacting under mild conditions with the C=C and C=N double bonds, forming cyclopropane and aziridine adducts (Table 2). According to the mechanism adopted,[16,19] the interactions with an alcohol and an amine (Table 2, experiments 8 and 9) proceed via the intermediate formation of ylide structures and lead to benzyl chloride and diphenylformamide respectively.

Dichlorocarbene reacts selectively with geraniol and geranyl acetate (Table 2, experiments 6 and 7) at the terminal double bond. The above reactions are highly selective. Cathodic electrolysis (lead cathode, j = 1–3 mA cm^{-2}) of CBr_4 in the presence of NBu_4BF_4 as the supporting electrolyte in cyclohexene-containing AN leads to the exclusive formation of 7,7-dibromonorcarane,[20] while the electrolysis of CBr_4 in CH_2Cl_2 in the presence of benzyltriethylammonium chloride as the supporting electrolyte results in a mixture of 7,7-dibromo, 7-bromo-7-chloro-, and 7,7-dichloro-norcaranes in an overall yield up to 85%. A number of reactions, inititated by the interaction of the electrochemically generated dibromocarbene with a chloride ion, take place during the electrolysis:[20]

Scheme 8



By varying the nature of the supporting electrolyte, it is possible to obtain predominantly (up to 65%) a particular dihalogeno-derivative (Scheme 8) as a mixture with other dihalogeno-derivatives obtained in an overall yield of ~80%.

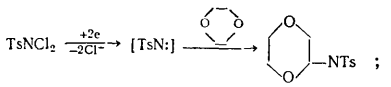
The examples considered above reveal good prospects for the creation of electrochemical processes for carbene synthesis, which may compete with traditional methods. It follows from the analysis of literature data that the formation of cyclopropane derivatives in high yields is promoted by carrying out the process at a relatively low current density (j = 1–5 mA cm^{-2}), a high alkene concentration relative to the source of the carbene, the use of halogenomethanes as solvents, and the use of tetraalkylammonium halides as supporting electrolyte salts, the readily soluble tetrabutylammonium salts being preferable. Furthermore, the replacement of NBu_4Br in the electrochemical synthesis of difluorocarbene from CF_2Br_2, for example, by NEt_4Br, promotes faster formation of a passivating layer of polytetrafluoroethylene on the electrode.[5] (We may note, however, that the question of the passivation of the electrode as well as the main causes of the low degree of conversion of the organic substrate has still been little investigated.)

2. Generation of carbene analogues

Nitrenes. The electrochemical reduction of organohalogen compounds makes it possible to generate also a nitrene, which is an important reaction intermediate.

On the basis of the results of preparative electrolysis in galvanostatic and potentiostatic regimes, the possibility of generating nitrenes from the corresponding *NN*-dichloro-derivatives at different electrodes (Pt, Zn, Cu, Hg, and C) has been demonstrated.[21–23] The electrochemical reduction of *NN*-dichloro-derivatives of toluene-*o*- and toluene-*p*-sulphonamides in the range of potentials 0.30–0.35 V takes place with transfer of two electrons.[21–23] As a result, the N–X (X = halogen) bond is ruptured in the first stage, as in the reduction of polyhalogenoalkanes. The fragmentation of the N-anion formed under these conditions (cf. Scheme 2) leads to a nitrene. Indeed, the electrochemical reduction of *NN*-dichlorosulphonamides at a platinum cathode in AN in the presence of $LiClO_4$ as the supporting electrolyte and 1,4-dioxane, with which nitrenes react,[24]

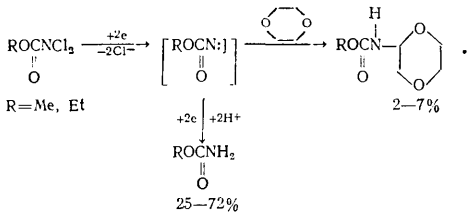
affording the products of insertion in a C–H bond, led to the formation of the corresponding adduct:



Ts = *p*-$MeC_6H_4SO_2$. 32%

Nitrenes can be generated similarly also in the cathodic reduction of *NN*-dichlorocarbamates under the same conditions,[22,23] but in this case the yield of the product of the insertion of the nitrene in a C–H bond of dioxane proved to be fairly low and the main reaction product was the corresponding carbamate:

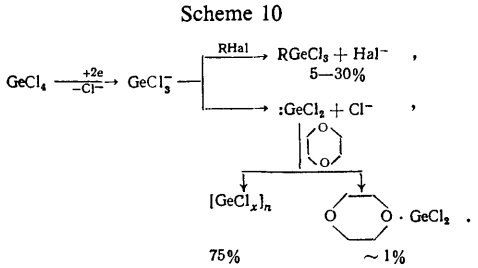
Scheme 9



Such a ratio of the electrolysis products is most probably due to the increased lability of the intermediate anion $ROCONCl^-$. In the case considered, the anion (IIa) (see Scheme 2) can fragment at the instant of its formation in the immediate vicinity of the surface of the electrode. The electron-deficient carbene-type or nitrene-type intermediate formed under these conditions is rapidly reduced at the electrode without having sufficient time to enter into the chemical reaction with the added substrate. The latter process can, in principle, partly compete with the reduction process. This (or a similar) situation evidently actually occurs in the electrolysis of *NN*-dichlorocarbamates (Scheme 9).

Germylenes. The electrochemical approach proved to be promising also for the generation of carbene analogues such as germylenes. This approach is based[25] on the electrochemical reduction of the readily available tetrachlorogermane, which had not been investigated previously. It has been established by methods involving the rotating disc electrode with a ring and electrolysis at a controlled potential [Pt cathode, AN with NEt_4ClO_4 as the supporting electrolyte, $E = -0.5$ V (rel. Ag/Ag^+)] that two electrons are transferred in the first stage of the electrochemical reduction of $GeCl_4$ with formation of the thermodynamically unstable anion $GeCl_3^-$:

Scheme 10



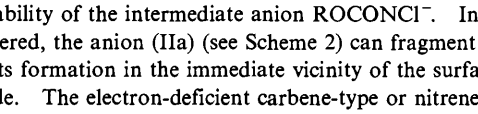
The formation of $GeCl_3^-$ has been confirmed,[26] in particular, by its interaction with organic halogeno-compounds added to the electrolysed solution. In the absence of RX (X = halogen), the $GeCl_3^-$ anion fragments with formation of a labile dichlorogermylene and then germanium subchlorides in 75% yield.[21] The intermediate formation of dichlorogermylene is demonstrated by its familiar[27] reaction with dioxane (Scheme 10), which leads to the formation of a stable complex.

3. The reduction of carbenes and nitrenes

It is quite evident that, since carbenes are electron-deficient species, they should be readily reduced. Therefore the very possibility of the cathodic generation of carbenes, which is at first sight surprising, depends on the lifetime of the intermediate carbanion (IIa) (see Scheme 2). In the case of extremely unstable anions, the carbene (or nitrene—see Section 2) formed on their fragmentation disappears rapidly via a cathodic reaction without having sufficient time to interact with a suitable substrate.

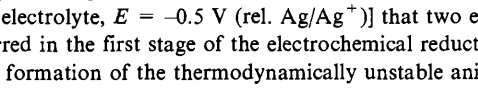
The mechanism of the cathodic reduction of carbenes was first discussed by McDonald and co-workers.[28,29] The authors chose as objects of their investigation diazo-compounds and no longer polyhalogeno-derivatives. It was postulated that the addition of an electron [$E_{p/2} = -1.68$ V (sat. c. e.), Pt cathode, DMF, NEt_4Br] initiates the fragmentation of these substances with evolution of a N_2 molecule, as happens, for example, during thermolysis. Their investigations made it possible to put forward the following mechanism of the reduction of diphenyldiazomethane:[28]

Scheme 11



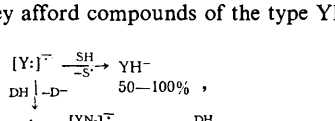
A similar mechanism has been proposed for the formation and subsequent reactions of the fluorenylidene radical-anion.[29] However, a more careful investigation of this process by high-temperature cyclic voltammetry showed that diazofluorene is reduced via a stage involving the dimerisation of the radical-anion of the diazo-compound.[30]

In subsequent studies,[31,32] it was shown by chronoammetry and low-temperature controlled potential electrolysis that the reduction of $(EtO_2C)_2CN_2$ and 2-diazo-5,5-dimethylcyclohexa-1,3-diene (diazodimedone) does indeed proceed with formation of the radical-anions of diazo-compounds. These radical-anions subsequently eliminate a N_2 molecule via a first-order reaction ($k = 8 \pm 2$ s^{-1} and 1.0 ± 0.1 s^{-1} at –38° and –84 °C respectively), forming carbene radical-anions:



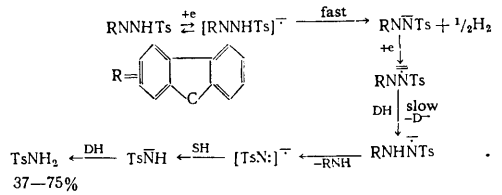
(*a*) $E_{p/2} = -1.0$ V [rel. Cd(Hg)/$CdCl_2$), cathode—vitreous carbon, DMF, NBu_4ClO_4; (*b*) $R_{p/2} = -1.82$ V (rel. Pt), Pt cathode, PrCN, NBu_4ClO_4.

In the absence of a proton donor, the above carbene radical-anions $[Y:]^-$ abstract preferentially a hydrogen atom, which leads to YH^-, while in the presence of benzoic acid, guanidinium perchlorate, or $(CF_3)_2CHOH$ they afford compounds of the type YH_2:



The carbene radical-anion $[PhC(O)\ddot{C}Ph]^-$, whose most characteristic reaction is the abstraction of a hydrogen atom from the solvent, is formed via a similar mechanism.[31] The formation

of the tosylnitrene radical-anion in the electrochemical reduction of fluorenone tosylhydrazone [$E_{p/2}$ = –0.28 V (sat. c. e.), Pt cathode, DMF, NBu_4ClO_4] was demonstrated recently with the aid of cyclic voltammetry, chronoammetry, and electrolysis at a controlled potential:[32]



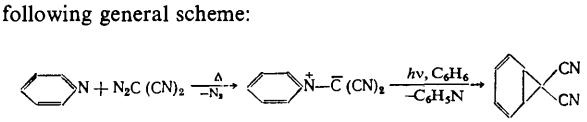
Thus the data presented above indicate the possibility of the generation and investigation of the properties of carbene and nitrene radical-anions. It may be expected that studies in this field will continue, especially to determine the oxidation-reduction as well as the electrophilic properties of carbenes and nitrenes.

III. Oxidation processes

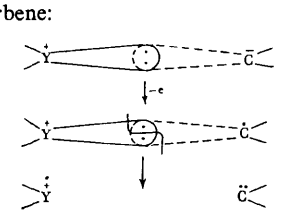
In the examples quoted above (see Section II), the electrochemical approach to the investigation of carbenes and their analogues was achieved in almost all cases via the generation of the corresponding thermodynamically unstable anions. However, from the methodological standpoint, one may be concerned with the electrochemical generation of not only anionic intermediates but also any other intermediates, whose fragmentation would be accompanied by the formation of carbenes. Data for the formation of such intermediates in the electrochemical oxidation of organic substances available at present are examined below.

1. Generation of carbenes

Ylides are known[1] to be formed or to behave as intermediates in many reactions of carbenes, carbenes with electron-accepting substituents leading to stable ylides. At the same time, even stable ylides can again become sources of carbenes on irradiation or under the influence of heat. For example, the processes described by Rieser and Friedrich[35] and by Streith et al.[36] can be represented by the following general scheme:



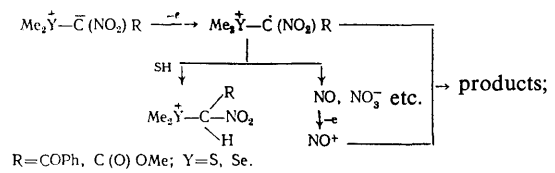
Thus the problem of generating carbenes from stable ylide structures reduces to breaking the ylide linkage in the required way by employing some kind of method involving a physical influence. One of such possibilities consists in the electrochemical oxidation of the ylide to the corresponding radical-cation, whose fragmentation would lead to a carbene:



Nitromethylides were selected as the objects of study.[37–39] The interest in these compounds was due to the possibility of generating a nitrocarbene in this way. The attempts to obtain nitrocarbenes from the corresponding α-nitrodiazo-compounds[40,41] or the alkali metal salts of polynitro- and halogenopolynitro-alkanes[42,43] proved unsuccessful.‡ Perhaps only the report[44] of the probable generation of arylnitrocarbenes from the silver salts of aryldinitromethanes is well founded: the thermolysis (at 100 °C) of these salts in the presence of alkenes leads mainly to isoxazoline *N*-oxide—the product of the 1,3-dipolar addition of an arylnitrocarbene.

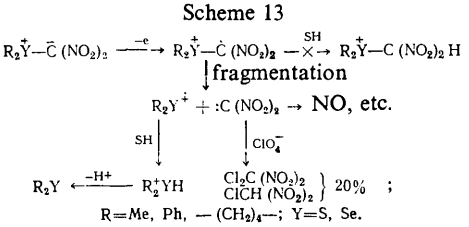
It has been shown[45] that on the polarisation curves for sulphonium§ and selenonium mononitromethylides, recorded at a platinum anode in AN in the presence of $LiClO_4$ as the supporting electrolyte, there is a single oxidation wave with $E_{1/2}$ = 1.4–1.5 V (rel. Ag/0.1 N Ag^+), its position depending on the structure of the ylide. However, the interaction of the radical-cations produced by the one-electron oxidation of the above ylides at E = 1.6 V (rel. Ag/0.1 N Ag^+) with the solvent, in which a hydrogen atom is abstracted and onium structures are formed, is faster than their fragmentation:[45]

Scheme 12



A number of indirect data[45] have indicated the possibility of the partial fragmentation of the mononitromethylide radical-cations during prolonged electrolysis, but the Y–C bond (Scheme 12) is not then involved. Thus the attempts to obtain nitrocarbenes by the anodic oxidation of nitromethylides were unsuccessful. The electrochemical oxidation of dinitromethylides (Scheme 13) yielded different results:

Scheme 13



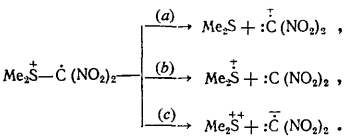
In the course of a study by the disc electrode method with a ring at an annular electrode, the formation of Me_2S was detected at the instant when dimethylsulphonium dinitromethylide was oxidised at the disc electrode; furthermore chloro-derivatives of dinitromethane were isolated from the products of the electrolysis [E = 1.9 V (rel. Ag/0.1 N Hg^+)] of the above dinitromethylide.[37] These data permit the conclusion that the intermediate radical-cation (see

‡ After the present review had been written, the formation of a nitrocarbene intermediate in the interaction of nitrodiazomethane with electron-enriched alkenes in the presence of rhodium acetate became known (P E O'Bannon, W P Dailey, *Tetrahedron Lett.*, 1988, **29** 987).

§ These conditions were standard for all the experiments described in this Section.

Scheme 13) fragments with retention of the sulphide and dinitromethyl fragments, i.e. at the Y—C bond.

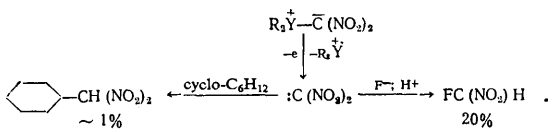
Scheme 14



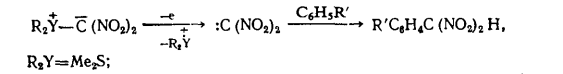
The enthalpies of the possible fragmentation pathways have been calculated in relation to the dimethylsulphonium dinitromethylide radical-cation by the MINDO/3 method.[37] The calculation showed that pathways (*a*) and (*c*) are more endothermic by 268 ± 63 and 1239 ± 63 kJ mol^{-1} than pathway (*b*) leading to the formation of a dinitrocarbene (Scheme 14). According to the calculated data, the dinitrocarbene has a singlet ground state, which is more favourable than the triplet state (the difference is 26 kJ mol^{-1} [37]).

A convenient criterion for the quantitative description of the electrophilicity of carbenes is known[46,47] to be the energy of the LUMO. This permits the calculation, within the framework of the MINDO/3 method, of the electronic structures of a series of singlet carbenes of the type :CR_2 [R = OH, F, Cl, CN, C(O)H, or NO_2] and makes it possible to demonstrate[37] that dinitrocarbene is the most electrophilic carbene in the series considered, because it has the lowest energy of the LUMO. This conclusion was then justified experimentally by introducing the electrochemically generated dinitrocarbene into reactions characteristic of electrophilic carbenes.[38,39]

The carbene mechanism explains satisfactorily the nature of the products formed in the electrochemical oxidation of dinitromethylides in the presence of cyclohexane and the fluoride ion:[38]

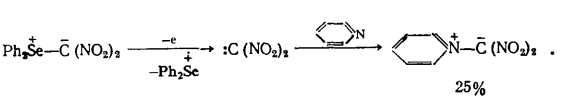


Like other electrophilic carbenes, dinitrocarbene interacts with the aromatic ring. The formation of the corresponding aryldinitromethanes can be explained by the insertion of dinitrocarbene in a C—H bond of the aromatic ring:[38]

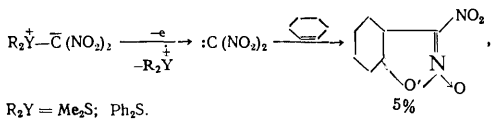


$R_2Y = Me_2S$;
R′ = H (yield 50%), Cl (40%), CN (15%), NO_2 (10%).

This process occurs even in the presence of substrates deactivated with respect to electrophilic attack. The electrolysis of dinitromethylides in the presence of pyridine entails the transylidation process:[39]



Another process characteristic of carbenes is their addition to a C=C bond. Calculation by the MINDO/3 method[38] for the interaction of dinitrocarbene with ethylene showed that the 1,3-addition of dinitrocarbene is preferable to the cyclopropane formation reaction. This conclusion agrees with data for the anodic electrolysis of dinitromethylides in the presence of cyclohexene:[38]

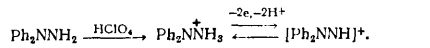


$R_2Y = Me_2S$; Ph_2S.

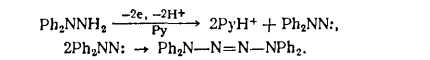
For comparison we may note that the dinitromethyl radical, which is also a highly electrophilic species,[48] generated by the electrochemical oxidation of the dinitromethane anion, either does not enter at all into reactions similar to those discussed above or it forms products in much lower yields.

2. Generation of carbene analogues

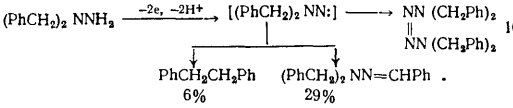
Nitrenes. Under anodic oxidation conditions, it is possible to generate also species such as nitrenes. As early as the beginning of the 1970's, investigators[49,50] studying the electrochemical oxidation of 1,1-disubstituted hydrazines concluded that this process includes a stage involving the intermediate formation of nitrenes. In this case, the anodic activation of the substrate is accompanied by fragmentation of a different type from that described in subsection 1, namely the elimination of protons. This conclusion is confirmed by data for the oxidation of 1,1-diphenylhydrazine at a platinum anode. In acidified (by the addition of $HClO_4$) AN, this process leads to the quantitative formation of the diphenyldiazenium cation (a protonated nitrene), which can be fully reconverted into the initial hydrazine by electrochemical reduction:[49]



On the other hand, in the presence of pyridine (Py), which facilitates the deprotonation of the intermediate radical-cations, the oxidation of 1,1-diphenylhydrazine proceeds via the formation of a nitrene, which rapidly dimerises to afford a quantitative yield of tetraphenyltetrazene:



Subsequently it was shown[51–53] that the electrochemical oxidation of *NN*-dibenzylhydrazine at E = 0.16 V (rel. Ag/Ag^+) at a platinum anode in AN in the presence of NBu_4BF_4 as the supporting electrolyte leads to bibenzyl, 1,1,4,4-tetrabenzyl-2-tetrazene, and benzaldehyde dibenzylhydrazone in material yields of 6, 10, and 29% respectively.[51] The mechanism of the formation of these substances includes stages with participation of a nitrene as a reactive intermediate:

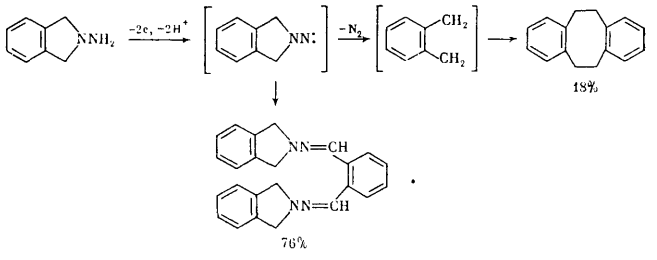


When the process is carried out on graphite (E = 0.37 V), tetrazene and the hydrazone are formed in 11 and 49% yields respectively, while bibenzyl is formed only in trace amounts.[51].

The electrochemical oxidation of *N*-aminodihydroisoindole at a platinum anode in the aprotic medium (AN) in the presence of the NBu_4BF_4 supporting electrolyte leads to 1,2,5,6-dibenzo-1,5-cyclooctadiene and a substituted *o*-xylylene[51,52] in current yields of 18 and 76% respectively. It is suggested that the two-electron oxidation of *N*-aminodihydroisoindole proceeds via the formation of a metastable

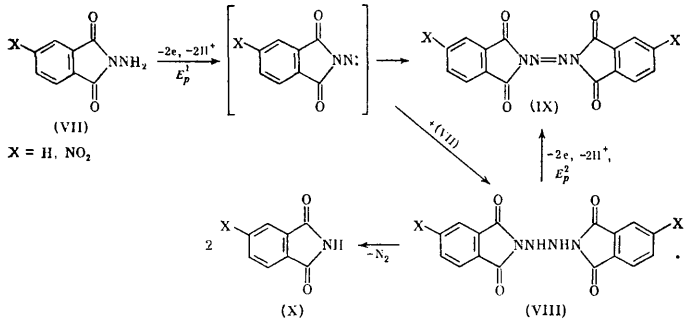
nitrene-type intermediate. The latter either splits off a N_2 molecule, forming a biradical whose dimerisation leads to a cyclooctadiene derivative, or gives rise to an *o*-xylene derivative via a complex mechanism:

Scheme 15



The electrochemical oxidation of *N*-aminophthalimide and of its tetrachloro- and 3-nitro-derivatives has been investigated[53] by cyclic voltammetry and electrolysis at a controlled potential (Pt anode, 0.1 N NBu_4BF_4 or 0.4 N $LiClO_4$ supporting electrolyte in AN). It was established that these compounds are oxidised in the first stage [E_p^1 = 0.99, 1.31, and 1.20 V (rel. Ag/Ag^+) respectively] with transfer of two electrons and two protons to the corresponding nitrenes, whose subsequent reactions lead to 1,4-diphthalotetrazans and 1,4-diphthalotetrazenes. In the second stage ($E_p^2 \geqslant 1.68$ V), the tetrazan is oxidised to the tetrazene. The overall process is described by Scheme 16:

Scheme 16



The yields and ratios of the products depend on the electrolysis conditions (Table 3). The tetrazene (IX) can be obtained also under conditions excluding the possibility of the electrochemical oxidation of the tetrazan (VIII) to the tetrazene (IX) (the controlled electrolysis potential is in the range of the E_p^1 potentials), which confirms the intermediate formation of a nitrene. During electrolysis, the tetrazan (VIII) decomposes partly with elimination of N_2, affording the product (X).

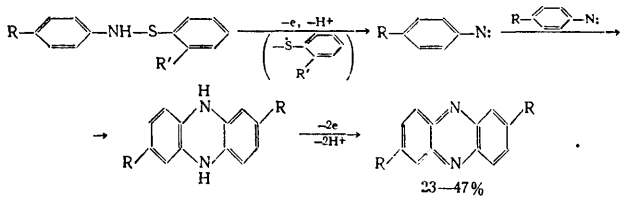
Table 3 shows that electrolysis at higher anodic potentials leads mainly to the formation of the tetrazene (IX), because the tetrazan (VIII), formed as a result of the insertion of the nitrene in a N—H bond of the initial aminophthalimide, is oxidised at the electrode to the tetrazene (IX). It is of interest to note that electrolysis at the potentials of the first wave in the presence of the NBu_4BF_4 supporting electrolyte leads preferentially to the formation of the tetrazan (VIII), while in the presence of the $LiClO_4$ supporting electrolyte the tetrazene (IX) is formed preferentially. Evidently ionic association effects influence significantly the mode of the reactions with participation of the intermediate nitrene. This question merits special consideration. At any rate, the examples presented demonstrate clearly the possibility of controlling the oxidation process (Scheme 16) depending on the electrolysis conditions.

Table 3. Yields of the products of the anodic oxidation of *N*-aminophthalimide (RH) and its nitro-derivative (RNO_2).[53]

Starting material	Supporting electrolyte	*E* in electrolysis, V(rel. Ag/Ag^+)	*Q*, F mol^{-1}	Current (material) yield		
				(VIII)	(IX)	(X)
RH	0.1 *N* NBu_4BF_4	1.3	0.5	80 (40)	—	—
RH	0.1 *N* NBu_4BF_4	1.9	0.5	0	64 (16)	—
RH	0.4 *N* $LiClO_4$	1.3	0.8	9 (6)	66 (27)	15 (12)
RH	0.4 *N* $LiClO_4$	2.0	1.0	0	86 (43)	10 (10)
RNO_2	0.4 *N* $LiClO_4$	1.3	0.8	0	51 (21)	29 (24)
RNO_2	0.4 *N* $LiClO_4$	2.0	1.0	0	64 (32)	21 (21)

Note. The oxidation was carried out at a platinum anode in AN.

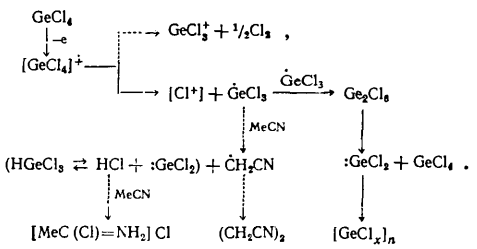
The nitrene can be generated under the conditions of anodic electrolysis also by the electrochemical oxidation of 2,4′-substituted benzenesulphenanilides.[52] On a graphite cathode in AN in the presence of the $NaClO_4$ supporting electrolyte, this process takes place with abstraction of one electron and leads to the cleavage of the S—N bond in the intermediate radical-cation (see Section II. 1). The nitrene formed enters into a intermolecular reaction involving insertion in a C—H bond, producing an adduct, which is subsequently oxidised at the electrode with transfer of two electrons and two protons, affording a phenazine:[52]



It is noteworthy that the electrochemical oxidation of *N*-aminophthalimides (see above) can compete successfully with the chemical methods for the synthesis of relatively unstable 2,3-unsubstituted tetrazans and tetrazenes, while the electrochemical oxidation of 4-substituted benzenesulphenanilides constitutes in essence a new method of synthesis of 2,7-disubstituted phenazines, which are otherwise difficult to obtain.[54–59]

Germylenes. According to Petrosyan et al,[26] dichlorogermylene is formed not only in the cathodic reduction of $GeCl_4$, as a result of the fragmentation of the intermediate anion $GeCl_4^-$ (see Section II, subsection 2), but also in the anodic oxidation of $GeCl_4$. The mechanism of the electrochemical oxidation of $GeCl_4$ (Pt anode, AN, $LiClO_4$) can be described[26] by the following scheme (the dashed

lines indicate minor processes) on the basis of data obtained by methods involving a rotating disc electrode with a ring and electrolysis at a controlled potential:



The intermediate radicals $\dot{G}eCl_3$ dimerise rapidly, affording Ge_2Cl_6, which readily disproportionates with formation of dichlorogermylene. The latter has been detected as a stable complex with dioxane (see Section II, subsection 2). The preparative electrolysis is accompanied by the formation of germanium subchlorides from dichlorogermylene in 60% yield. The intermediate radicals $\dot{G}eCl_3$ are capable of abstracting a hydrogen atom from AN, giving rise to $\dot{C}H_2CN$ and $HGeCl_3$, which indicates the presence in the reaction mixture of trace amounts of $(CH_2CN)_2$ and $[CH_3C(Cl)=NH_2]Cl$.

In conclusion, we may note that the observed ability of $GeCl_4$ to function as a source of dichlorogermylene under the conditions of both cathodic and anodic processes merits special attention and the development of electrochemical studies on these lines should lead to new interesting findings. The latter may prove valid also for the tetrachlorides of other Group IV elements, which have been hardly studied hitherto.

References

1. M Makosha, M Fedorynski *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1979, **24**(5) 466
2. A V Bukhtiyarov, E A Chernyshev, O V Kuz'min, et al. *Dokl. Akad. Nauk SSSR*, 1984, **278**(5) 1127
3. S Wawsonek, R C Duty *J. Electrochem. Soc.*, 1961, **108** 1135
4. H P Fritz, W Kornrumpf *Liebigs Ann. Chem.*, 1978, 1416
5. H P Fritz, W Kornrumpf *J. Electroanal. Chem. Interfacial Electrochem.*, 1979, **100** 217
6. H P Fritz, W Kornrumpf *J. Electrochem. Soc.*, 1980, **127** 128
7. G P Girina, V A Kokorekina, L G Feoktistov, et al. *IX Vsesoyuznoe Soveshchanie po Polyarografii: Tezisy Dokladov* (IX All-Union Conference on Polarography), Ust'-Kamenogorsk, 1987, Part 1, p. 137
8. M M Baizer, J L Chruma *J. Org. Chem.*, 1972, **37** (12) 1951
9. A J Fry, R G Reed *J. Am. Chem. Soc.*, 1972, **94**(24) 8475
10. E H Mottus, M R Ort *J. Electrochem. Soc.*, 1970, **117** 885
11. V A Afanas'ev, O S Korneva, G N Nesterenko, et al. *IV Vsesoyuznaya Konferentsiya po Khimii Karbenov: Tezisy Dokladov* (The IV All-Union Conference on the Chemistry of Carbenes: Abstracts of Reports), Izd. Nauka, Moscow, 1987, p. 112
12. R C Duty, G Biolchini, W Matthews *Anal. Chem.*, 1974, **46** 167
13. R C Duty, B V Pepich *J. Electrochem. Soc.*, 1980, **127** 1261
14. V A Petrosyan, M E Niyazymbetov, T K Baryshnikova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 91
15. T K Baryshnikova, M E Niyazymbetov, V S Bogdanov, V A Petrosyan *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2325
16. J Tabushi, Z Yoshida, N Takahashi *J. Am. Chem. Soc.*, 1971, **93** 1820
17. M Makosza, A Kacprowicz *Rocz. Chem.*, 1975, **49** 1627
18. W E Parham, J R Potoski *Tetrahedron Lett.*, 1966, 2311
19. M Saunders, R W Murray *Tetrahedron*, 1960, **11** 1
20. V A Petrosyan, M E Niyazymbetov, T Yu Rudashevskaya, L V Adaevskaya *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2183
21. T Fuchigami, T Nonaka, K Iwata *J. Chem. Soc., Chem. Commun.*, 1976, 951
22. T Fuchigami, T Nonaka *Chem. Lett.*, 1977, 1087
23. T Fuchigami, T Nonaka *Inform. Mater. Energy Theory Life*, 1985, **53** 582
24. D S Breslow *Nitrenes* (Edited by W Lwowski), Intersci. Publ., 1970, p. 287
25. V A Petrosyan, M E Niyazymbetov, S P Kolesnikov, V Ya Li *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 461
26. V A Petrosyan, M E Niyazymbetov, S P Kolesnikov, V Ya Li *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 1889
27. O M Nefedov, S P Kolesnikov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1966, 201
28. R N McDonald, J R January, K J Borhani, M D Hawley *J. Am. Chem. Soc.*, 1977, **99** 1268
29. R N McDonald, K J Borhani, M D Hawley *J. Am. Chem. Soc.*, 1978, **100** 995
30. V D Parker, D Bethell *Acta Chem. Scand. Ser. B*, 1980, **34** 617
31. D A van Galen, M P Young, M D Hawley, R N McDonald *J. Am. Chem. Soc.*, 1985, **107** 1465
32. D A van Galen *J. Electrochem. Soc.*, 1986, **133** 441
33. D Bethell, L J McDowall, V D Parker *J. Chem. Soc., Chem. Commun.*, 1984, 308
34. D A van Galen, J H Barnes, M D Hawley *J. Org. Chem.*, 1986, **51** 2544
35. J Rieser, K Friedrich *Liebigs Ann. Chem.*, 1976, **764** 666
36. J Streith, A Blind, J M Cassal, C Sigwalt *Bull. Soc. Chim. Fr.*, 1969, 948
37. V A Petrosyan, M E Niyazymbetov, V D Semenov, et al. *IV Vsesoyuznaya Konferentsiya po Khimii Karbenov: Tezisy Dokladov* (The IV All-Union Conference on the Chemistry of Carbenes: Abstracts of Reports), Izd. Nauka, Moscow, 1987, p. 112
38. V A Petrosyan, M E Niyazymbetov, V V Semenov, et al. *IV Vsesoyuznaya Konferentsiya po Khimii Karbenov: Tezisy Dokladov* (The IV All-Union Conference on the Chemistry of Carbenes: Abstracts of Reports), Izd. Nauka, Moscow, 1987, p. 116
39. V A Petrosyan, V N Solkan, M E Niyazymbetov, et al. *IV Vsesoyuznaya Konferentsiya po Khimii Karbenov: Tezisy Dokladov* (The IV All-Union Conference on the Chemistry of Carbenes: Abstracts of Reports), Izd. Nauka, Moscow, 1987, p. 114
40. U Schöllkopf, P Markush *Liebigs Ann. Chem.*, 1971, **753** 143
41. U Schöllkopf, P Markush *Liebigs Ann. Chem.*, 1971, **753** 147
42. K Torssell, R Rynode *Ark. Kemi.* , 1965, **25**(6) 625
43. A Rahman, L Clapp *J. Org. Chem.*, 1976, **41** 122
44. E Contouli-Argyropoulon, N E Alexandron *J. Org. Chem.*, 1980, **45** 4158
45. M E Niyazymbetov, V A Petrosyan, V V Semenov, S A Shevelev *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1332
46. R Moss *Acc. Chem. Res.*, 1980, **13** 58
47. S Stinson *Chem. Eng. News*, 1979, **57** 20

48. V A Petrosyan, M E Niyazymbetov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 368
49. G Gauguis, M Genies *Tetrahedron Lett.*, 1970, 2903
50. G Gauguis, B Chaband, M Genies *J. Electroanal. Chem. Interfacial Electrochem.*, 1972, **40** 6
51. T Fuchigami, T Sato, T Nonaka, J K Lee *J. Chem. Soc. Jpn., Chem. Ind. Chem.*, 1984, (11) 1769
52. T Fuchigami, T Nonaka *Denki Kagaku*, 1983, **51**(1) 133
53. T Fuchigami, T Sato, T Nonaka *Electrochem. Acta*, 1986, **31** 365
54. H Sayo, K Mori, A Ueda, N Morimoto *Chem. Pharm. Bull.*, 1977, **25** 525
55. H Sayo, K Mori, A Ueda, T Michida *Chem. Pharm. Bull.*, 1978, **26** 1682
56. H Sayo, K Mori, T Michida *Chem. Pharm. Bull.*, 1979, **27** 2316
57. H Sayo, K Mori, T Michida *Chem. Pharm. Bull.*, 1980, **28** 3707
58. H Sayo, K Mori, T Michida *Chem. Pharm. Bull.*, 1981, **29** 2598
59. H Sayo, K Mori, T Michida *Chem. Pharm. Bull.*, 1982, **30** 3782

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Halogen-containing carbenes

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ABSTRACT. The electronic and steric influence of the substituents at a multiple bond and of the presence of a heteroatom in the molecule on the reactivity of compounds in relation to halogenocarbenes is examined. The mechanisms of the interaction of carbenes with single bonds are discussed and data on new methods for the generation of halogenocarbenes are reported.

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I. Introduction

Halogenocarbenes are used more often than other carbenes because of both their relatively ready availability and the synthetic importance of halogenocyclopropanes and other compounds obtained with the aid of halogenocarbenes. In terms of the extent to which these carbenes have been investigated as regards their thermodynamic properties, their structure (by quantum-chemical methods), and their simplest gas-phase reactions, this group of carbenes is inferior only to methylene and, partly, phenylcarbenes.

It has been shown in recent years that all mono- and di-halogenocarbenes have a singlet ground state. According to non-empirical calculations, the energy differences between the singlet and triplet states of carbenes are as follows (kJ mol^{-1}; the experimental values are given in brackets): CH_2 −46(−38);[1] CHF 55 ± 8 (< 63); CHCl 23 ± 8; CHBr 17 ± 8;[2] CF_2 205; CCl_2 71; CBr_2 46.[3] The enthalpies of formation ΔH_f^0 (singlet) of a number of carbenes have been determined experimentally (kJ mol^{-1}): CH_2 425 ± 2; CF_2 −180 ± 8; CClF 46 ± 4; CCl_2 238. We may also indicate the ionisation potentials of the same carbenes (eV): CH_2 (triplet) 10.396; CF_2 12.24 ± 0.01; CFCl 10.9 ± 0.3; CCl_2 9.76.[4] There have been numerous studies in which the geometrical structures of halogenocarbenes have been determined experimentally or calculated.[1–4]

This review deals with questions of the reactivity of halogenocarbenes generated in the liquid phase, namely the influence of electronic and steric factors and also the influence of the heteroatom in the substrate on the rate of reaction. Data are presented on new methods for the generation of halogenocarbenes.

II. Reactions with unsaturated compounds

This process has been investigated in greatest detail. The interaction of halogenocarbenes with unsaturated compounds leads to halogen-containing strained cyclic systems, which can be used as synthons in organic synthesis. On the other hand, this reaction is the simplest cheletropic process and has therefore attracted the attention of theoretical chemists.

1. The influence of the electronic effects

In order to determine the reactivity of double bonds in relation to halogenocarbenes, the method of competing reactions was already used in the first investigations. It was established that the relative rate constants are correlated with the σ^+ constants of the substituents in the aromatic ring for the reactions of dichlorocarbene with ring-substituted styrenes (−0.42),[5] 1-arylbuta-1,3-dienes (−0.42),[6] 2-arylbuta-1,3-dienes (−0.36),[7] 2-arylpropenes (−0.38),[8] 2-arylbut-1-enes (−0.37),[7] methyl esters of substituted cinnamic acids (−0.33), and arylideneanilines (−0.36).[9] The type of the correlation equation and the negative sign of the ρ constant (given above in brackets) indicate a transition state in which the reaction centre is positively charged and is involved in a direct polar conjugation with the substituent.

In the interaction with diene, triene, and tetraene hydrocarbons, dichlorocarbene adds to the terminal double bond. Its reactivity in the series buta-1,3-diene (0.48), *trans*-hexa-1,3,5-triene (1.27), styrene (1.0), 1-phenylbuta-1,3-diene (1.87), 1-phenylhexa-1,3,5-triene (2.02), 1-phenylocta-1,3,5,7-tetraene (2.02), and 2-phenylbuta-1,3-diene (4,38) is satisfactorily correlated with the localisation energies of the methylene carbon atom (L_r^+) calculated by the SCF PPP method as the difference between the energies of the π electrons of the hydrocarbon and the carbonium formed from it after the removal of the CH_2 fragment:[10,11]

$$\lg k_{\text{rel}}^{CCl_2} = -(0.57 \pm 0.05)L_r + 11.7; \quad r = 0.978; \quad s = 0.07, \; n = 7.$$

Similar correlations with the ionisation potentials (IP) have been observed for conjugated hydrocarbons ($\lg k = 4.53 - 0.53\text{IP}$; $r = 0.99$) and for non-conjugated hydrocarbons ($\lg k = 10.17 - 1.05\text{IP}$; $r = 0.99$).

For the estimation of the selectivity of the carbene, Moss proposed the carbene selectivity index m_{CXY} (relative to dichlorocarbene) calculated from the equation[12]

$$m_{CCl_2}^{CXY} = \lg (k_i/k_0)^{CXY} / \lg (k_i/k_0)^{CCl_2}. \quad (1)$$

The values of m_{CXY} can be calculated from the constants σ_R^* and σ_I of the substituents at the carbene centre by the equation[13,14]

$$m_{CXY} = -1.10 \sum_{XY} \sigma_R^+ + 0.53 \sum_{XY} \sigma_I - 0.31. \quad (2)$$

The selectivity of the carbene increases with increasing π-donor and σ-acceptor effects of the substituents at the carbene centre (Table 1). For $m_{CXY} \leqslant 1.5$, the carbene exhibits electrophilic properties (dihalogenocarbenes). Carbenes with nucleophilic properties [dimethoxycarbene, dimethylamino(methoxy)carbene] have a selectivity index $\geqslant 2.2$. Carbenes having a selectivity index in the range $1.5 < m_{CXY} < 2.2$ are ambiphilic: they react as electrophilic species with nucleophilic alkenes and they react as nucleophiles with an electrophilic double bond. Such carbenes include chloro(methoxy)carbene,[15,16] chloro(phenoxy)carbene,[17,18] fluoro(phenoxy)carbene,[19] and fluoro(methoxy)carbene.[13,14]

Table 1. The selectivity indices (m_{CXY}) of halogenocarbenes in reactions with alkyl- and aryl-ethylenes.

Carbene	Alkylethylenes				Arylethylenes	
	(1)	(2)	(3)	(4)	(1)	(2)
$BrCCO_2Et$	0.29	0.26	—	—	—	—
ClCClC=CCl_2	0.38*	0.34*	—	—	—	—
cyclo-C_3H_5CCl	0.41	0.73**	—	—	—	—
MeCCl	0.50	0.58	0.59	—	—	—
PhCBr	0.70	0.64	1.40 (0.50) ***	—	—	—
PhCCl	0.83	0.71	1.43 (0.59) ***	—	—	—
CBr_2	0.65	0.82	1.84	0.62	0.64	0.66
PhCF	0.89	0.96	1.59 (0.95)***	—	—	—
CFBr	0.96	1.18	—	1.03	0.80	0.83
CCl_2	1.00	0.97	0.98	1.00	1.00	1.00
CFCl	1.28	1.22	1.25	1.23	0.94	0.91
CF_2	1.48	1.47	1.48	1.43	0.83	0.79
ClCOMe	—	1.59****	—	—	—	—
ClCOPh	—	1.59****	—	—	—	—
FCOPh	—	1.74****	—	—	—	—
FCOMe	—	1.85	—	—	—	—

Note. The indices m_{CXY} have been calculated from Eqns. (1)–(4); the ratios k_i/k_0 in Eqn. (1) were taken from the literature.[13,14,22,23]

* According to the data of Kostikov and de Miegere.[20]

** According to Moss et al.,[21] the difference from the value obtained by Eqn. (1) is due to the different conformation of the carbene as a result of steric interactions.

*** Calculated for the conformation with the benzene ring rotated by 90°.

**** The ambiphilicity of carbenes was demonstrated.[15,19]

The dependence of the selectivity of the carbene on the series of alkenes selected for its determination has been demonstrated for the reactions of dihalogenocarbenes with alkylethylenes and styrenes.[5] Difluoro- and chlorofluoro-carbenes exhibit a greater selectivity in reactions with alkylethylenes than dichlorocarbene, while in reactions with ring-substituted styrenes they actually show a lower selectivity (Table 1).

Schoeller and co-workers[24–26] demonstrated within the framework of the one-electron perturbation theory that the selectivity index S can be defined by the following equation

$$S \equiv \partial(\Delta E)/\partial\Delta = \partial(\delta E_I + \delta E_{II})/\partial\Delta \,, \qquad (3)$$

where

$$\delta E_I = \langle\pi|H|p\rangle^2 \cdot (E_p - E_\pi)^{-1};\ \delta E_{II} = \langle\sigma|H|\pi^*\rangle^2 \cdot (E_\sigma - E_{\pi^*})^{-1};\ E_\sigma,\ E_p,\ E_\pi,$$

and E_σ, E_p, E_π, and E_{π^*} are the energies corresponding to the HOMO and LUMO of the carbene and the alkene. The selectivity indices calculated by Eqn. (3) are listed in Table 1. The values obtained agree well with the experimental data and data calculated by Eqn. (2). In the case of halogeno(phenyl)carbenes, a good agreement has been obtained for the conformation in which the benzene ring has been rotated by 90° (the values are given in brackets). The application of the molecular orbital perturbation method permits the calculation of the selectivity index of the carbene by means of the equation

$$m_{CXY} = d^X d^Y \Delta_{i0}^{CXY}/\Delta_{i0}^{CCl_2}, \qquad (4)$$

where d^X and d^Y are empirical constants of the substituents at the carbene centre, $\Delta_{i0}^{CXY} = (\varepsilon_{HOMO}^{i} - \varepsilon_{LUMO}^{CXY})^{-1} - (\varepsilon_{HOMO}^{0} - \varepsilon_{LUMO}^{CXY})^{-1}$ and ε_{HOMO}^{i}, ε_{HOMO}^{0}, and ε_{LUMO}^{CXY} are respectively the orbital energies of the HOMO of the ith and standard alkenes and of the LUMO of the carbene (Table 1).

Calculations by non-empirical methods have confirmed the dependence of the selectivity of the carbene on the relative positions of the frontier orbitals of the carbene and the alkene.[13] For electrophilic carbenes, the main contribution comes from the interaction of the unoccupied p orbital of the carbene with the HOMO (π) of the alkene, while for nucleophilic carbenes the main contribution is that of the interaction of the HOMO (σ) of the carbene with the LUMO (π*) of the alkene. For ambiphilic carbenes, the selectivity is appreciably influenced by the substituents at the double bond of the alkene: electron-donating substituents promote the manifestation of the electrophilic properties by the carbene, while electron-accepting substituents promote the manifestation of nucleophilic properties.

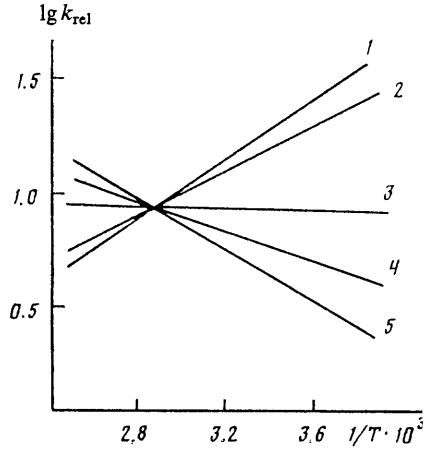


Figure 1. Temperature dependence of the relative reactivities of dihalogenocarbenes ($\lg k_{rel}$) for the 2,3-dimethylbut-2-ene/2-methylpropene pair[27]: *1*, :CF_2; *2*, :CFCl; *3*, :CCl_2; *4*, :CBrCl; *5*, :CBr_2.

The systematic study of the selectivity of dihalogenocarbenes at different temperatures undertaken by Giese and co-workers[27–29] demonstrated that the selectivity of dichlorocarbene in relation to the 2,3-dimethylbut-2-ene/2-methylpropene pair does not vary, while for

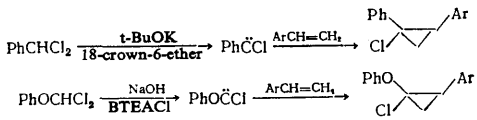
other carbenes it depends on temperature (Fig. 1). At 90° + 10 °C, the selectivity of all the dihalogenocarbenes is the same, while at higher temperatures fluorine-containing carbenes proved to be less selective than other carbenes but dibromocarbene is more selective. Thus, for the chosen pair of alkenes the reaction with dichlorocarbene can be assigned to the isoenthalpic series. This has to be set against the finding that the enthalpy of activation for the reaction of dibromocarbene with isobutene is higher than for the reaction with tetramethylethylene ($\Delta\Delta H^{*}$ = 6 kJ mol^{-1}). On the other hand, the enthalpy of activation for the reaction of difluorocarbene with isobutene is smaller than for the reaction with tetramethylethylene ($\Delta\Delta H^{\#}$ = −11 kJ mol^{-1}), which suggests that the entropy of activation plays the main role. The selectivity of dichlorocarbene in relation to the series of 2-arylpropenes is also independent of temperature ($\Delta\Delta H^{\#}$ = 0). On the other hand, the enthalpies of activation for the reactions of alkylpropenes increase with increase in the degree of branching of the alkyl group.[30] The selectivity index of dibromocarbene (m_{CBr_2}) depends on the degree of substitution at the double bond and assumes the following values: 1.1 for monosubstituted alkenes, 0.86 for disubstituted alkenes, and 0.73 for trisubstituted alkenes, which corresponds to the usual relation between activity and selectivity: a less reactive alkene exhibits a greater selectivity.[31]

Table 2. The relative rate constants for the reactions of chloro(phenyl)- and chloro(phenoxy)-carbenes with ring-substituted styrenes ($RC_6H_4CH=CH_2$) at different temperatures.[17,18]

R	PhCCl at different T (K)			PhOCCl at different T (K)			
	260	300	320	280	300	320	298*
p-MeO	1.44	1.65	2.22	0.42	0.74	0.83	1.95
p-Me	1.18	1.38	1.46	0.68	0.88	0.91	1.32
H	1.0	1.0	1.0	1.0	1.0	1.0	1.0
p-Cl	0.65	0.61	0.54	1.77	1.12	1.02	1.17
m-Br	—	—	—	2.39	1.53	1.24	—
ρ	−0.58	−0.76	−1.06	1.11	0.40	0.23	—

*Photolysis of chloro(phenoxy)diazirine.[17,18]

The selectivity of chloro(phenyl)carbene in reactions with styrene increases with increasing temperature,[32] while the selectivity of chloro(phenoxy)carbene, generated from dichloro(phenoxy)methane and NaOH, diminishes (Table 2):[33]



where BTEACl = benzyltriethylammonium chloride.

It may be that the different temperature dependences of the selectivities of these carbenes are because chloro(phenyl)carbene is electrophilic while chloro(phenoxy)carbene is nucleophilic. It has been shown[17,18] that chloro(phenoxy)carbene, generated by the photolysis of chloro(phenoxy)diazirine, is ambiphilic in the reactions with both styrenes (see Table 2; k_{rel} = 1.42 and 1.33 for *p*-trifluoromethylstyrene and *p*-nitrostyrene) and with other alkenes (for example, k_{rel} is 0.36 for hex-1-ene, 1.00 for pent-2-ene, 7.3 for isobutene, 3.0 for tetramethylethylene, 3.7 for methyl acrylate, and 7.3 for acrylonitrile).

The absolute rate constants for the interaction of arylhalogenocarbenes, generated by the flash photolysis of the corresponding arylhalogenodiazirines, with unsaturated compounds have been measured.[34] It follows from the temperature dependence of the absolute rate constants for the reactions of chlorophenylcarbene with a series of alkenes that the reactions have a negative ethalpy and entropy of activation and that the changes in the enthalpy of activation are responsible for the observed series of reaction rate constants (Table 3).[35]

Table 3. Thermodynamic parameters of the reactions of chloro(phenyl)carbene with alkylethylenes.[35]

Alkene	$\Delta\Delta H^{\neq}$, kJ mol^{-1}	$\Delta\Delta S^{\neq}$, J mol^{-1} K^{-1}	$\Delta\Delta G^{**}$, kJ mol^{-1}	k_{abs}^{*}, litre mol^{-1} s^{-1}	k_{rel}^{*}
2,3-Dimethylbut-2-ene	−18.4	−96	9.2	$3.3\cdot10^{8}$	1.0
2-Methylbut-2-ene	−15.5	−92	11.3	$1.6\cdot10^{8}$	0.48
trans-pent-2-ene	−6.6	−84	18.0	$1.0\cdot10^{7}$	0.030
Hex-1-ene	−6.3	−88	18.8	$3.8\cdot10^{6}$	0.012

*At 25 °C.
**From k_{abs}.

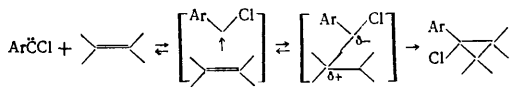
In order to account for the negative activation energy, the hypothesis was put forward that an intermediate complex between the carbene and the alkene is formed and that it can subsequently either decompose into the initial reactants or can give rise to cyclopropane. In all probability, this is either a π-complex of the carbene with the alkene or a "close pair" of the reactants in the solvent cage:

$$\ddot{\text{C}}\text{Cl}_2 + \text{alkene} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \ddot{\text{C}}\text{Cl}_2/\text{alkene},$$

$$\ddot{\text{C}}\text{Cl}_2/\text{alkene} \xrightarrow{k_2} \text{cyclopropane},$$

$$k_{obs} = k_1k_2/(k_{-1}+k_2).$$

The rate constants for the reactions of halogenophenylcarbenes with alkenes increase with increasing pressure in the reaction system and are independent of the solvent employed, which is consistent with the reversible formation of a carbene–alkene complex or an early transition state:



The introduction of electron-donating substituents into the aromatic ring stabilises the carbene and lowers its reactivity, while the introduction of electron-accepting substituents increases the reactivity (Table 4). Electron-accepting substituents favour the

conversion of the transition state into the final cyclopropane, stabilising the negative charge on the carbene atom, while the dissociation of the complex into the initial carbene and alkene is hindered. On the other hand, if the substituent is electron-donating, the degree of dissociation of the complex into the initial reactants increases. However, the data in Table 4 show that the selectivity of the carbene hardly changes when the substituent in the aromatic ring is altered. On the other hand, it does depend significantly on the character of the halogen atom at the carbene centre.[38] It is seen from Table 4 that the rate of addition to the double bond increases with decrease in the selectivity of the carbene in the sequence $F\ddot{C}Ph > Cl\ddot{C}Ph > Br\ddot{C}Ph$.

Table 4. The absolute rate constants for the addition of 4-$RC_6H_4\ddot{C}X$ to alkenes (k_{abs}, litre mol^{-1} s^{-1}) at 25 °C.[37,38]

X	R	10^6k			
		2,3-dimethylbut-2-ene	2-methylbut-2-ene	*trans*-but-2-ene	hex-1-ene
F	H	160	53	2.4*	0.93
Br	H	380	180	12*	4.0
Cl	MeO	14	7.7	0.44	0.13
Cl	Me	120	49	1.8	0.62
Cl	H	280	130	5.5	2.2
Cl	Cl	330	180	7.5	2.3
Cl	CF_3	1500	680	49	18
$\rho(\sigma^+)$ for $RC_6H_4\ddot{C}Cl$		1.5	1.4	1.5	1.6

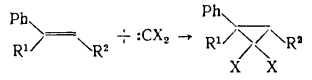
* Values for *trans*-pent-2-ene.

According to non-empirical calculations, complexes are not formed in the reactions of halogenocarbenes with alkenes (only complexes in a solvent cage are possible) and there is no activation barrier to cycloaddition.[39] The observed negative activation energies are probably a common feature of the reactions of all species with a high energy. In such cases the enthalpic activation barrier is absent and there is an entropic barrier. At low temperature, dichloro-, bromochloro- and dibromo-carbenes should then be non-selective and their reactions with alkenes should be diffusion-controlled.

The determination of the relative reactivities of deuterio-substituted 1-monosubstituted and 1,1-disubstituted ethylenes in relation to dichlorocarbenes showed that the "reverse" secondary isotope effect is observed for the CH_2 group in the given reaction ($k_H/k_D \simeq 0.73-0.80$), whereas for the CH group it is close to unity (0.90–0.94).[40] This result indicates a mechanism of the addition of the carbene to the C=C bond in which the carbene locks onto the methylene carbon atom of the double bond to a greater extent than onto the neighbouring atom.

2. The influence of steric effects

The study of reactions of dichloro- and dibromo-carbenes with α- and β-substituted styrenes showed that the reactivity of the double bond depends both on the type of its substitution and on the steric effects of alkyl groups:[41]



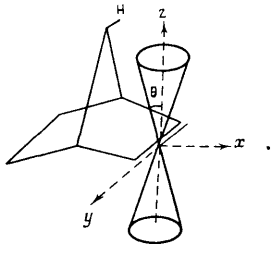
$$\lg k^{\beta}_{CCl_2} = -0.46 + 0.76 \lg k^{\alpha}_{CCl_2},$$
$$\lg k^{\alpha}_{CBr_2} = -0.20 + 0.84 \lg k^{\alpha}_{CCl_2},$$
$$\lg k^{\beta}_{CBr_2} = 0.94 \lg k^{\beta}_{CCl_2}.$$

The correlations obtained from the data in Table 5 between the reactivities of dichloro- and dibromo-carbenes show that α-alkylstyrenes are more sensitive than β-alkylstyrenes to changes in the substituent both at the double bond and at the carbene atom. This can be explained by the fact that in the transition state the carbene and the methylene group attacked by it are apparently in the *anti*-planar conformation.

Table 5. Relative rate constants k_{rel} for the reactions of substituted styrenes $Ph(R^1)C=CHR^2$ with dichloro- and dibromo-carbenes.[41]

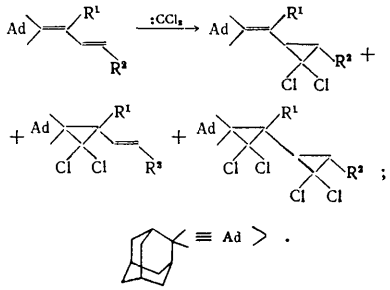
R^1	R^2	k_{rel}	
		CCl_2	CBr_2
Me	H	8.6±0.9	4.0±0.2
Et	H	5.7±0.4	2.6±0.2
iso-Pr	H	3.0±0.3	1.6±0.1
t-Bu	H	0.009±0.001	0.012±0.003
H	Me	1.9±0.2	1.8±0.2
H	Et	1.39±0.08	1.45±0.08
H	iso-Pr	0.67±0.03	0.69±0.05
H	t-Bu	0.010±0.005	—

The determination of the reactivities of the double bonds in bicyclic alkenes containing a *cis*-1,2-disubstituted C=C bond led to the conclusion that the approach of the carbene to the bond can be achieved only in a specific region of space, which can be represented by a cone whose axis (0*z*) passes through the centre of the double bond and is at right angles to it:[42]



The minimum angle of the cone (2θ) is about 60°. If any group (H atom) enters the cone located above the double bond, then the approach of the carbene is hindered. Fig. 2 presents the dependence of the reactivity of the double bond in relation to dichlorocarbene on the angle θ calculated for hydrogen atoms closest to the 0*z* axis for different molecules. With increase in the angle θ, the reactivity of the double bond rises, in agreement with the increase in the accessibility of the bond to the approach of the carbene. It is seen from the values of k_{rel} that the rate of addition of the carbene is a maximum for $\theta > 60°$ and that the reaction does not occur if $\theta < 30°$.

The additivity of the influence of the steric effects of the substituents at the double bond on the reactivity of the latter in the reaction of dichlorocarbene with adamantylidene-substituted 1,3-dienes and allenes has been established.[43] The reactivity of the double bond adjoining the adamantane ring is then low and mainly adducts involving the double bond remote from it are formed:



≡ Ad >.

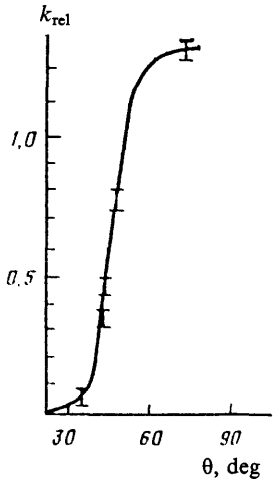
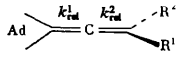


Figure 2. Dependence of the reactivity of the 1,2-disubstituted C=C bond on the angle θ.[40]

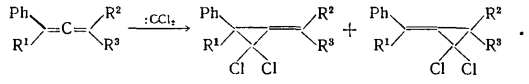
Comparison of the values of k_{rel} for allenes of the adamantane series shows that the reactivity of the double bond closest to the ring diminishes in proportion to the increase in the number of methyl groups at the C(3) atom, while the reactivity of the remote bond then increases.



R^1	R^2	k^1_{rel}	k^2_{rel}
H	H	0.47	0
H	Me	0.28	0.32
Me	Me	0	3.2

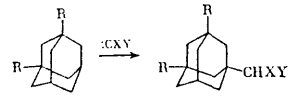
Comparison of the values of k_{rel} for the above allenes with model methylallenes has shown that the influence of the substituents at the C(3) atom of the allene system on the reactivity of the C(1)=C(2) bond can be represented by the equation $k_{rel} = (s'/s'')k_i$, where k_i is the relative rate constant for the reaction of the carbene with the C(1)=C(2) bond of the allene without a substituent at the C(3) atom and s' and s'' are coefficients taking into account the steric shielding of the double bond of the allene by the substituents at the C(3) atom from different sides of the plane of the C(1)=C(2) bond (s_H = 1, s_{Ad} = 0.36, s_{Me} = 0.16).

Adducts involving the most substituted double bond are formed exclusively in the interaction of dihalogenocarbenes with allene hydrocarbons containing aromatic substituents.[44] The reactivity of the bond adjoining the phenyl group can be estimated from the above equation in which the coefficient s for the substituents at the C(3) atom are 1.00 (H), 0.16 (Me), and 0.0 (Ph):

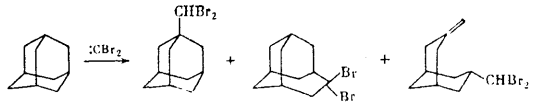


III. Reactions with saturated compounds

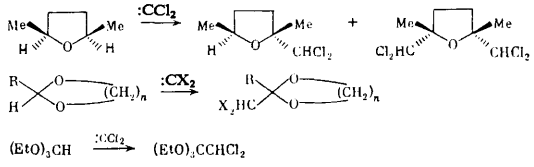
The interaction of halogenocarbenes with single bonds has been investigated much less than the interaction with a double bond. Halogenocarbenes are inserted fairly readily only in a tertiary C–H bond. Thus the reaction of dichlorocarbene, generated under phase-transfer conditions, with adamantane and 1-methyl- and 1,3-dimethyladamantanes leads to the formation of insertion products in high yields.[45] The reaction of dibromocarbene with adamantane results in the formation, apart from the product of insertion in a tertiary C–H bond, also of products involving the expansion and cleavage of the ring:[47]



R=H, Me, X=Y=Cl (Ref.45);
R=H, X=Y=Br (Ref.45);
R=H, X=Cl, Y=CCl=CCl$_2$ (Ref.46).



Dihalogenocarbenes are inserted, with moderate yields, in the C–H bonds of alkyl-substituted aromatic hydrocarbons: ethylbenzene, cumene, and diphenylmethane.[48,49] The carbene is easily inserted in a C–H bond in the α-position with respect to a C–O bond, for example in tetrahydrofuran,[50] dioxolan,[51,52] dioxane,[52] and ethers:[51]

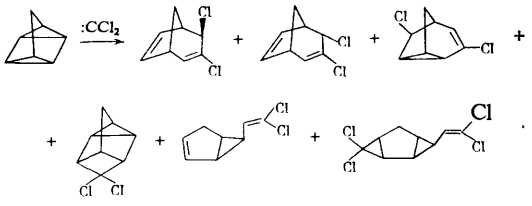


The interaction of dichlorocarbene with alkoxides leads to products of the insertion of the carbene in the α-CH bond in satisfactory yields:[53]

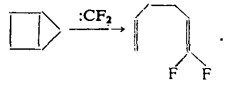
$$RCH_2OLi \xrightarrow[THF]{CHCl_3,\ t\text{-}BuOLi} RCH(OH)CHCl_2,$$

R=Ph, CH=CH$_2$, CH=CHPh.

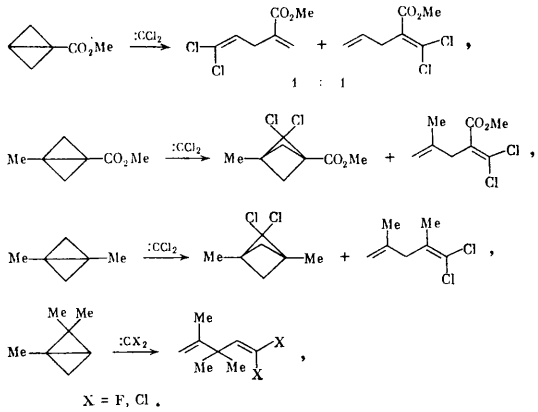
The interaction of dihalogenocarbenes with quadricyclane affords a low yield of a mixture of the same adducts as with norbornadiene but in other proportions:[54,55]



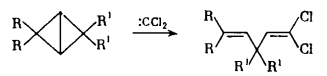
Difluorocarbene, generated from bromodifluoromethyltriphenylphosphonium bromide in the presence of KF, reacts with bicyclo[2.1.0]pentane, producing a very low yield (0.5%) of 1,1-difluorohexa-1,5-diene.[56] An adduct is not formed with bicyclo[3.1.0]hexane:



The interaction of 1,3-disubstituted bicyclobutane derivatives with dichlorocarbene leads to bicyclo[1.1.1]pentane or penta-1,4-diene derivatives depending on the nature of the substituents. The methyl ester of bicyclobutane-1-carboxylic acid reacts with dichlorocarbenes, forming only 1,1-dichloro-2-methoxycarbonylpenta-1,4-diene and the corresponding 4-methoxycarbonyl derivatives,[57] the reaction of the methyl ester of 3-phenylbicyclobutane-1-carboxylic acid gives rise to bicyclopentane derivatives, while the methyl ester of 3-methylbicyclobutane-1-carboxylic acid affords a mixture of substituted bicyclopentane and penta-1,4-diene.[58,59] The reaction of 1,3-dimethylbicyclobutane with dichlorocarbene produces a mixture of 2,2-dichloro-1,3-dimethylbicyclo[1.1.1]pentane and 1,1-dichloro-2,4-dimethylpenta-1,4-diene, whose ratio depends on the method of generation of the carbene.[60] The reaction of 1,2,2-trimethylbicyclobutane with both dichlorocarbene[61] and difluorocarbene[56] produces only a 1,1-dihalogeno-3,3,4-trimethylpenta-1,4-diene:



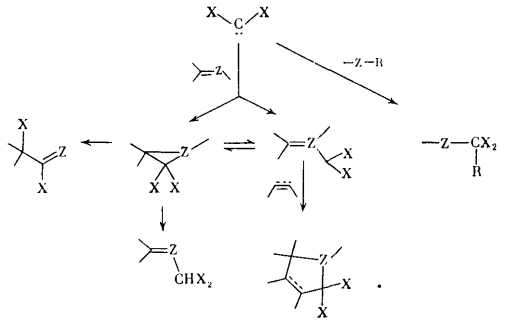
The reaction of 2,2,4,4-tetraalkylbicyclobutanes with dichlorocarbene afford only substituted penta-1,4-dienes:[62]



According to quantum-chemical calculations, the interaction of singlet carbene with bicyclobutane can proceed as a result of the attack by the free 2*p* orbital of the carbene on the HOMO of the bicyclobutane, which is located mainly on the C(1)–C(3) bond. The approach of the carbene "from the side", leading to the formation of penta-1,4-diene, is then more favourable than attack "from above", which leads to bicyclopentane.[56]

IV. Reactions with compounds containing heteroatoms

When the molecule contains a heteroatom having an unshared electron pair, the carbene can interact with the latter, forming an ylide. The possible pathways in the reactions of a carbene with compounds containing a heteroatom are indicated schematically below:



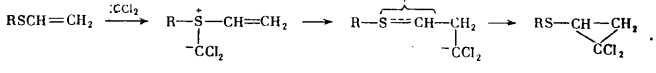
1. Oxygen- and sulphur-containing compounds

The ethers of 2,2-dihalogenocyclopropanols are formed in the reactions of dihalogenocarbenes with vinyl ethers.[63,64] In their reactions with dichlorocarbene, vinyl ethers are 10–20 times more reactive than the corresponding carbon analogues (alk-1-enes), which indicates an appreciable mesomeric involvement of the oxygen atom in the stabilisation of the transition state. It has been shown for a series of α-heterosubstituted styrenes $PhCX=CR^1R^2$, where X = OAlk, Cl, or Br, that the following relation holds:[65]

$$\lg k_{rel} = 10.41 - 18.2\ 2\Delta\varepsilon_j - 2.16m,$$

where $\Delta\varepsilon_f = \varepsilon_{\text{styrene HOMO}} - \varepsilon_{\text{carbene LUMO}}$ and m is the number of substituents at the β-carbon atom of the double bond.

The interaction of dichlorocarbene with unsaturated sulphides affords both cyclopropane derivatives[66,67] and the products of the dehydrochlorination of the latter.[67,68] Table 6 lists the relative rate constants for the addition of dichlorocarbene to vinyl ethers and vinyl sulphides. It is seen from these data that vinyl sulphides are 5–6 times more reactive than the corresponding vinyl ethers. This result cannot be explained solely by the different electronic influences of the group RX on the double bond. In its reactions with the sulphides, dichlorocarbene probably interacts not with the double bond but with the sulphur atom, forming an ylide, which then undergoes a 1,3-sigmatropic shift, affording a dipolar ion, which cyclises to cyclopropane:[69]

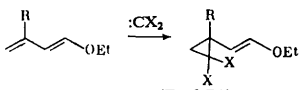


This hypothesis agrees with the correlation between the constants k_{rel} for the reactions of dichlorocarbene with vinyl sulphides, on the one hand, and the ionisation potentials of the unshared electron pair (IP) and the coefficient c_S of the sulphur atom involved in the

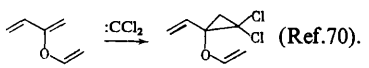
HOMO of the sulphides, on the other, in accordance with the equation

$$\lg k_{rel} = -(4.79 \pm 0.5) + (17.8 \pm 1.7) c_S^2/(IP - 6.8).$$

In reactions of dihalogenocarbenes with dienes containing an alkoxy-group, the carbene adds to the double bond at the end of the conjugation system or to a "cross-conjugated" bond:



R = H, Me; X = Cl (Ref.71)
R = H, X = Br (Ref.72)



In the reactions with dichloro- and dibromo-carbenes, 1,1-diethoxy-ethylene produces cyclopropanone ketals, which are converted into halogenoacrylic acid esters on heating. On the other hand, the spirocyclic dibromoketal is stable and can be used in syntheses:[73]

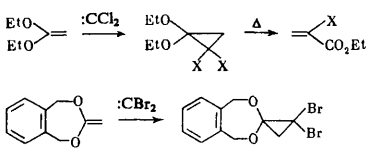
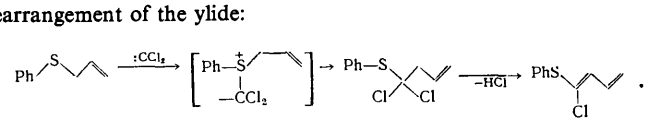


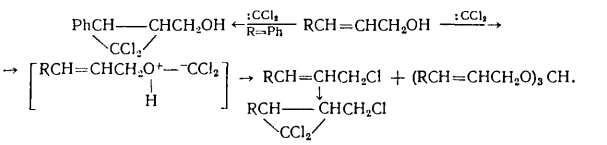
Table 6. The relative rate constants for the addition of dichlorocarbene to sulphides and ethers of the type $RXCH=CH_2$ relative to cyclohexene.

R	k_{rel}	
	X=S (Ref.69)	X=O (Ref.70)
Me	7.1	1.5
Et	—	1.7
n-Bu	10.1	1.7
iso-Bu	8.2	1.4
t-Bu	5.5	6.2
Ph	3.3	0.69
$CH_2=CH$	2.9	0.6

The interaction of dichlorocarbene, generated by the phase-transfer method, with allyl phenyl sulphide led to the isolation of 1-chloro-1-phenylthiobuta-1,3-diene,[74] obtained as a result of the dehydrochlorination of the product of the [2,3]sigmatropic rearrangement of the ylide:

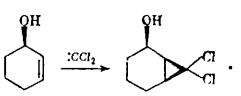


Dichlorocarbene, generated by the phase-transfer method, reacts with substituted allyl alcohols to form substituted (2,2-dihalogeno-cyclopropyl)carbinols in high yields.[75] The thermolysis of (bromodichloromethyl)phenylmercury in allyl alcohol yields allyl chloride, allyl formate, and chloroform.[76] The interaction of dichlorocarbene, generated under the conditions of phase-transfer catalysis, with allyl and cinnamyl alcohols proceeds via two pathways, involving the double bond and the hydroxy-group; in the case of allyl alcohol, 2,2-dichloro-1-chloromethylcyclopropane, triallyloxymethane, and allyl chloride are formed. The main product of the reaction with cinnamyl alcohol is 3,3-dichloro-1-hydroxy-methyl-2-phenylcyclopropane; in addition, 3-chloro-1-phenylprop-1-ene and 3,3-dichloro-1-chloromethyl-2-phenylcyclopropane are formed:[77]

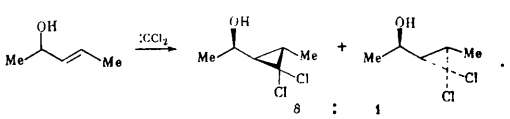


It has been shown by the methods of competing reactions that the ratios of the activities of the hydroxy-group (in both alcohols) and double bonds in cinnamyl alcohol, allyl alcohol, cinnamyl chloride, and allyl chloride are approximately 1 : 1.2 : 0.04 : 0.3 : 0.01 in reactions with dichlorocarbenes.

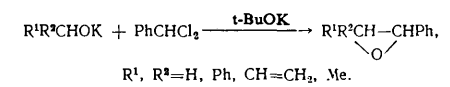
The reactions of cyclic allyl alcohols with dichlorocarbene readily give rise to dichlorocyclopropane derivatives. In conformity with the directing effect of the hydroxy-group, the reaction of 2-cyclohexenol gives rise to a mixture of the *syn*- and *anti*-products in proportions of 13 : 1, whereas 2-cycloheptanol and 2-cyclooctenol afford only the *anti*-adducts:



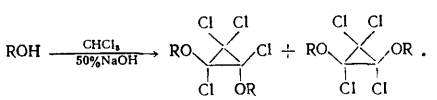
In the case of acyclic allyl alcohols, the most stable rotational isomer is converted into a dichlorocyclopropane and the reaction takes place predominantly from the side of the hydroxy-group:[78]



Chloro(phenyl)carbene, generated from benzylidene dichloride on treatment with potassium t-butoxide, reacts with alkoxides to form oxirans:[79]

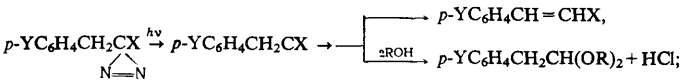


When dichlorocarbene was generated by the phase transfer method using ethanol-containing chloroform, 1,1,2,3-tetrachloro-2,3-diethoxycyclopropane was obtained.[80] A mixture of stereoisomeric 2,3-dialkoxy-1,1,2,3-tetrachlorocyclopropanes is also formed in the reactions with isobutyl and neopentyl alcohols,[81] while benzyl and phenylethyl alcohols afford the corresponding ortho-esters:



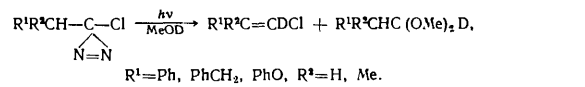
It follows from kinetic experiments that the reaction of benzylchlorocarbenes, obtained from the corresponding diazirines, with alcohols involves the insertion of the carbene in the O—H bond

of the alcohol dimer or oligomer via the electrophilic attack of the carbene on the unshared electron pair of the oxygen atom with the reversible formation of an ylide intermediate:[82,83]



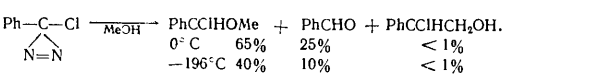
X=Cl, Br; Y=H, Me, Cl;
R=Me, Et, CH_2.

The study of the reactions of substituted benzylchlorocarbenes with MeOD showed that the carbene is partly protonated by the alcohol and that the subsequent elimination of the proton leads to an alkene or an ether:[84]

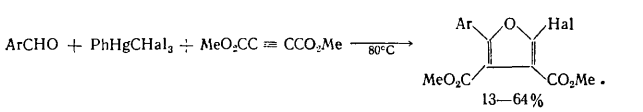


R^1=Ph, $PhCH_2$, PhO, R^2=H, Me.

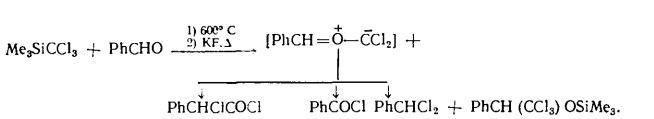
The photolysis of chloro(phenyl)diazirine in methanol at 0 °C and in a matrix at –196 °C showed that an increase in the yield of the products of the insertion of singlet chloro(phenyl)carbene in a C–H bond is not observed when the temperature is reduced and the principal reaction pathway remains the insertion in the O–H bond:[85]



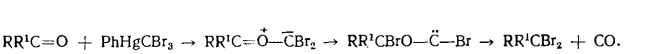
In the reactions of dichloro- and dibromo-carbenes, generated from phenyltrihalogenomethylmercury derivatives, with benzaldehydes, dihalogenocarbonyl ylides are formed. These have been detected in reactions with dipolarophiles:[86,87]



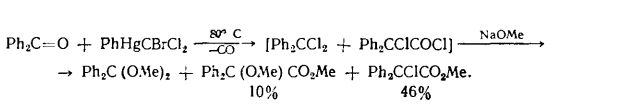
Vacuum flash pyrolysis of Me_3SiCCl_3 involves the formation, together with benzaldehyde, of dichlorocarbonyl ylide,[88] which then reacts according to the following mechanism:



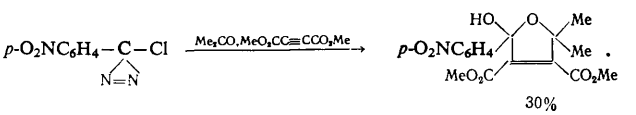
When $PhHgCBr_3$ is heated in the presence of aldehydes and ketones, a deoxygenation reaction is observed:[89]



In contrast to the reactions of dichlorocarbene derived from $PhHgCBrCl_2$ with aromatic aldehydes, it was not possible to detect carbonyl ylides in the reactions with aromatic ketones.[90] It has been suggested that for steric reasons the latter are readily converted in this instance into oxirans, whose reactions lead to the final products:[90]

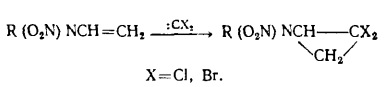


The reaction of chloro(*p*-nitrophenyl)carbene with acetone produces an ylide, whose formation has been detected by means of the reactions with dipolarophiles:[91]



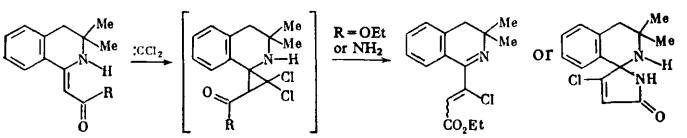
2. Nitrogen-containing compounds

Substituted aminocyclopropanes have been obtained in the reactions of halogenocarbenes with enamines. The reactions of *N*-nitroenamines with dichlorocarbenes[92] and dibromocarbenes[92,93] lead to the formation of the corresponding dihalogenocyclopropanes in yields ranging from 20 to 60%:

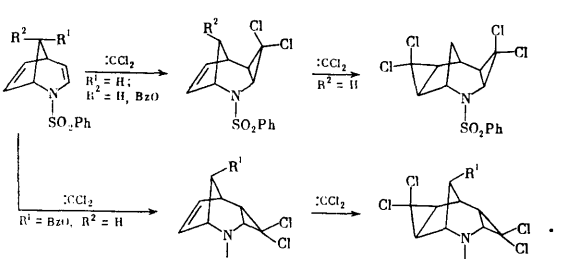


X=Cl, Br.

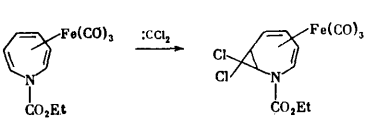
The dichloropropanes formed in the interaction of dichlorocarbene with 1-(R-carbonylmethylene)-3,3-dimethyl-1,2,3,4-tetrahydroisoquinolines are converted into a 1-azadiene or a spirolactam under the reaction conditions:[94]



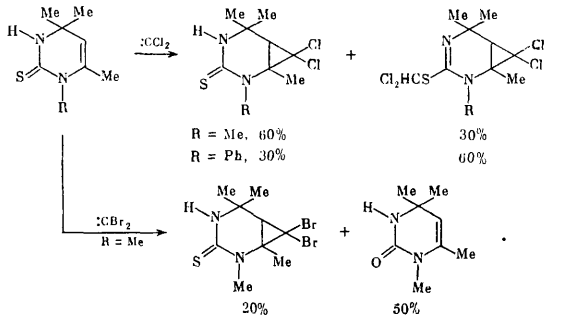
The influence of the stereochemistry of the enamine on the stereoselectivity of the cycloaddition of dihalogenocarbenes has been investigated. *N*-(Benzenesulphonyl)-2-azabicyclo[3.2.1]octa-3,6-dienes react with dichlorocarbene predominantly via the C(3)=C(4) bond, whereupon the stereochemistry of the cycloaddition is determined by the substituent at the C(8) atom:[95]



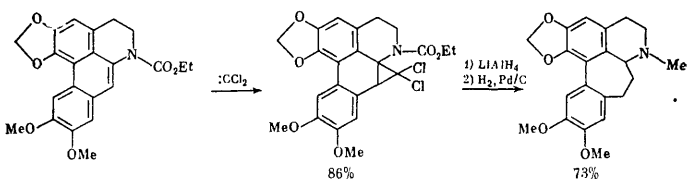
The addition of dichlorocarbene to tricarbonyl[*N*-(ethoxycarbonyl)-azepine]iron takes place selectively:[96]



The reactions of 1-substituted 4,4,6-trimethyl-1,4-dihydropyrimidine-2(3*H*)-thiones with dihalogenocarbenes lead to the corresponding cyclopropane derivatives:[97]



The addition of dichlorocarbene to the enamine double bond with subsequent ring expansion has been used to synthesise homoaporphines:[98]

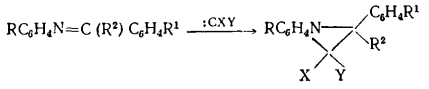


A similar strategy, involving the addition of a dihalogenocarbene to the double bond in 1,2-dihydroisoquinolines and subsequent cleavage of the three-membered ring at the bond opposite to the CX_2 group, has been used in the synthesis of benzazepines.[99–101] In these cases, the dihalogenocarbene added to the enamide group:

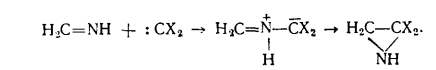


$R^1, R^2 = O$, $R^3 = Me$; $R^1 = H$, $R^2 = Ph$, $R^3 = Ac$; X = Cl, Br.

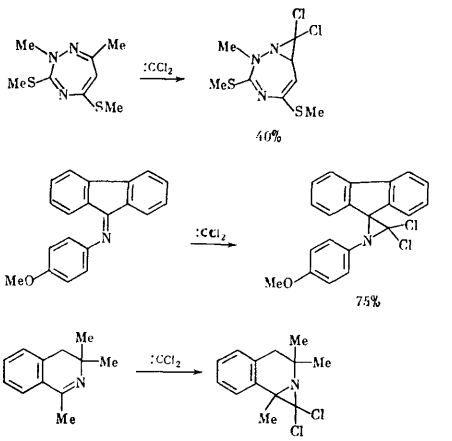
The reactions of bromine-, fluorine-, and chlorine-containing dihalogenocarbenes with aromatic azomethines, leading to the formation of *gem*-dihalogenoaziridines, have been studied in detail.[9] The relative reactivities of the azomethines in the reactions with dibromo- and dichloro-carbenes are then correlated with the basicities of the azomethines. Asymmetric carbenes react stereoselectively:[9]



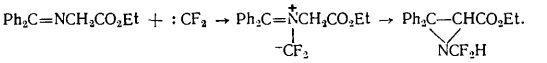
Quantum-chemical calculations for the interaction of methylene and dichlorocarbene with formaldimine have shown that in all cases the reaction begins with the formation of an ylide (without an activation barrier), which then cyclises to aziridine with a small activation barrier:[102]



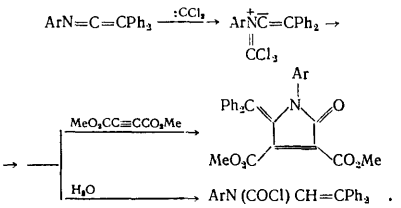
Dichlorocarbene reacts with *trans*-cinnamylideneaniline only at the C=N bond with formation of 3,3-dichloro-1-phenyl-2-(*trans*-2-phenylvinyl)aziridine.[9] 2,2-Dibromo-3-(4-nitrophenyl)-1-phenylaziridine[103] as well as a substituted triazepine[104] and spirocyclic aziridines[94,105] have been synthesised by the reactions of azomethines with dihalogenocarbenes generated under the conditions of phase-transfer catalysis:



The reactions of acetophenone anils with dichlorocarbene, generated by treating $CHCl_3$ with potassium t-butoxide, afforded the corresponding *gem*-dichloroaziridines in 40–80% yields.[106] Perfluorinated carbenes do not form aziridines on reaction with fluorinated azomethines, while $(CF_3)_2C=NH$ reacts with bis(trifluoromethyl)carbene to give the product of insertion in a H–N bond.[107] On the other hand, the reaction of difluorocarbene with the imine derivative of glycine leads to an aziridine, which is formed as a result of the rearrangement of the primary difluoroazomethine-ylide:[108]

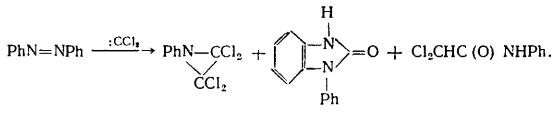


The reactions of keten imines with dichlorocarbene, generated by the thermal catalytic decomposition of sodium trichloroacetate, involve only the C–N bond and lead to the formation of the corresponding carbamoyl chlorides as a result of the hydrolysis of the intermediate keten imine-ylides.[109,110] The relative reactivities of compounds containing cumulated C=C and C=N bonds in the reactions with dichlorocarbene, obtained from chloroform and potassium t-butoxide at 0 °C (k_{rel} is 1.0 for $PhN=C=CPh_2$, 0.7 for p-$ClC_6H_4N=C=CPh_2$, 1.1 for p-$MeOC_6H_4N=C=CPh_2$, and 0.44 for PhN=CHPh), have been measured for the first time.[110] The formation of keten imine-ylides has been confirmed by their reactions with olefinic and acetylenic dipolarophiles:[111]

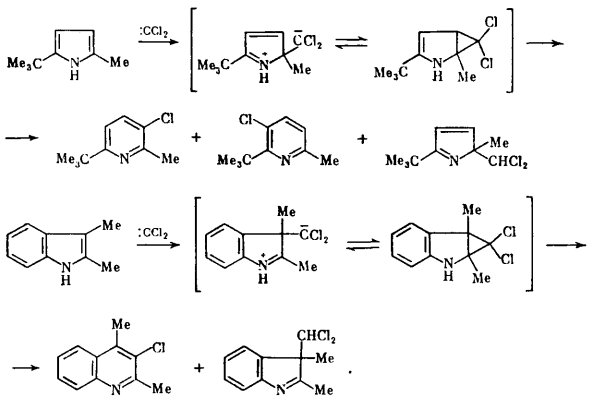


1-Phenylbenzimidazol-2-one has been isolated in the reaction of azobenzene with dichlorocarbene, generated under the conditions of phase-transfer catalysis together with tetrachloroaziridine, which is also formed in the reactions of azobenzene with phenyltrihalogenomethylmercury reagents.[112,113] 1-Phenylbenzimidazol-2-one is

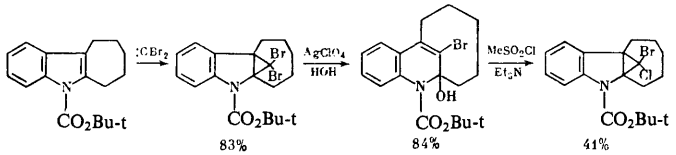
formed via the intermediate *gem*-dichlorodiaziridine:



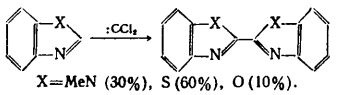
The study of the mechanism of the interaction of dichlorocarbene, generated from $PhHgCCl_3$ and NaI, with 2,5-dialkylpyrroles and 2,3-dialkylindoles[114,115] showed that, in a neutral (aprotic) or weakly alkaline (protic) medium, the reaction proceeds via the same intermediate:



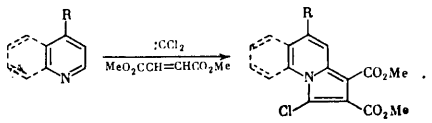
In the reaction of dibromocarbene with cycloheptenoindole, a tetracyclic adduct was obtained and was converted by a ring opening process into the corresponding dihydroquinoline, undergoing an unusual retrocyclisation:[116]



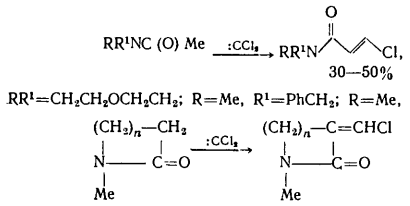
In dichlorocarbene generating systems, benzazoles afford bibenzazoles:[117]



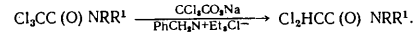
It has been established recently that six-membered azaheterocycles react with dichlorocarbene to form unstable cyclic immonium ylides, whose cycloaddition leads to 3-chloroindolizines which are otherwise difficult to obtain:[118]



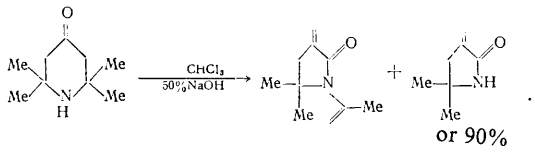
The corresponding (*E*)-3-chloroacetamides and α-chloromethylenelactams have been obtained from tertiary acetamides and lactams:[119]



Under the conditions of the thermal catalytic decomposition of sodium trichloroacetate in chloroform, trichloroacetamides are reduced to dichloroacetamides as a result of the chlorophilic CCl_3 elimination reaction:[120]

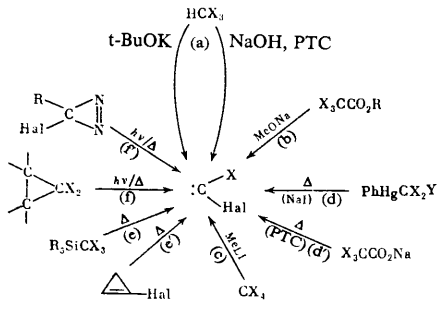


The interaction of dichlorocarbene with 2,2,6,6-tetramethylpiperidin-4-one results in ring contraction:[121,122]



V. Methods for the generation of halogenocarbenes

Numerous methods for the preparation of halogenocarbenes are now known. A general scheme illustrating the methods of generation is presented below and includes the following: (a) classical methods for the formation of dihalogenocarbenes from haloforms with the aid of potassium t-butoxide or 50% sodium hydroxide solution in the presence of a phase-transfer catalyst (PTC): (b) treatment of trihalogenoacetic acid esters with sodium methoxide: (c) the interaction of organolithium compounds with tetrahalogenomethanes: (d) thermal decomposition of phenyltrihalogenomethylmercury derivatives or sodium trihalogenoacetates (a catalyst may be used to reduce the temperature at which the decomposition takes place): (e) thermal decomposition of trihalogenomethylsilyl derivatives or 1-halogenocyclopropenes: (f) the photolysis or thermolysis of halogenocyclopropanes or halogenodiazirines.



Halogenocarbenes can be generated in this way in both neutral and alkaline media and thermolysis or photolysis can be used for this purpose.

New ways of generating halogenocarbenes appeared recently and these will be examined below.

Dichlorocarbene has been obtained by treating CCl_4 with KOH in t-butyl alcohol and dimethyl sulphoxide.[123] The addition of carbene to alkenes takes place stereospecifically and the yields of cyclopropanes are 48–93%.

Dichlorocarbene is formed under the conditions of phase-transfer catalysis from trimethylsilyl trichloroacetate in the presence of KF.[124] The yields of cyclopropanes reach 70% when CH_2Cl_2 is used as the solvent and $NBu_4^+I^-$ or 18-crown-6-ether are used as catalysts. Dichlorocarbene is also formed in the vacuum flash thermolysis of trimethyl(trichloromethyl)silane at 600 °C.[88] Dichloro- and dibromo-carbenes have been generated by the photolysis of 11,11-dichloro- or 11,11-dibromo-tricyclo[4.4.1.0^{1,6}]-undeca-2,4,8-triene at 25 °C; the yield of the corresponding cyclopropanes in the reaction with cyclooctene reaches 80%.[125]

New methods have been proposed recently for the generation of difluorocarbenes—for example, by the reaction of phosphines and phosphites with bromodifluoromethyl(triphenyl)phosphonium salts:[126]

$$Ph_3P^+CF_2BrBr^- + Ph_3P + Me_2C{=}CMe_2 \rightarrow \underset{\underset{CF_2}{\diagup\diagdown}}{Me_2C{-}CMe_2}\ .$$
35%

Difluorocarbene, obtained from the complex $(CF_3)_2Cd.glyme$, reacts stereospecifically with alkenes:[127]

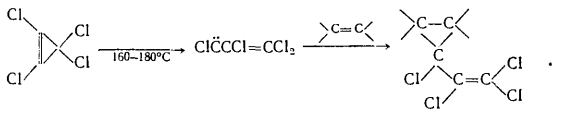
$$(CF_3)_2Cd.glyme + AcBr + Me_2C{=}CMe_2 \xrightarrow{-30°C} \underset{\underset{CF_2}{\diagup\diagdown}}{Me_2C{-}CMe_2} + AcF$$
70% 96%.

The mechanism of the generation of $:CF_2$ from $PhHgCF_3$ on treatment with the iodide anion has been investigated.[128] The formation of difluorocarbene has been postulated in the reaction of HCF_2SO_2F with nucleophiles.[129] The interaction of HCF_2SO_3H with P_2O_5 yielded $HCF_2SO_3CHF_3$, which was formed as a result of the insertion of $:CF_2$ in the initial compound.[130] The influence of the conditions in the reaction of HCF_2SO_2R (R = F, OPh, $OCH_2CF_2CHF_2$, C_6F_5, $OCHF_2$, NHPh, or NMePh) with bases and acids on the intermediate formation of difluorocarbene, the latter giving rise to an adduct with 2,3-dimethylbut-2-ene, has been investigated.[131]

Chloro(trifluoromethyl)carbene has been generated by the photolysis of the corresponding diazirine at 25 °C.[132] The addition of $F_3C(Cl)C:$ to *cis*- and *trans*-but-2-enes takes place stereospecifically but the yields of the corresponding cyclopropanes are low. Chloro(phenoxy)carbene has been obtained similarly on photolysis of diazirine.[17] Cyclopropanes have been obtained in the presence of alkenes in 10–30% yield. Fluoro(methoxy)carbenes have been generated by the thermolysis and photolysis of fluoro(methoxy)-diazirine;[133] in the presence of acrylonitrile and methyl acrylate, the corresponding cyclopropanes were obtained in low yields. The intermediate formation of halogenocarbenes has been postulated in the stereoselective synthesis of 1-halogeno-2-siloxyalkenes:[134]

$$X_3CCHR^2OSiMe_2R^1 \xrightarrow{BuLi} X\ddot{C}CHR^2OSiMe_2R^1 \rightarrow \underset{H}{\overset{X}{\diagup}}C{=}C\underset{R^2}{\overset{OSiMe_2R^1}{\diagdown}}$$
68–96%; X=Cl, Br

In recent years, increased attention has been paid to the study of halogeno(vinyl)carbenes, whose synthetic value is associated with the fact that it is possible to construct with their aid one of the main structural elements of pyrethroids—the vinylcyclopropane fragment. The thermolysis of tetrachlorocyclopropene (> 150 °C) results in the formation of perchlorovinylcarbene,[20,47,135,136] which reacts with alkenes to form the corresponding cyclopropanes (in approximately 60° yield) or is inserted in C–H bonds of heptane and adamantane:



Other halogenovinylcarbenes, namely $Cl_2C{=}CCl\ddot{C}F$, $Cl_2C{=}CH\ddot{C}Cl$, and $Cl_2C{=}CCl\ddot{C}Cl$ obtained by treating the corresponding halogenoalkenes with lithium amides, form halogenovinylcyclopropanes in low yields.[137] The formation of $Me_2C{=}CCl\ddot{C}Cl$ has been postulated in the reaction involving the treatment of 2,2,3-trichloro-1,1-dimethylcyclopropane with MeLi.[138] New (2-chlorovinyl)carbenes have also been obtained by the reaction of $MeClC{=}CHCHCl_2$ and 2-chloro-1-(dichloromethyl)cyclopentene with potassium t-butoxide.[139] The addition of these carbenes to *cis*-but-2-ene takes place entirely stereospecifically. Chloro(2-furyl)- and chloro(2-thienyl)-carbenes have been obtained by treating 2-dichloromethyl-substituted furan and thiophen derivatives with potassium t-butoxide and dibenzo-18-crown-6 ether.[140]

References

1. M Jones, R A Moss *Reactive Intermediates,* Wiley, New York, 1981, Vol. 2, p.60
2. G E Scuseria, M Duran, R G A Maclagan, H F Schaefer *J. Am. Chem. Soc.,* 1986, **108** 3248
3. C W Bauschlicher *J. Am. Chem. Soc.,* 1980, **102** 5492
4. A K Mal'tsev *Novoe v Khimii Karbenov* (New Advances in the Chemistry of Carbenes), Izd. Nauka, Moscow, 1973, p. 10
5. R R Kostikov, A P Molchanov, G V Golovanova, I G Zenkevich *Zh. Org. Khim.,* 1977, **13** 1846
6. R R Kostikov, V S Aksenov, I A D'yakonov *Zh. Org. Khim.,* 1974, **10** 2099
7. R R Kostikov, A P Molchenov, K A Ogloblin *Zh. Org. Khim.,* 1973, **9** 2451
8. I H Sadler *J. Chem. Soc. B,* 1969, 1024
9. R R Kostikov, A F Khlebnikov, K A Ogloblin *Zh. Org. Khim.,* 1977, **13** 1857
10. R R Kostikov, A P Molchanov, I A D'yakonov *Zh. Org. Khim.,* 1977, **13** 2297
11. R R Kostikov, A P Molchanov *Zh. Org. Khim.,* 1984, **20** 1003
12. R A Moss, C B Mallon *J. Am. Chem. Soc.,* 1975, **97** 344
13. N G Rondan, K N Houk, R A Moss *J. Am. Chem. Soc.,* 1980, **102** 1770
14. R A Moss *Acc. Chem. Res.,* 1980, **13** 58
15. R A Moss, A C Munjal *Tetrahedron Lett.,* 1979, 4721
16. R A Moss, M Fedorynski, W-C Shieh *J. Am. Chem. Soc.,* 1979, **101** 4736
17. R A Moss, L A Perez, J Wlostowska, et al. *J. Org. Chem.,* 1982, **47** 4177
18. R A Moss, L A Perez *Tetrahedron Lett.,* 1983, **24** 2719
19. R A Moss, G Kmieckik-Lawrynowicz, K Krogh-Jespersen *J. Org. Chem.,* 1986, **51** 2168

20. R Kostikov, A de Miejere *J. Chem. Soc., Chem. Commun.*, 1984, 1528
21. R A Moss, M Vezza, W Guo, R C Munjal *J. Am. Chem. Soc.*, 1979, **101** 5088
22. R A Moss, B Gerstl *J. Org. Chem.*, 1967, **32** 2268
23. R A Moss, M A Joyce, J K Huselton *Tetrahedron Lett.*, 1975, 4621
24. W W Schoeller *Tetrahedron Lett.*, 1980, **21** 1505
25. W W Schoeller *Tetrahedron Lett.*, 1980, **21** 1509
26. W W Schoeller, N Aktetin, H Friege *Angew. Chem., Int. Ed. Engl.*, 1982, **21** 932
27. B Giese, W-B Lee *Angew. Chem., Int. Ed. Engl.*, 1980, **19** 835
28. B Giese, W-B Lee *Tetrahedron Lett.*, 1982, **23** 3561
29. B Giese, W-B Lee *Chem. Ber.*, 1981, **114** 3306
30. B Giese, C Neumann *Tetrahedron Lett.*, 1982, **23** 3557
31. B Giese, W-B Lee, S Stiehl *Tetrahedron Lett.*, 1983, **24** 881
32. W Brück, H Durr *Tetrahedron Lett.*, 1982, **23** 2175
33. W Brück, H Durr *Angew. Chem., Int. Ed. Engl.*, 1982, **21** 916
34. N J Turro, J A Butcher, R A Moss, et al. *J. Am. Chem. Soc.*, 1980, **102** 7576
35. N J Turro, G F Lehr, J A Butcher, et al. *J. Am. Chem. Soc.*, 1982, **104** 1754
36. N J Turro, M Okamoto, I R Gould, et al. *J. Am. Chem. Soc.*, 1987, **109** 4973
37. R A Moss, L A Perez, N J Turro, et al. *Tetrahedron Lett.*, 1983, **24** 685
38. D P Cox, I R Gould, N P Hacker, et al. *Tetrahedron Lett.*, 1983, **24** 5313
39. K N Houk, N G Rondan, J Mareda *Tetrahedron*, 1985, **41** 1556
40. R R Kostikov, A P Molchanov *Dokl. Akad. Nauk SSSR*, 1977, **236** 110
41. R R Kostikov, A P Molchanov *Zh. Org. Khim.*, 1978, **14** 355
42. R R Kostikov, A P Molchanov *Dokl. Akad. Nauk SSSR*, 1984, **20** 1426
43. R R Kostikov, E N Grishina, Ya M Slobodin *Zh. Org. Khim.*, 1984, **20** 1426
44. R R Kostikov, I S Vorob'eva, A P Molchanov *Zh. Org. Khim.*, 1983, **19** 256
45. W von E Doering, W Henderson *J. Am. Chem. Soc.*, 1958 **80** 5274
46. I Tabushi, Z Yoshida, N Takabashi *J. Am. Chem. Soc.*, 1970, **92** 6670
47. W Weber, A de Meijere *Chem. Ber.*, 1985, **118** 2450
48. Ya M Slobodin, L A Ashkenazi, G I Klimchuk *Zh. Org. Khim.*, 1984, **20** 1238
49. E K Fields *J. Am. Chem. Soc.*, 1962, **84** 1745
50. S-H Goh, K C Chan, T-S Kam, H-L Chong *Aust. J. Chem.*, 1975, **28** 381
51. K Steinbeck *Tetrahedron Lett.*, 1980, **21** 2149
52. V I Boev *Zh. Org. Khim.*, 1981, **17** 1340
53. K Steinbeck *Tetrahedron Lett.*, 1978, 1103
54. T Harada, E Akiba, A Oku *J. Am. Chem. Soc.*, 1983, **105** 2771
55. C W Jefford, J Roussilhe, M Papadopoulos *Helv. Chim. Acta*, 1985, **68** 1557
56. U Misslitz, M Jones, A de Miejere *Tetrahedron Lett.*, 1985, **26** 5403
57. J E Jackson, U Mizzlitz, M Jones, A de Miejere *Tetrahedron*, 1987, **43** 653
58. K B Wiberg, G M Lampman, R P Guila, et al. *Tetrahedron*, 1965, **21** 2749
59. D E Applequist, J W Wheeler *Tetrahedron Lett.*, 1977, 3411
60. D E Applequist, T L Renken, J W Wheeler *J. Org. Chem.*, 1982, **47** 4985
61. A E Grigor'ev, A V Tarakanova, E N Mil'vitskaya, et al. *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1980, **2** 498
62. G B Mock, M Jones *Tetrahedron Lett.*, 1981, **22** 3819
63. A P Molchanov, Yu B Koptelov, R R Kostikov *Zh. Org. Khim.*, 1988, **24** 390
64. A Ledwith, H J Woods *J. Chem. Soc. B*, 1967, 973
65. R R Kostikov, E A Drygailova, E A Golovkina, et al. *Zh. Org. Khim.*, 1987, **23** 2170
66. W E Parham, L Christensen, S H Groen, L M Dodson *J. Org. Chem.*, 1964, **29** 2211
67. W Ando, H Higuchi, T Migita *J. Org. Chem.*, 1977, **42** 3365
68. W E Parham, S H Groen *J. Org. Chem.*, 1965, **30** 728
69. R R Kostikov, A P Molchanov, S V Amosova, B A Trofimov *Izv. Akad. Nauk SSSR, Ser Khim.*, 1980, 1354
70. R R Kostikov, A P Molchanov, O A Tarasova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 1286
71. A Kh Khusid, L A Yanovskaya *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 2790
72. A Kh Khusid, N Yu Sorokina *Zh. Org. Khim.*, 1983, **19** 263
73. P Dowd, C Kaufman, P Kaufman, Paik Vi Hyon *Tetrahedron Lett.*, 1985, **26** 2279
74. A V Anisimov, T A Kolosova, E V Viktorova *Zh. Org. Khim.*, 1983, **19** 1121
75. K Kleveland, L Skattebol, L K Sydnes *Acta Chem. Scand., Ser. B*, 1977, **31** 463
76. D Seyferth, Y-A Mui, J Mui, K W Darragh *J. Org. Chem.*, 1966, **31** 4079
77. A P Molchanov, R R Kostikov *Zh. Org. Khim.*, 1987, **23** 69
78. R H Ellison *J. Org. Chem.*, 1980, **45** 2509
79. F Mohamadi, W C Still *Tetrahedron Lett.*, 1986, **27** 893
80. C Rucker *Chem. Ber.*, 1985, **118** 2137
81. E V Dehmlow, R Neuhaus *Z. Naturforsch., B*, 1987, **42** 796
82. M T H Lui, R Subramanian *J. Chem. Soc., Chem. Commun.*, 1984, 1962
83. M T H Liu, R Subramanian *J. Chem. Soc., Perkin Trans. II*, 1986, 1233
84. H Tomioka, N Hayashi, T Sugiura, Y Izawa *J. Chem. Soc., Chem. Commun.*, 1986, 1364
85. H Tomioka, Y Ozaki, Y Izawa *Chem. Lett.*, 1982, 843
86. H S Gill, J A Landgrebe *Tetrahedron Lett.*, 1982, **23** 5099
87. H S Gill, J A Landgrebe *J. Org. Chem.*, 1983, **48** 1051
88. J F Gisch, J A Landgrebe *J. Org. Chem.*, 1985, **50** 2050
89. Z Huan, J A Landgrebe, K Peterson *Tetrahedron Lett.*, 1983, **24** 2829
90. C W Martin, H S Gill, J A Landgrebe *J. Org. Chem.*, 1983, **48** 1898
91. T Ibata, M T H Liu, J Toyoda *Tetrahedron Lett.*, 1986, **27** 4383
92. V P Ivshin, M S Komelin, N P Belik *Zh. Org. Khim.*, 1980, **16** 980
93. V P Ivshin, M S Komelin, G B Sofronova, T V Zykova *Zh. Org. Chem.*, 1980, **16** 101
94. A F Khlebnikov, R R Kostikov, V S Shklyaev, et al. *Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Khimii Karbenov* (Abstracts of Reports at the IV All-Union Conference on the Chemistry of Carbenes), Moscow, 1987, p. 11

95. H Inoue, K Tokisato, K Umano *Bull. Chem. Soc. Jpn.*, 1982, **55** 1661
96. T Ishizu, K Harano, N Hori, et al. *Tetrahedron*, 1983, **39** 1281
97. H Singh, P Singh *Tetrahedron*, 1981, **37** 1215
98. J L Castro, L Castedo, R Riguera *Tetrahedron Lett.*, 1985, **26** 1561
99. H P Soetens, U K Pandit *Recl. Trav. Chim. Pays-Bas*, 1980, **99** 271
100. C D Perchonock, I Lantos, J A Finkelstein, K G Holden *J. Org. Chem.*, 1980, **45** 1950
101. I Lantos, D Bhattacharjee, D S Eggleston *J. Org. Chem.*, 1986, **51** 4147
102. V Ya Bespalov, R R Kostikov *Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Khimii Karbenov* (Abstracts of Reports at the IV All-Union Conference on the Chemistry of Carbenes), Moscow, 1987, p. 132
103. A F Khlebnikov, R R Kostikov *Khim. Geterotsikl. Soedin.*, 1984, 912
104. A Hasnaoui, M El Messaoudi, J-P Lavergne *Rec. Trav. Chim. Pays-Bas*, 1985, **104** 129
105. I S Prostakov, L A Gaivoronskaya, S K Sarkar, et al. *Khim. Geterotsikl. Soedin.*, 1986, 895
106. N S Kozlov, V D Pak, V M Bakulev, V V Mashevskii *Vestn. Akad. Nauk SSSR, Ser. Khim.*, 1985, 110
107. D Sohn, W Sundermeyer *Chem. Ber.*, 1982, **115** 3334
108. J R McCarthy, C L Barney, M J O'Donnell, J C Huffman *J. Chem. Soc., Chem. Commun.*, 1987, 469
109. A F Khlebnikov, M S Novikov, R R Kostikov *Zh. Org. Khim.*, 1985, **21** 2227
110. A F Khlebnikov, M S Novikov, R R Kostikov *Zh. Org. Khim.*, 1986, **22** 1706
111. A F Khlebnikov, M S Novikov, R R Kostikov *Khim. Geterotsikl. Soedin.*, 1987, 1336
112. S Sekiguchi, T Fujiu *Bull. Chem. Soc. Jpn.*, 1984, **57** 3337
113. T Fujiu, K Izumi, S Sekiguchi *Bull. Chem. Soc. Jpn.*, 1985, **58** 1055
114. A Gambacorta, R Nicoletti, S Cerrini, et al. *Tetrahedron*, 1980, **36** 1367
115. M Botta, F De Angelis, A Gambacorta *Tetrahedron*, 1982, **38** 2315
116. D Dhanak, R Kuroda, C B Reese *Tetrahedron Lett.*, 1987, **28** 1827
117. J S Rao, D S Inyengar, U T Bhalerao, S N Rao *Heterocycles*, 1987, **26** 1161
118. A F Khlebnikov, R R Kostikov *Khim. Geterotsikl. Soedin.*, 1987, 856
119. M Markos, J L Castro, L Castedo, R Riguera *Tetrahedron*, 1986, **42** 649
120. A F Khlebnikov, E I Kostik, M S Novikov, R R Kostikov *Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Khimii Karbenov* (Abstracts of Reports at the IV All-Union Conference on the Chemistry of Carbenes), Moscow, 1987, p. 12
121. H Lind, T Winkler *Tetrahedron Lett.*, 1980, **21** 119
122. J T Lai, J C Westfahl *J. Org. Chem.*, 1980, **45** 1513
123. C D Poon, P-W Yuen, T-O Man, et al. *J. Chem. Soc., Perkin Trans. I*, 1984, 1561
124. E V Dehmlow, W Leffers *J. Organomet. Chem.*, 1985, **288** 41C
125. J F Hartwig, M Jones, R A Moss, W Lawrynowich *Tetrahedron Lett.*, 1986, **27** 5907
126. D J Burton, D G Naac, R M Flynn, et al. *J. Org. Chem.*, 1983, **48** 3616
127. L J Krause, J A Morrison *J. Am. Chem. Soc.*, 1981, **103** 2995
128. H Koroniak *J. Fluorine Chem.*, 1984, **24** 503
129. Q Chen, S Zhu *Ioutsi Hsua Hsueh*, 1984, 434; *Ref. Zh. Khim.*, 1985, 10Zh362
130. Q Chen, S Zhu *Hua Hsueh Hsueh Pao*, 1985, **43** 546; *Ref. Zh. Khim.*, 1986, 3B4080
131. Q Chen, S Zhu *Hua Hsueh Hsueh Pao*, 1986, **44** 92; *Ref. Zh. Khim.*, 1986, 3B4080
132. R A Moss, W Guo, D Z Denney, et al. *J. Am. Chem. Soc.*, 1981, **103** 6164
133. R A Moss, M Fedorinski, J Terpinski, D Z Denney *Tetrahedron Lett.*, 1986, **27** 419
134. M C Pirrung, J R Hwu *Tetrahedron Lett.*, 1983, **24** 565
135. W Weber, A de Meijere *Angew. Chem.*, 1980, **92** 135
136. T Liese, G Splettstoesser, A de Meijere *Tetrahedron Lett.*, 1982, **23** 3341
137. S Keyaniyan, W Gothling, A de Meijere *Chem. Ber.*, 1987, **120** 395
138. N Slougui, G Rousseau *Tetrahedron Lett.*, 1987, **28** 1651
139. K N Shavrin, I E Dolgii, O M Nefedov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1214
140. I E Dolgii, K N Shavrin, I V Krylova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 2644

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Carbene synthesis and chemical reactions of cyclopropene-3-carboxylate esters—promising intermediates for organic synthesis

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ABSTRACT. The data on the methods of synthesis and chemical reactions of cyclopropene-3-carboxylate esters have been correlated and classified. Particular attention has been given to the direct carbene synthesis of cyclopropene esters, which provides an accessible route to compounds of this series. In studying the chemical reactions particular attention has been given to selective reactions that provide the opportunity of using cyclopropene-3-carboxylate esters in organic synthesis to obtain various types of compounds.

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I. Introduction

The preparation of cyclic molecules containing three carbon atoms by the reaction of aliphatic diazo compounds with unsaturated acceptors using the diazo method and a study of their chemical reactions constitute one of the most productive trends in the use of carbene reactions in organic synthesis.

In 1956 D'yakonov[1] used the synthesis of ethyl 2-methyl-3-phenylcyclopropene-3-carboxylate to demonstrate the possibility of employing the diazo method to obtain these compounds which were very novel at that time from readily available acetylenes. At the end of the 1950s and the beginning of the 1960s a series of studies was carried out by Breslow[2–4] into the synthesis using the diazo method and an investigation of the simplest chemical properties of cyclopropene esters.

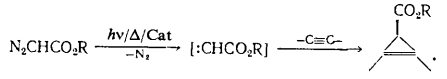
However, a systematic and detailed study of the reactions of cyclopropene-3-carboxylate esters only became feasible during the 1970s when the D'yakonov method was substantially improved by Soviet[5–7] and foreign[8] research workers, which led to cyclopropene-3-carboxylate esters becoming the most readily available class of carbofunctional cyclopropene compounds. During these years the varied reactivity of cyclopropene esters was demonstrated, which was an indication of their future potential in organic synthesis to obtain derivatives of cyclopropane, cyclopropene and cyclobutane, various furans, γ-butyrolactones and α-pyrans, and also many acyclic carbofunctional compounds.

Despite the large number of experimental studies in the literature, there are no review publications on the chemistry of cyclopropene-3-carboxylate esters. The last review on the chemistry of cyclopropene compounds[9] dates back to 1966 and contains very limited information on the properties of cyclopropene-3-carboxylate esters.

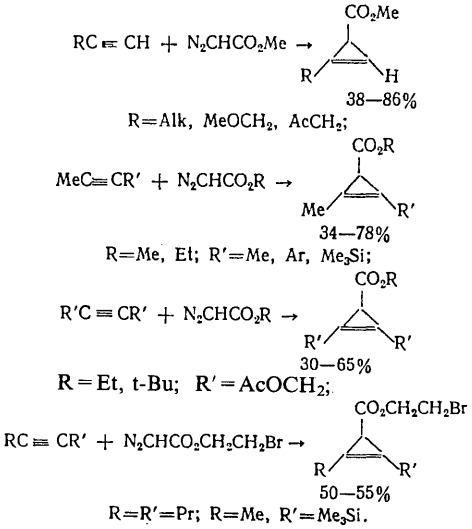
The present work is the first attempt to give a systematic account of the literature material including the studies of the present authors on the synthesis and chemical reactions of cyclopropene-3-carboxylate esters and it reflects the state of this topic at the end of 1987.

II. Synthesis of cyclopropene-3-carboxylate esters by the diazo method

The diazo method is based on the carbene decomposition reaction of alkyl diazoacetates (ADA) that takes place on exposure to radiation, heating, or catalysts (Cat). Addition of the resulting free or complexed carbenes to triple bonds gives cyclopropene-3-carboxylate esters:[10]

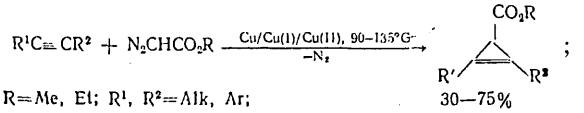


The most important preparative synthesis is the thermocatalytic method for decomposition of alkyl diazoacetates. By using rhodium compounds (for example, rhodium acetate) as catalysts for this process, it is possible to obtain cyclopropene-3-carboxylate esters in high yield even at room temperature from both terminal and internal (including those substituted with functional groups) acetylenes:[8,11–16]

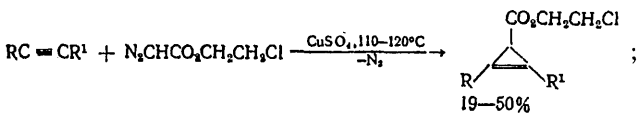


In order to suppress the secondary formation of fumarate and maleate esters—formal dimers of the carbenes—the reaction is carried out with a 2.5–3-fold molar excess of acetylene.

The use of traditional copper catalysts requires a temperature of 90–140 °C for the decomposition of ADA and gives satisfactory yields of cyclopropene esters only in the case of disubstituted acetylenes which are usually employed in 2–10-fold molar excess relative to ADA:[13,17–23]



R=Me, Et; R¹, R²=Alk, Ar; 30—75%

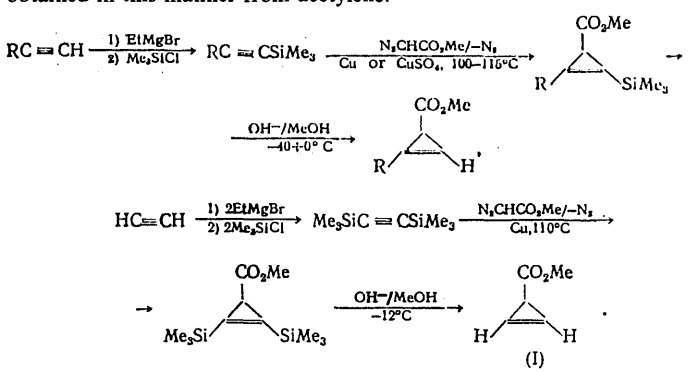


19—50%

R=Pr, R¹=Pr, Me_3Si; R=cyclo-C_3H_5, R¹=Me_3Si.

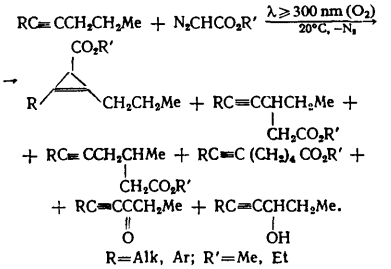
The yield of products and the selectivity of the process depend to a significant extent on the concentration of catalyst. For example, in the case of copper bronze a molar ratio of catalyst to acetylene of 0.02 : 1 is the otpimum,[22] while when using copper salts the optimum ratio is 0.001 : 1.[21]

When ADA are reacted with terminal acetylenes in the presence of copper compounds, the corresponding cyclopropene-3-carboxylate esters are formed in yields not greater than 16%.[7,24] The synthesis of such cyclopropenes can be carried out more effectively by using the so-called silyl protection method, which is based on the ready hydrolytic cleavage of the C–Si bond in trimethylsilyl-substituted cyclopropene-3-carboxylate esters.[6,25–29] In particular, the methyl ester (I) of the simplest cyclopropene-3-carboxylic acid † was obtained in this manner from acetylene.[26]



Significant disadvantages of this method are its multistage nature and the insufficiently high overall yields of cyclopropene esters (25–30%).

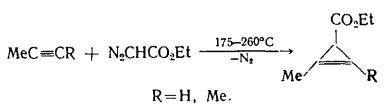
In the photolytic initiation of the reaction between acetylenes and ADA, products derived from the introduction of carbenes into the C–H bond—the corresponding esters of acetylenic acids—are formed together with cyclopropenes, while in the presence of air acetylenic ketones and alcohols are further formed. As a result the yield of cyclopropene esters from internal acetylenes does not usually exceed 40%,[11,12] only in rare cases does it reach 60%,[32] while from terminal acetylenes it is 17–20%.[22]



The preparation of cyclopropene-3-carboxylate esters purely by a thermal reaction between ADA and disubstituted acetylenes requires a temperature of 130 °C or above[24,31] and it is usually accompanied by destruction and oligomerisation of the initial and final products as well as by a number of other side reactions, as a result of which the yields of cyclopropene esters do not exceed 20%.[31,32]

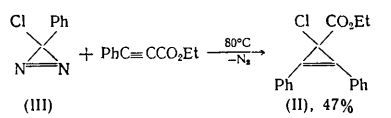
Cyclopropene-3-carboxylate esters that are unsubstituted or monosubstituted at the double bond cannot be obtained at all under normal conditions by thermal reaction of ADA with acetylene or 1-alkynes. Acetylene and its derivatives when heated with ADA to 100 °C form only pyrazoles,[33–36] and at higher temperatures (150–200 °C) the initial and final products are almost completely converted into tar.[24]

However, by carrying out the process in a flow reactor, a short residence time of the products in the hot zone and a large dilution of the reaction mixture with the initial acetylene can be achieved so that cyclopropene esters are obtained in preparative yields (30–35%).[7,24] This method in particular was used to synthesise ethyl 1-methyl- and 1,2-dimethyl-cyclopropene-3-carboxylates (yields 28–30%) from gaseous acetylenes and ethyl diazoacetate:[7,24]



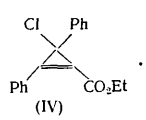
R=H, Me.

In the cyclopropenation of unsaturated compounds, diazirines can be used as diazo components.[37] However, only one example of the use of the latter to obtain cyclopropene esters is known—the synthesis of ethyl 1,2-diphenyl-3-chlorocyclopropene-3-carboxylate (II) from chlorophenyldiazirine (III) and ethyl propiolate:[38]



(III) (II), 47%

Unfortunately, DeBoer[38] did not discuss the reasons for the formation of ester (II) instead of the expected ester (IV)



(IV)

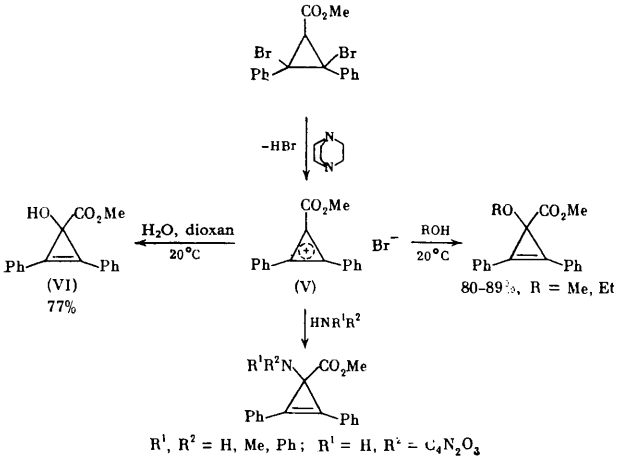
It is possible that the reaction, without involving phenylchlorocarbene, takes place as a [1,3]-dipolar addition of diazobenzyl chloride N_2=C(Cl)Ph, which is an isomer of (III),[37,39] to ethyl propiolate followed by elimination of nitrogen and migration of chlorine.

† Ester (I) was obtained as a solution in CCl_4.[26,27]

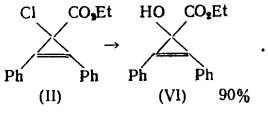
III. Other methods for synthesising cyclopropene-3-carboxylate esters

As well as the development of the diazo method, alternative processes for the synthesis of cyclopropene-3-carboxylate esters have been elaborated. Thus, according to the findings of Komendantov et al.,[40,41] 3-hydroxy-, 3-alkoxy-, and 3-aminocyclopropene-3-carboxylate esters can be obtained from methyl 1,2-dibromo-1,2-diphenylcyclopropane-3-carboxylate by a scheme that involves formation of the cyclopropenyl bromide (V) (Scheme 1).

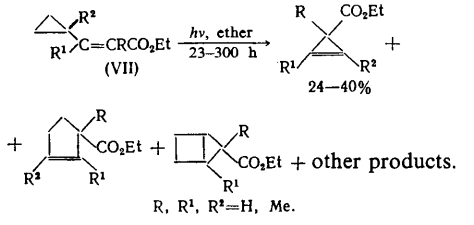
Scheme 1



In addition to this method, 1,2-diphenyl-3-hydroxycyclopropene-3-carboxylate esters (VI) can be obtained from the corresponding 3-chlorocylopropene-3-carboxylate esters (II) by treatment of a solution of (II) in acetone at 25 °C with sodium bicarbonate:[38]



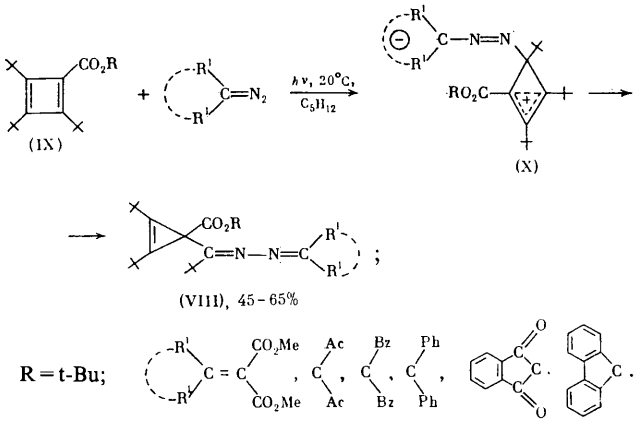
Cyclopropene esters are also obtained by the photolytic decomposition of cyclopropylvinylcarboxylate esters (VII).[42]



However, the reaction is not selective, and the yields of cyclopropenes do not exceed 40%.

Examples are known of the synthesis of tetrasubstituted cyclopropene-3-carboxylate esters (VIII) by photochemical reaction of a cyclobutadienecarboxylate ester (IX) with diazo compounds.[43]

It has been suggested that the reaction takes place via an intermediate betaine structure (X)



However, these methods are specific in nature and do not have wide importance for preparative synthesis.

IV. Chemical reactions of cyclopropene-3-carboxylate esters

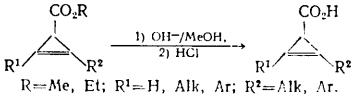
Cyclopropene-3-carboxylate esters constitute a class of alicyclic compounds with unique properties since they contain several interdependent reaction sites in the molecule—an ester group, a ring double bond and a strained three-carbon ring. In a number of cases by choosing the conditions it is possible to achieve reaction selectivity on one of the reaction sites. This fact is of importance for preparative synthesis since it is possible to obtain synthons with a three-carbon ring or carbofunctional acyclic compounds.

1. Reactions taking place with preservation of the three-carbon ring

(a) Reactions involving the ester group

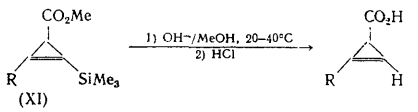
Cyclopropene-3-carboxylate esters undergo reactions that are typical for esters—alkaline and acid hydrolysis, reduction, nucleophilic addition of organometallic compounds. In the majority of cases these reactions take place with preservation of the three-carbon ring and can give other cyclopropene derivatives from accessible cyclopropene esters.[11,14,16,32,44-46]

Hydrolysis. Methyl and ethyl cyclopropene-3-carboxylates when treated with alcoholic or aqueous alkaline solutions at 20–40 °C are readily saponified to the corresponding acids (yields of 40% to 92%).[11,13,18,19,21,31,32,47,48]



When the temperature is lowered to 0 °C, the rate of hydrolysis decreases substantially,[26,27] and when it is increased to 90–120 °C, as well as saponification of the ester group exocyclic migration of the cyclopropene double bond occurs (when there is an alkyl substituent on the double bond), giving the corresponding alkylidenecyclopropanecarboxylic acids (see IV, 1b).

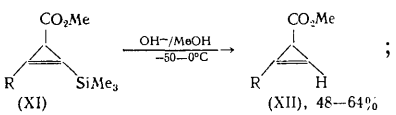
Hydrolysis of 1- or 1,2-silyl-substituted cyclopropene-3-carboxylate esters has several special features as a result of the presence of the labile C–Si bond in the molecule, and depending on the temperature and substituent in the silyl group gives different products.[26,27] Thus, at temperatures above 20 °C hydrolysis of 1-trimethylsilyl-2-alkylcyclopropene-3-carboxylate esters (XI) in methanol gives the corresponding alkylcyclopropene-3-carboxylic acids with yields of up to 95%.[26,27,32]



(XI)

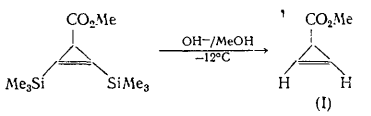
R=Alk.

On the other hand, at temperatures, of 0 °C and below only cleavage of the C–Si bond occurs in esters (XI) without saponification of the ester group. As a result, cyclopropene-3-carboxylate esters (XII) or (I) that are monosubstituted at the double bond are selectively formed:[25–29]



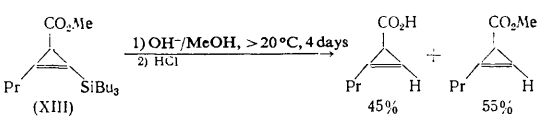
(XI) (XII), 48–64%

R=Alk.



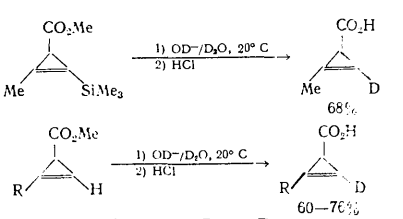
(I)

Replacement of the $SiMe_3$ group by $SiBu_3$ inhibits cleavage of the Ci–Si bond in ester (XIII) to such an extent that the reaction only takes place at temperatures above 20 °C, being accompanied by hydrolysis of the ester group and formation of a mixture of 1-propylcyclopropene-3-carboxylic acid and its methyl ester in approximately equal amounts:[26,27]



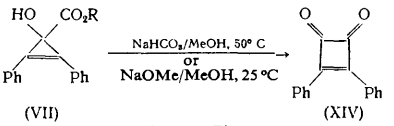
(XIII) 45% 55%

Removal of the silyl protecting group by hydrolysis in deuterated solvents gives 1-alkyl-1-deutero-substituted cyclopropene-3-carboxylic acids (the latter can also be obtained directly from the corresponding 1-alkylcyclopropene-3-carboxylate esters):[49]



R-iso-Pr, n-Bu, t-Bu.

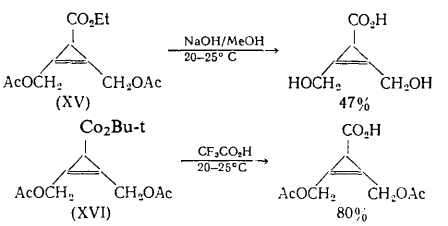
The alkaline hydrolysis of 3-hydroxycyclopropene-3-carboxylate esters (VII) takes place in an unusual manner. When these compounds are treated with bases, they undergo a reverse benzil rearrangement at the same time as hydrolysis of the ester group, as a result of which the cyclobutenedione (XIV) is formed in almost quantitative yield:[38,40]



(VII) (XIV)

R=Me, Et.

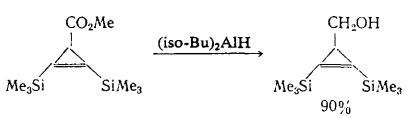
In contrast to methyl and ethyl esters, t-butyl esters are stable to bases and only form the corresponding acids by acidic hydrolysis, which can be of use for synthetic purposes. Thus, while all the ester groups present are saponified even at room temperature when ethyl ester (V) undergoes alkaline hydrolysis, acid hydrolysis of the corresponding t-butyl ester (XVI) under mild conditions can give the corresponding acid in 80% yield.[14]



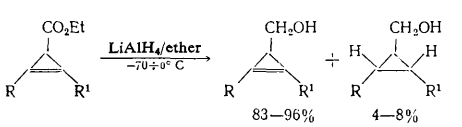
(XV)

(XVI)

Reduction to alcohols. The ester group of cyclopropene-3-carboxylates can be reduced selectively to an alcohol with diisobutylaluminium hydride.[50]



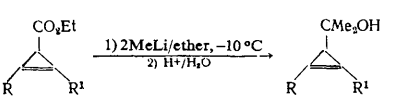
Reduction of the ester group with $LiAlH_4$ only takes place selectively at temperatures not exceeding 0 °C. In this case the cyclopropene double bond is also partially reduced.[11,51–53]



R, R^1=Alk, R=Me; R^1=$SiMe_3$.

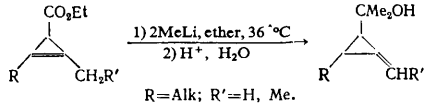
Above 0 °C only cyclopropylcarbinols are formed (see IV, 1b).

Nucleophilic addition to the alkoxycarbonyl group. The only examples of this type of reaction for cyclopropene-3-carboxylate esters are those that occur with methyllithium and butyllithium. Thus, at –10 °C the reaction of ethyl 1,2-dialkylcyclopropene-3-carboxylates with methyllithium in ether gives the corresponding tertiary alcohols (yields of 60–75%).[47,48]



R, R^1=Alk.

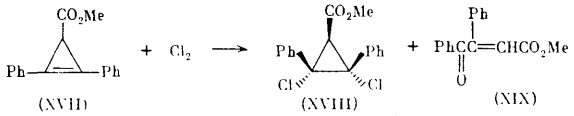
At higher temperatures, exocyclic migration of the cyclopropene double bond occurs together with alkylation, resulting in formation of the corresponding alkylidenecyclopropyldimethylcarbinols in yields of up to 70% (see IV, 1b).[47,48,54]



(b) Reactions involving the ring double bond

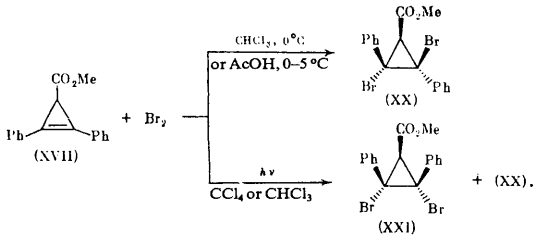
Addition of electrophiles. The presence of the ring double bond is responsible for the ability of cyclopropene-3-carboxylate esters to add on electrophilic reagents. In this case the ester group present has a stabilising effect on the three carbon ring,[55] and it assists in preservation of the ring and formation of the corresponding polyfunctional cyclopropanes.

Chlorination of the double bond of methyl 1,2-diphenylcyclopropene-3-carboxylate (XVII) occurs by a *cis*-addition in a *trans*-orientation relative to the ester group, and the yield of methyl dichlorocyclopropanecarboxylate (XVIII) varies from 35% to 71% depending on the reaction conditions.[56] The process is accompanied to a slight extent by opening of the cyclopropene residue and formation of the butenoate (XIX).



71% (*h*ν, CCl_4)
41% (diffuse light, 0 °C, CCl_4)
35% (AcOH, 15°C)

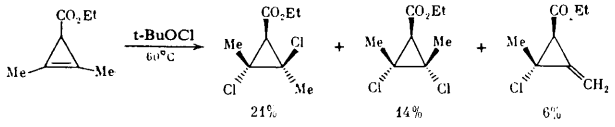
The stereochemistry of the addition of bromine to the ring double bond depends on the experimental conditions, *cis*- or *trans*-addition occurring with a *trans*-orientation relative to the ester group. Thus, bromination of ester (XVII) in chloroform or acetic acid in the dark or diffuse light takes place exclusively by *trans*-addition, giving methyl 1,2-dibromo-*cis*,*trans*-1,2-diphenylcyclopropane-3-carboxylate (XX) in 40% yield.[40]



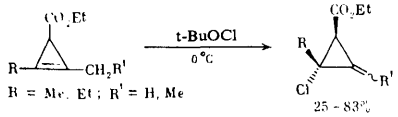
On the other hand, in tetrachloromethane or chloroform on irradiation *cis*-addition of bromine mainly takes place with formation of methyl 1,2-dibromo-*cis*,*cis*-1,2-diphenylcyclopropane-3-carboxylate (XXI) in 80% yield. In this case the isomeric ester (XX) is formed in very small quantities.[40]

It was assumed[40] that the dependence of the yields of halogenation products on the reaction conditions is due to different mechanisms for addition of chlorine or bromine to ester (XVII). An ionic mechanism is assumed in diffuse light and in a polar solvent and a radical mechanism in the presence of radiation. The higher yields of dichloro- and dibromo- cyclopropanes (XVIII) and (XXI) obtained by irradiation may be due to the higher stability of an intermediate cyclopropyl radical compared to the stability of a cyclopropyl cation or the corresponding chloronium or bromonium cations.[40,56]

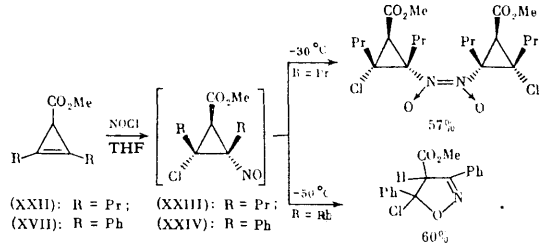
Halogenation of cyclopropene esters may also be carried out using t-butyl hypochlorite. However, in this case at 60 °C addition of chlorine is not selective and gives a mixture of *cis*- and *trans*-isomers of dichlorocyclopropanes together with methylenechlorocyclopropanes—substitution and isomerisation products.[57,58]



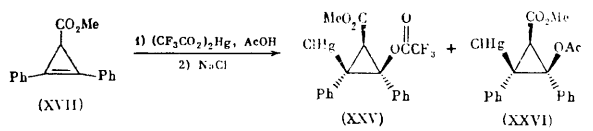
By reducing the temperature to 0 °C the reaction can be mainly directed towards formation of methylenechlorocyclopropanes; in a number of cases this can be important for preparative synthesis.[57,58]



Cyclopropene esters (XXII) and (XVII) can add on nitrosyl chloride. However, the nitrosyl chlorides (XXIII) and (XXIV) formed in this process have low stability and depending on their structure either dimerise or undergo opening of the three-carbon ring:[59]

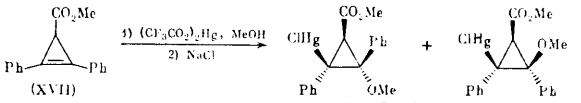


Mercuration of cyclopropene-3-carboxylate esters takes place with preservation of the cyclopropane residue,[60,61] and the reaction conditions have a considerable effect on both the stereochemistry of addition of mercury salts to the ring double bond and the nature of the resulting products formed. Thus, addition of mercuric trifluoroacetate to the diphenylcyclopropene ester (XVII) in acetic acid occurs by a *cis*-mechanism in a *cis*-orientation relative to the ester group and gives (as a result of subsequent treatment with NaCl) the 1-chloromercuro-2-trifluoroacetoxycyclopropanecarboxylate ester (XXV) together with a small quantity of the solvolysis adduct (XXVI); the ratio of (XXV) : (XXVI) = 87 : 13.[61]

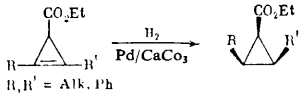


Reaction of the same ester (XVII) with mercuric trifluoroacetate in methanol leads exclusively to solvolysis adducts—the corresponding 1-chloromercuro-2-methoxycyclopropanes (XXVII)— with the

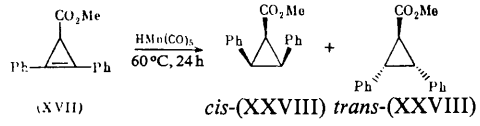
trans,cis-isomer, which is formed by *trans*-addition, predominating [ratio of *trans,cis*-(XXVII) : *cis,cis*-(XXVII) = 85 : 15).[60,61]



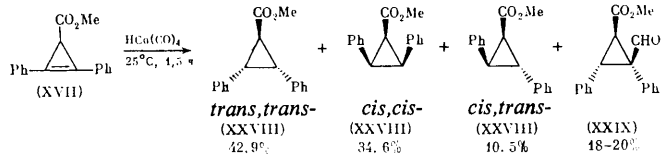
Reduction. The ring double bond of cyclopropenecarboxylate esters is reduced by metal carbonyl hydrides, lithium aluminium hydride, and hydrogen in the presence of catalysts. The most selective and frequently used method is reduction of cyclopropene esters by catalytic hydrogenation using palladium supported on $CaCO_3$ as the catalyst. As a result, only *cis,cis*-1,2-dialkylcyclopropane-3-carboxylate esters are formed in yields up to 98%.[18,19,42,62,63]



Reduction of methyl diphenylcyclopropenecarboxylate (XVII) with manganese pentacarbonyl hydride is not stereospecific and gives a mixture of isomeric cyclopropanecarboxylate esters in quantitative yield, although the *cis*-isomer is mainly formed [ratio of *cis*-(XXVIII) : *trans*-(XXVIII) = 7 : 1]: [64]

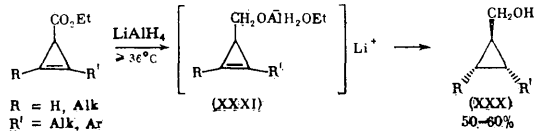


Reduction of the same ester (XVII) with cobalt carbonyl hydride is not selective and all possible isomeric 1,2-diphenylcyclopropane-3-carboxylate esters (XXVIII) are formed with a total yield of 88%.[65]



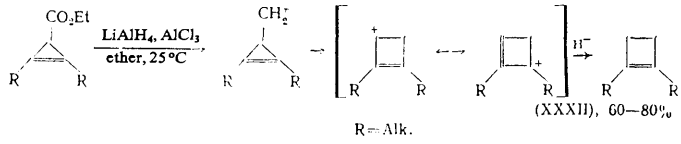
In this case hydroformylation of ester (XVII) is a competing process, resulting in the formation of ester (XXIX) with a yield of about 22%.

In contrast to the reagents considered above, lithium aluminium hydride mainly reduces the ester group in cyclopropene esters, and depending on the temperature reduction can also be accompanied by hydrogenation of the ring double bond. Thus, at 0 °C only cyclopropene alcohols are formed (see IV, 1a), while at higher temperatures the corresponding cyclopropylcarbinols are formed, only as a single *trans,trans*-isomer (XXX).[51-53]



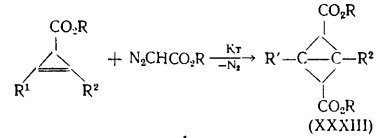
The stereospecific formation of (XXX) is due, according to Vincens et al.,[51,53] to the intramolecular nature of the reduction of the double bond in the intermediate alkoxyaluminium hydride (XXXI).

In the presence of $AlCl_3$ reduction of cyclopropene esters with $LiAlH_4$, which occurs via intermediate carbocations, is accompanied by expansion of the three-membered ring and formation of cyclobutenes (XXXII).[66]



Cycloaddition. Because of the presence of the double bond, cyclopropene-3-carboxylate esters undergo a cycloaddition reaction with various enophiles to give the corresponding bicyclo[*n*.1.0]-carboxylate esters (n = 1–4). In a number of cases these reactions are important for preparative synthesis.

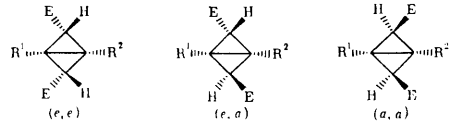
[1 + 2]-Cycloaddition. The only known example of reactions of this type is the addition of alkoxycarbonylcarbenes, which are generated by catalytic decomposition of alkyl diazoacetates, to the double bond of cyclopropene esters. In this process the corresponding bicyclobutane adducts (XXXIII) are formed in 25–42% yield:[67-70]



R = Me, Et, t-Bu; R^1 = H, Pr, Bu, Ph; R^2 = Pr, Bu, Ph, $SiMe_3$; Cat = Cu (110 °C), $Rh(OAc)_2$ (25 °C).

In certain cases diesters (XXXIII) are formed as by-products (2–5%) in the preparation of cyclopropene esters from acetylenes and alkyl diazoacetates.[14,28,71]

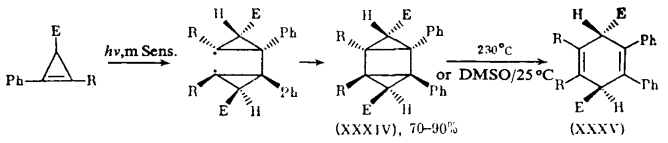
As regards the stereoselectivity of this reaction, it is known that di-t-butyl esters (XXXIII) are only formed as a single (*e,e*)-isomer,[14] while the dimethyl and diethyl esters are formed as two (*e,e*)- and (*e,a*)-isomers, the ratio of which varies from 3 : 1 to 1 : 1 depending on the nature of the substituents R^1 and R^2.[28,67-70,71] The sterically hindered (*a,a*)-isomer is not formed in a single case.



E = CO_2Me, CO_2Et, CO_2Bu-t

[2 + 2]-Cycloaddition. Reactions of this type involving cyclopropene-3-carboxylate esters only occur on photolysis and have limited importance for preparative synthesis. In particular, homodimerisation of cyclopropene esters to the corresponding tricyclohexanedicarboxylate esters (XXXIV) in the presence of a sensitiser (for example, trioxanone) takes place stereospecifically via biradical intermediates which are characterised by the greatest delocalisation of electrons.[72-76] Esters (XXXIV) when heated to

230 °C or when dissolved in dimethyl sulphoxide at 25 °C are quantitatively converted to cyclohexadienedicarboxylate esters (XXXV).[72]

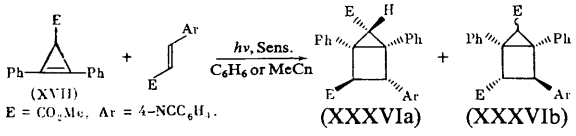


R = Me, Ph; E = CO_2Me.

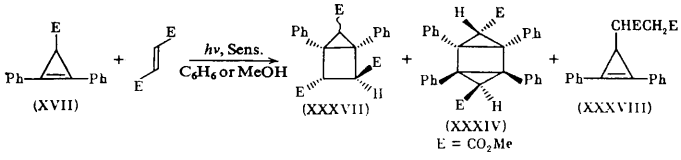
In two studies[77,78] there are reports about the possible formation of tricyclohexanes (XXXIV) together with the isomeric cyclohexadienes (XXV) [77] by carrying out this reaction with direct photolysis. However, attempts to reproduce the reported results[77,78] proved unsuccessful;[72–76] cyclopropene esters underwent opening of the three-carbon ring with formation of alkoxyfurans. This difference in the behaviour of cyclopropene esters under conditions of direct and sensitised photolysis is attributed[72–76] to the different multiplicity of the excited state of cyclopropene.

According to the results of two studies[72,79] photochemical cyclodimerisation of 3-substituted cyclopropene-3-carboxylate esters doe not occur because of considerable steric hindrance.

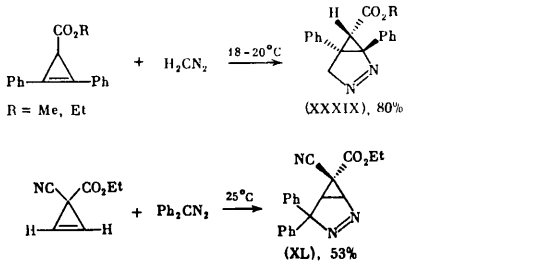
There are known examples of the cross-[2 + 2]-cycloaddition of cyclopropene esters to electron-deficient olefins taking place by sensitised photolysis.[74] Thus, the photochemical reaction of ester (XVII) with methyl *p*-cyanocinnamate gives the corresponding bicyclopentane adducts (XXXVIa, b) with an *exo*-configuration of the alkoxycarbonyl group.



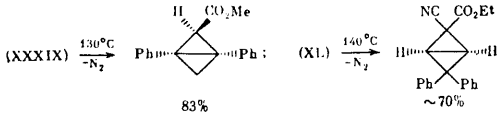
However, the reaction of the same ester (XVII) with dimethyl fumarate is less sensitive, and both the bicyclopentane *exo*- and *endo*-isomers (XXXVII) are formed.



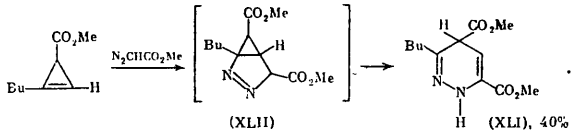
[3 + 2]-Cycloaddition. In the absence of decomposition catalysts diazoalkanes react at room temperature with cyclopropene-3-carboxylate esters by a [3 + 2]-cycloaddition to give the corresponding pyrazolines solely as their *exo*-isomers.[80–82]



The reaction can have preparative value for the synthesis of bicyclo[1.1.0]butanecarboxylate esters, which are formed in high yield by thermolysis of pyrazolines (XXXIX) or (XL).[80,82]

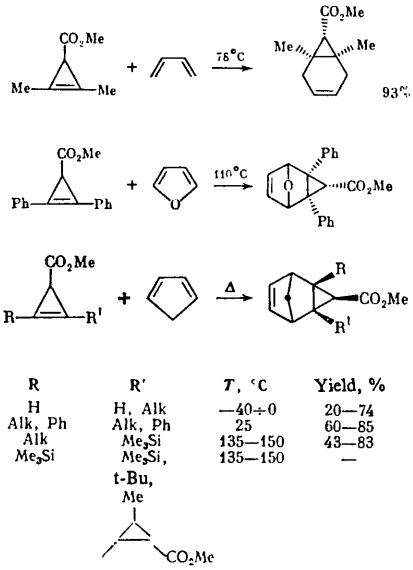


The reaction of methyl 1-butylcyclopropene-3-carboxylate with methyl diazoacetate in the absence of catalysts also apparently takes place by a [3 + 2]-cycloaddition [via the initially formed bicyclic pyrazoline (XLII)] to give the pyridazine (XLI):[70]



[4 + 2]-Cycloaddition. These are the most characteristic of all the cycloaddition reactions of cyclopropene-3-carboxylate esters and are those the most frequently used in synthesis.

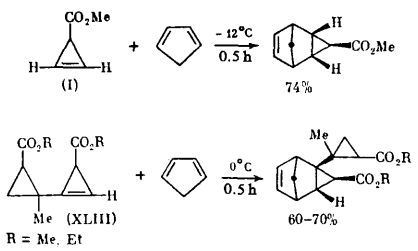
Cyclopropene esters react with butadienes,[83,84] cyclopentadiene,[27–29,30,84–87] and furan[85,87] to form the corresponding adducts, the reactions with cyclic dienes taking place with strict selectivity. When cyclopropene esters are reacted with cyclopentadiene, the *endo*-adducts are exclusively formed, and with furan the corresponding *exo*-adducts are formed.



R	R'	*T*, °C	Yield, %
H	H, Alk	—40÷0	20—74
Alk, Ph	Alk, Ph	25	60—85
Alk	Me_3Si	135—150	43—83
Me_3Si	Me_3Si, t-Bu, Me	135—150	—

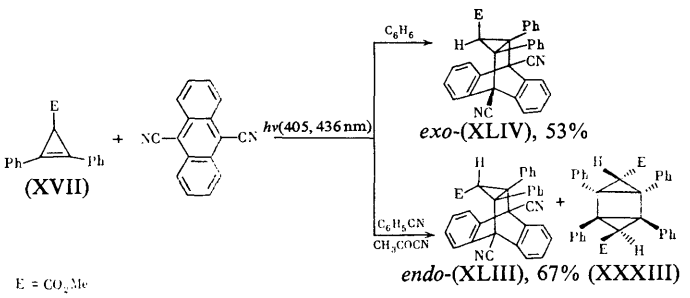
The activity of cyclopropene esters as dienophiles is determined by the nature of the substituents on the ring double bond and the steric accessibility of this bond. Thus, unsubstituted and monosubstituted cyclopropene-3-carboxylate esters are the most active, reacting with cyclopentadiene even at 0 °C and below.[27,29,86] Because of this it was possible to use cyclopentadiene as a trap for cyclopropene esters that have low stability under normal conditions. It was this method that

was used to "capture" the simplest methyl cyclopropene-3-carboxylate (I) and esters (XLIII), which are unstable in a pure state above 0 °C.[27,29,86]



The least active dienophiles are cyclopropene esters with a trimethylsilyl group on the double bond, which form the corresponding adducts only on boiling in xylene for many hours; and the introduction of a further trimethylsilyl or other bulky substituent on to the ring double bond completely prevents a reactions with cyclopentadiene.[27,28,86]

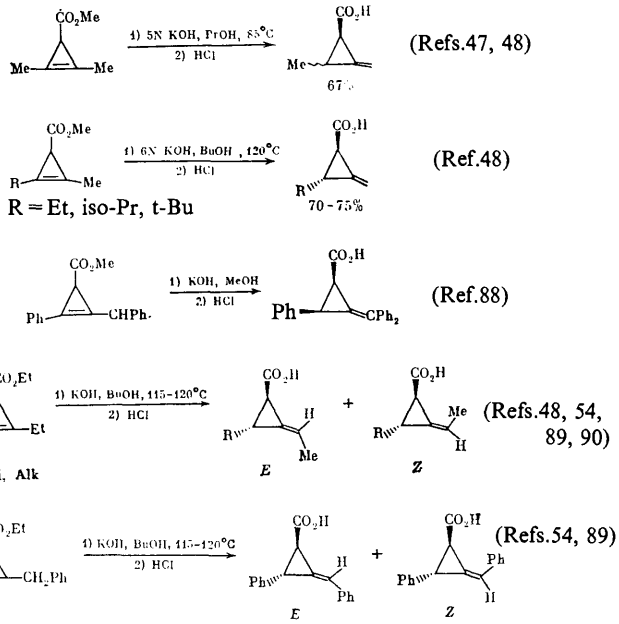
[4 + 2]-Cycloaddition reactions of cyclopropene esters with electron-deficient dienes are also possible by photolysis, with the structure of the adducts formed depending to a considerable degree on the experimental conditions. Photochemical reaction of ester (XVII) with 9,10-dicyanoanthracene in benzene gives the *exo*-adduct (XLIV), while in acetonitrile or benzonitrile the sterically hindered *endo*-adduct (XLIII) is formed. In the latter case the cyclodimer (XXXIII) is also formed together with *endo*-adduct (XLIII).



This difference in the results of the reaction was attributed by Brown-Wensley et al.[74] to differences in the nature of the intermediates in relation to the polarity of the medium.

Exocyclic migration of the double bond. In a number of unsaturated compounds with a three-carbon ring, compounds with an *exo*-configuration of the double bond are thermodynamically more stable than the isomeric alkylcyclopropenes; this causes the latter to be isomerised to the corresponding alkylidenecyclopropanes by the action of bases.[55]

Exocyclic migration of the double bond in alkyl- or benzyl-substituted cyclopropene-3-carboxylate esters occurs, in addition to saponification of the ester group, on treatment with alcoholic alkali solutions at 85–120 °C.[47,48,54,88–90] As a result, 1-methylenecyclopropane-3-carboxylate esters are formed from 1-methylcyclopropene-3-carboxylate esters, while 1-ethyl- or 1-benzyl-substituted cyclopropene-3-carboxylate esters give 1-ethylidene- or 1-benzylidene-cyclopropane-3-carboxylate esters as mixtures of their (*Z*)- and (*E*)-isomers with the latter predominating.



Potassium t-butoxide and sodium methoxide in absolute solvents do not cause cyclopropene esters to react in these ways.[91]

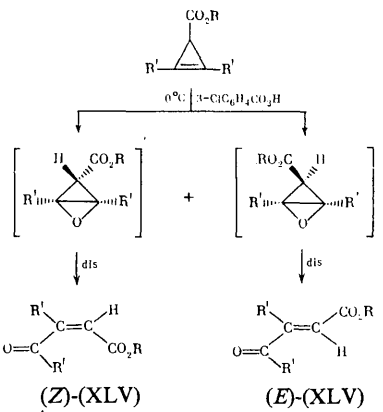
2. Reactions of cyclopropene-3-carboxylate esters with opening of the three-carbon ring

The reactions discussed in the previous section indicate that the three-carbon ring of cyclopropene-3-carboxylate esters, in particular for those disubstituted on the double bond, is quite stable. However, acids, oxidising agents or transition metals can cause the ring to open with formation of acyclic compounds.

(a) Oxidation

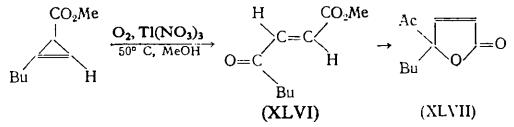
Oxidation of cyclopropene-3-carboxylate esters with chloroperbenzoic acid at 0 °C takes place via an epoxidation stage and gives isomeric unsaturated ketones (XLV) in almost quantitative yields (Scheme 2).[92–95]

Scheme 2



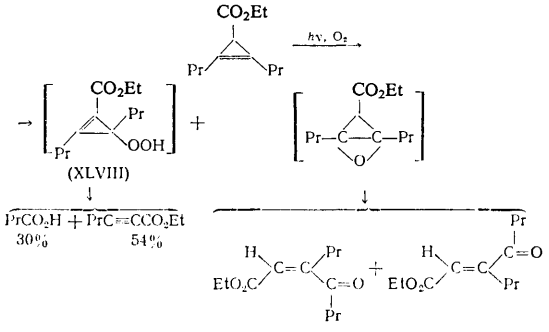
Peracetic and perbenzoic acids do not cause cyclopropene esters to react at all.[94]

The formation of vinylketone (XLVI) occurs in the oxidation of methyl 1-butylcyclopropene-3-carboxylate with oxygen in the presence of thallium nitrate at 50 °C in methanol. However, (XLVI) is gradually converted during the reaction to lactone (XLVII).[70]



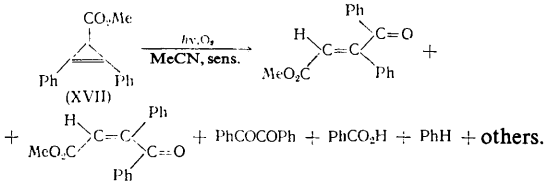
(XLVI) (XLVII)

In the oxidation of cyclopropene esters with oxygen by sensitised photolysis, the yield of vinylketones does not exceed 15%. The main products of the photooxidation of 1,2-dipropylcyclopropene-3-carboxylate esters are butyric acid and ethyl hex-2-ynoate, which are formed as a result of decomposition of the initially generated hydroperoxide (XLVIII).[95]



(XLVIII)

The photooxidation of ester (XVII) is not selective and leads to a complex mixture of products.[74]

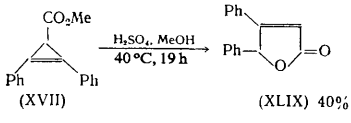


(XVII)

(b) Reactions with acids

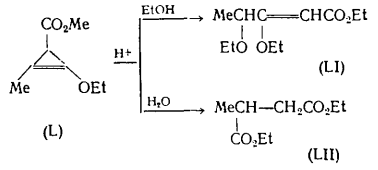
Cyclopropene-3-carboxylate esters are fairly stable towards acids. At 20–25 °C they withstand prolonged contact (up to 40 h) with concentrated hydrochloric, hydrobromic, sulphuric, and hydrofluoric acids.[96,97] However, on boiling with alcoholic or aqueous acid solutions cyclopropene esters undergo ring-opening to form various carbofunctional compounds.

Thus, when ester (XVII) is boiled for many hours with a methanol solution of sulphuric acid, lactone (XLIX) is obtained.[96]



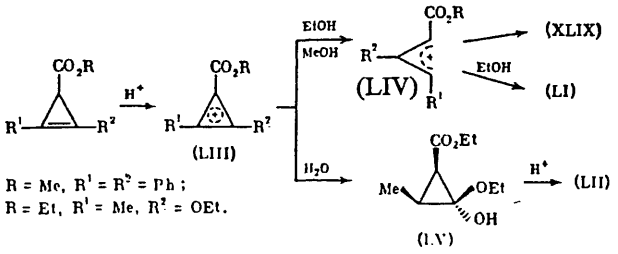
(XVII) (XLIX) 40%

Under similar conditions the ethoxycyclopropene-3-carboxylate ester (L) is converted to ethyl diethoxypentenoate (LI) in 50% yield, while in an aqueous solution of *p*-toluenesulphonic acid the diethyl ester (LII) is obtained in quantitative yield without formation of the corresponding furanone.[98]



(L) (LI) (LII)

It has been proposed[96,98] that the driving force of all these processes is protonation of the ring double bond to form the cyclopropyl cation (LIII), which isomerises in alcohol solution to the allylic cation (LIV), which then cyclises to lactone (XLIX) or reacts with the solvent to form acid (LI). In aqueous solution hydration of cation (LIII) gives ketal (LV), which is isomerised by the action of acid to ester (LII).

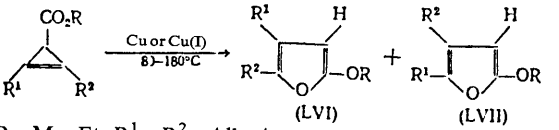


R = Me, R¹ = R² = Ph;
R = Et, R¹ = Me, R² = OEt.

(LIII) (LIV) (LV)

(c) Catalytic reactions of cyclopropene-3-carboxylate esters

Reactions of cyclopropene-3-carboxylate esters on treatment with copper compounds. The most numerous examples of catalytic reactions of cyclopropene esters are those occurring in the presence of copper compounds. Among these the isomerisation of cyclopropene-3-carboxylate esters to alkoxyfurans is the most familiar.[21,55,99,100]



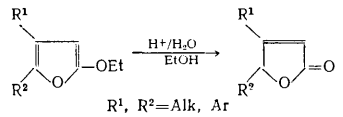
(LVI) (LVII)

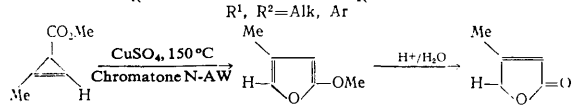
R = Me, Et, $R^1 = R^2$ = Alk, Ar;
R = Et, R^1 = Me, R^2 = Ph (LVI : LVII = 19 : 1), n-Bu (LVI : LVII = 1 : 1) t-Bu (LVI : LVII = 1.2 : 1);
R = Et, R^1 = Et, t-Bu, R^2 = H.

In an inert atmosphere with exclusion of moisture alkoxyfurans are the main reaction products, so this can be regarded as a preparative method.[55,99,100]

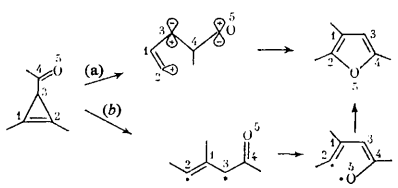
Asymmetrically substituted cyclopropene-3-carboxylate esters are converted to form two isomeric alkoxyfurans (LVI) and (LVII) in total yields of up to 90%, the ratio of which is determined by the substituents on the cyclopropene double bond.[100] Isomerisation of 1-substituted cyclopropene-3-carboxylate esters only gives product (LVI), which corresponds to cleavage of the C(2)–C(3) bond of the cyclopropene ring.[7,22] However, the yield of alkoxyfuran (LVI) does not exceed 20–25%, which is apparently due to oligomerisation of the initial cyclopropene ester and final alkoxyfuran during the reaction.

In the presence of traces of moisture and acids, alkoxyfurans are readily hydrolysed to the corresponding furanones,[19,100] which in specific cases[7] are the only identifiable reaction products.

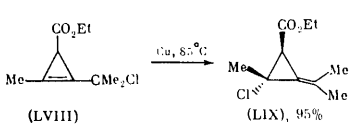




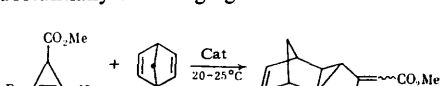
According to Komendantov et al.,[100] the formation of alkoxyfurans can take place either by a concerted [1,3]-sigmatropic rearrangement of cyclopropene esters [route (*a*)], which is no longer forbidden in the presence of a catalyst, or by a non-concerted route (*b*) via a biradical that is formed by opening of the three-membered ring. In this case the role of the catalyst is to reduce the energy of activation for isomerisation through the formation of an organocopper complex and hence weaken the σ-bonds.



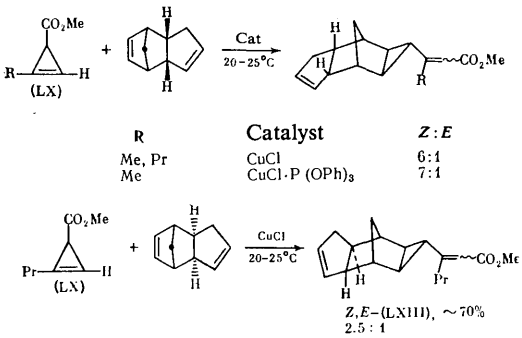
However, for cyclopropene ester (LVIII), which contains a chlorine atom in the α-position of the alkyl substituent on the double bond (in contrast to the esters considered above), in the presence of copper at 85 °C an exocyclic migration of the double bond and chlorine to form the ester (LIX) occurs rather than isomerisation to an alkoxyfuran.[101] The same reaction of ester (LVIII) occurs without copper but at a higher temperature (150 °C).



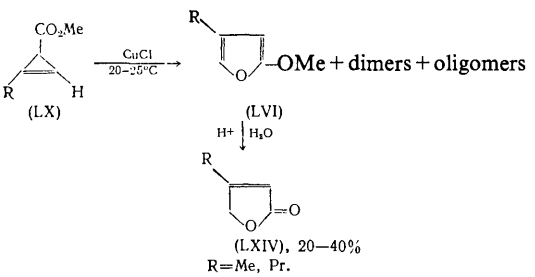
Comparatively recently[102,103] it was found that 1-alkylcyclopropene-3-carboxylate esters (LX) in the presence of Cu(I) compounds can selectively vinylcyclopropanate the strained ring double bond in norbornadiene and dicyclopentadiene to give cycloadducts (LXI)–(LXIII) exclusively as the *exo,anti*-isomers. In this case the ratio of (*Z*)- to (*E*)-isomers varies according to the nature of the substituent R in the cyclopropene ester, the structure of the unsaturated compound and the nature of the catalyst, increasing substantially on changing from CuCl to its complexes.[103]



R	Catalyst (Cat)	*Z*:*E*
Me	CuCl	1.3:1
	CuCl·2Me$_3$SiC≡CMe	2.5:1
	CuCl·P(OPh)$_3$	3:1
Pr	CuCl	1.7:1
	CuCl·2Me$_3$SiC≡CMe	2.5:1
	CuCl·P(OPh)$_3$	4:1
C_5H_{11}	CuCl	1.8:1
	CuCl·P(OPh)$_3$	7:1

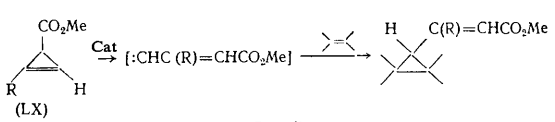


With other unsaturated compounds—1,5-cyclooctadiene, cyclohexene, methylenecyclobutane, methyl acrylate—esters (LX) do not give vinylcyclopropane adducts but are converted to lactones (LXIV), as a result of hydrolysis of the initially formed alkoxyfurans (see above), and oligomers.[103]



When esters (LX) are reacted with cyclopentadiene, diene adducts are formed in 70% yield.[103]

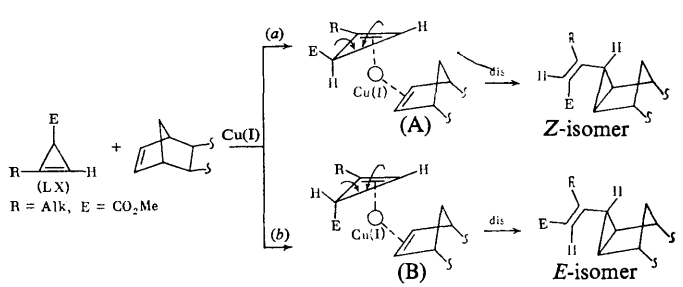
According to the results of three studies[102,104,105] the formation of cycloadducts (LXI)–(LXIV) may be due to addition to the double bonds of vinylcarbene intermediates which are generated by catalytic isomerisation of cyclopropenes (LX).



R=Alk.

However, the high regioselectivity and stereoselectivity for formation of the vinylcyclopropane adducts is more consistent with the reaction taking place within the coordination sphere of Cu(I) according to a concerted mechanism (Scheme 3).[103]

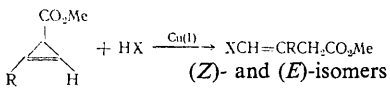
Scheme 3



In this case the exclusive *exo*-addition of the reaction species to the double bond of norbornadiene is due to *exo*-coordination of the copper atom with the initial cyclodiene. The selective formation of

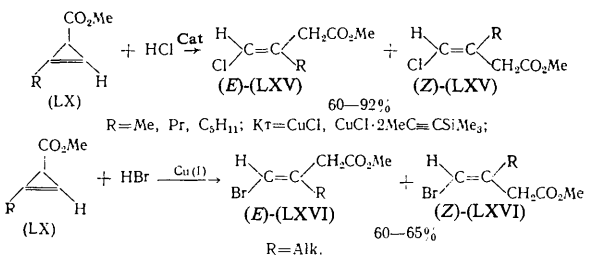
the *anti*-isomer and the ratio of (*Z*)- to (*E*)-isomers are established when cyclopropene (LX) coordinates with the olefin complex of univalent copper and is determined by the stereoselectivity of the subsequent conversions, being governed by the principle of conservation of orbital symmetry. The presence of bulky ligands in the coordination sphere of copper, particularly when changing from CuCl to the complex catalysts $2MeC{\equiv}CSiMe_3.CuCl$ and $(PhO)_3P.CuCl$, must reduce the probability of coordination of the type (B) in favour of (A), in other words, it leads to an increase in the yield of (*Z*)-isomer, which in actual fact occurs.

During the last few years we have discovered a new reaction of methyl 1-alkylcyclopropene-3-carboxylates (LX) with proton-donor reagents of the general type HX, which takes place on treatment with copper(I) chloride at room temperature. This reaction, which is undoubtedly of interest for preparative synthesis, leads to the formation of the corresponding (*Z*)- and (*E*)-isomers of 4-substituted methyl 3-alkylbutenoates.[97,106-108]



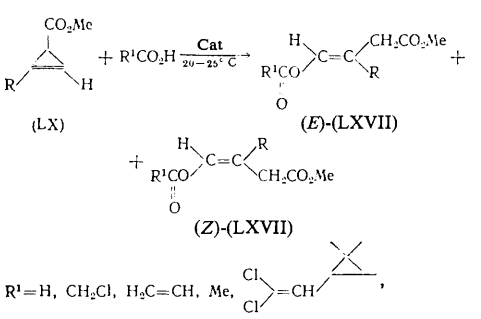
R=Alk, X=Cl, Br, R^1CO_2, ArO, CN, $R^2C{\equiv}C$.

Gaseous HBr, hydrochloric acid, and hydrogen chloride (whatever the method of generation) at 20–25 °C in the presence of copper (I) chloride or its complex readily add on to the C(2)–C(3) bond in (LX) to form methyl 4-bromo- or 4-chloro-butenoates (LXV) and (LXVI), mainly as their (*E*)-isomers.[97,106]



R=Alk.

Carboxylic acids whose pK_a values occur within the region 3 to 7 (monochloroacetic, formic, acrylic, acetic, permethrinic) react in a similar manner with cyclopropene esters (LX). In this case the yields of the resulting (*Z*)- and (*E*)-4-acyloxybutenoate esters (LXVII) amount to 58–95%.[97,106]

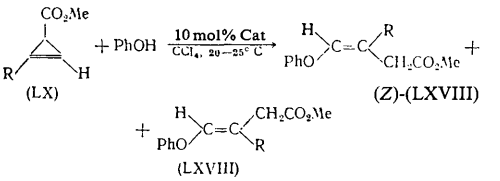


R=Alk, R^1=H, CH_2Cl, $H_2C{=}CH$, Me, ,

Cat = $CuCl.2MeC{\equiv}CSiMe_3$

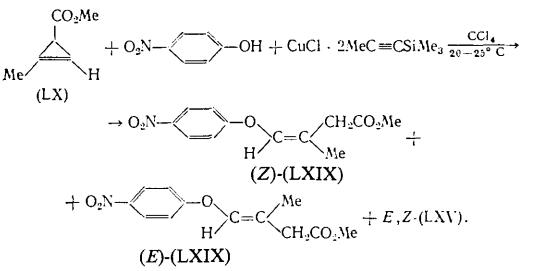
Stronger carboxylic acids that have pK_a values of 0–2 (trifluoro-, trichloro-, and dichloro-acetic acids as well as hydrofluoric acid) do not add on to cyclopropene esters (LX) in the presence of CuCl but rapidly convert them to 4-alkylfuranones (LXIV).[97]

On the other hand the catalytic addition of phenol to esters (LX) proceeds quite smoothly, giving methyl phenoxybutenoates (LXVIII) in 50–80% yield, mainly as the (*Z*)-isomer.[97,106]



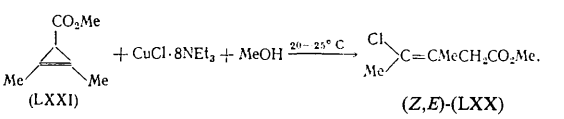
R = Me, C_5H_{11}; Cat = $CuCl.2MeC{\equiv}CSiMe_3$.

Reaction of esters (LX) with 4-nitrophenol under the same conditions gives mainly oligomeric products. However, in the presence of 100 mol% of an acetylene complex of copper(I) chloride, *p*-nitrophenol an add on to a cyclopropene ester (LX, R = Me) in a similar manner to phenol to form (*Z*)- and (*E*)-methyl 4-(*p*-nitrophenoxy)-3-methylbut-3-enoates (LXIX) (5 : 1) with a total yield of 30%. The main reaction products here are isomeric 4-chloro-3-methylbut-3-enoate esters (LXV) (total yield 45%),[97] in the formation of which nitrophenol appears only as a proton donor, while CuCl is a source of Cl, in other words, it acts as a reactant rather than a catalyst:



This trend is shown to an even greater extent for 2,4-dinitrophenol, methanol, butyl mercaptan, and 5-methyl-4-cyclohexene-1,2-dicarboximide. Their reaction with esters (LX) in the presence of the complex $CuCl.2MeC{\equiv}CSiMe_3$ gives only (*Z*)- and (*E*)-4-chlorobutenoate esters (LXV), the quantity of which increases as the amount of added CuCl increases.[97]

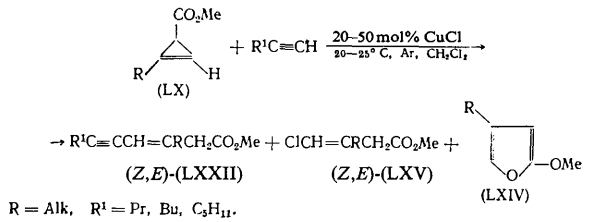
The only example of the catalytic addition of HCl units to 1,2-disubstituted cyclopropene-3-carboxylate esters is formation of the corresponding 4-chloropentenoate esters (LXX) by reaction of the cyclopropenoate ester (LXXI) with an equivalent quantity of the complex $CuCl.8NEt_3$ and methanol.[106]



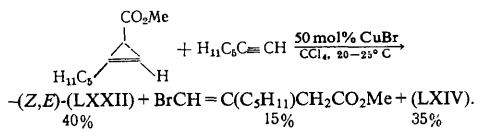
Esters (LXX) are formed in 30% yield mainly as the (*Z*)-isomer [(*Z*) : (*E*) = 5 : 2].

Among compounds that contain a mobile hydrogen atom on a carbon atom (terminal acetylenes, HCN, nitro- and trinitro-methane, ethyl cyanoacetate, bromoform) an [H–X]-addition reaction with 1-alkylcyclopropene-3-carboxylate esters can only be achieved with

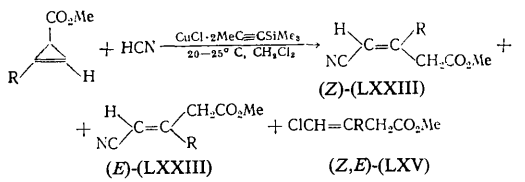
terminal acetylenes and HCN,[97,107] which, in contrast to the other compounds with a mobile hydrogen atom that were studied, are able to form complexes with CuCl. In this case esters (LX) and 1-alkynes in the presence of 20–50 mol% CuCl react to form the corresponding 3-alken-5-ynoate esters (LXXII) (yield ~65%) mainly as their (*Z*)-isomers[105] together with chlorobutenoate esters (LXV) (yields 10–20%) and methoxyfurans (LXIV) (yield 5–10%). The selectivity of the process and the yields of esters (LXXII) depend significantly on the reaction conditions, primarily on the ratio of reactants and the relative quantity of CuCl.[97,107]



The reaction of cyclopropene ester (LX, R = C_5H_{11}) with 1-heptyne in the presence of CuBr occurs in a similar manner:[97]



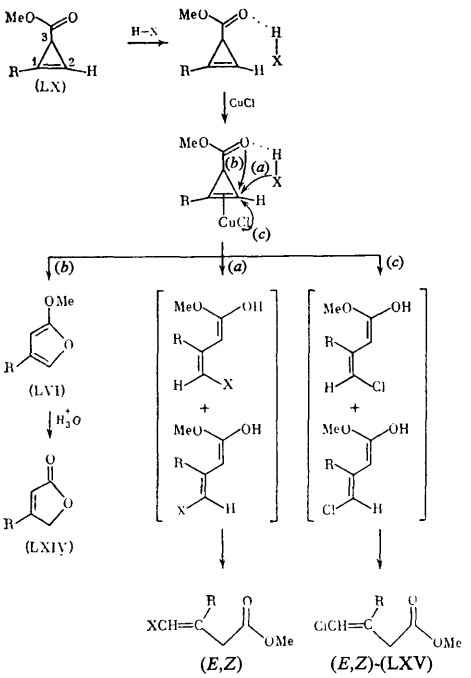
Addition of gaseous HCN in the presence of CuCl.2MeC≡CSiMe$_3$ to cyclopropenes (LX) also takes place fairly readily, the formation of 4-cyanoalkylbutenoate esters (LXXIII) also being accompanied by partial hydrochlorination of (LX) to chlorobutenoate esters (LXV). The maximum yield of esters (LXXIII) (60–65%) occurs with incomplete conversion of (LX) (66–70%) and a quantity of CuCl.2MeC≡CSiMe$_3$ equal to 20 mol%.[107]



Treatment of esters (LX) with trinitromethane, nitromethane, bromoform, or ethyl acetate at 25 °C in the presence of 10–100 mol% of $CuCl_2$.2MeC≡CSiMe$_3$ complex gives only chlorobutenoate esters (LXV).[97]

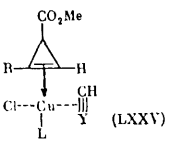
As regards the mechanism of the reaction between cyclopropene esters and proton-donor reagents HX (Scheme 4), it is most likely that the formation of 4-substituted 3-butenoate esters takes place within the coordination sphere of copper.[97] In the presence of the reagents HX (hydrogen halides, carboxylic acids, phenols) that are capable of solvating cyclopropene esters (LX) and thus become part of an organocopper complex, attack by nucleophile X on the C(2) atom of the ring becomes possible and (*Z*)- and (*E*)-methyl 4-X-3-alkyl-3-butenoates are formed [route (*a*)].

Scheme 4



This process is significant or fundamental (yield of products 30–95%) in the case of HCl, HBr, carboxylic acids with pK_a 3–7, phenol, and nitrophenol. In the presence of carboxylic acids with pK_a 0–2, isomerisation to a methoxyfuran is preferred [route (*b*)], apparently because of the low nucleophilicity of residue X.

The formation of addition product by catalytic reaction of cyclopropene esters with terminal acetylenes and HCN takes place according to the same scheme. However, in this case the reagents HX are drawn into the reaction zone by formation of a complex with CuCl:

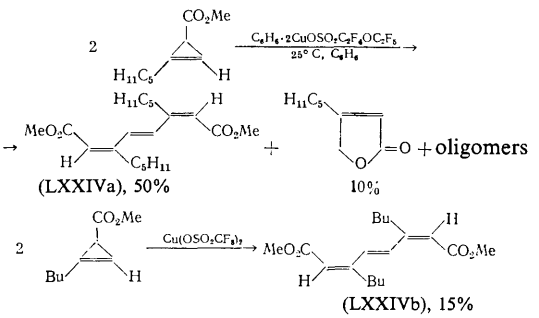


R = Alk,
Y = N or CR^1.

In the resulting organocopper intermediate (LXXV) coordination of the terminal acetylenes or HCN with CuCl leads to weakening of the C–H bond, an increase in the nucleophilicity of the C≡Y residue and convergence of the proton-donor reagent with the cyclopropene molecule, thus creating a favourable opportunity for nucleophilic attack on the C(2) atom to form the corresponding enynoate or cyanobutenoate esters (LXXII) and (LXXIII).[97]

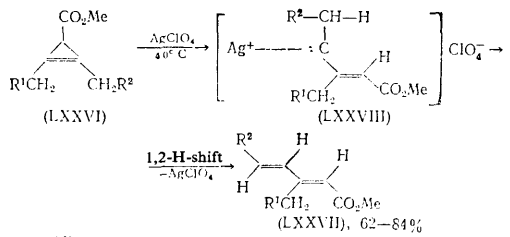
In the reaction of cyclopropene esters with HX reagents in the presence of CuCl, a competing process is also possible—addition of HCl units to the C(2)–C(3) bond to form (*Z*)- and (*E*)-methyl 4-chloro-3-alkyl-3-butenoates (LXV) [route (*c*)]. In this case the HX reagents only act as proton donors, while CuCl acts as the chlorine donor. This route is the main one for reactions of the esters in the presence of 20–100 mol% CuCl with methanol, 2,4-dinitrophenol, butyl mercaptan, cyclohexenedicarboximide, bromoform, trinitromethane, nitromethane, and ethyl cyanoacetate.

When CuCl or its complexes are replaced by $CuOSO_2C_2F_4OC_2F_5$ or copper(II) triflate, the main reaction route of 1-alkylcyclopropene-3-carboxylate esters is their stereoselective dimerisation with ring-opening to give hexatrienecarboxylate esters (LXXIV), which are the formal dimers of vinylcarbenes [:CHC(R)=CHCO$_2$Me] isomer with (LX).[70,109]



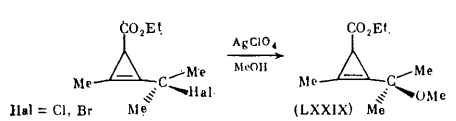
The same reaction of (LX) on treatment with $CuOSO_2C_2F_4OC_2F_5$ occurs in the presence of norbornadiene or acetic acid; neither vinylcyclopropene adducts (LXI) nor acyloxybutenoate esters (LXVII) (R^1 = Me) are formed in these cases.[97]

Reactions of cyclopropenecarboxylate esters in the presence of other metals. Apart from copper compounds the action of other metals, in particular, Ag, Pt,[110] Fe,[32] Rh,[16] on cyclopropene-3-carboxylate esters has been studied. Thus, in the presence of $AgClO_4$ (40 °C) or $AgBF_4$ (80 °C) or PtO_2 (220 °C), 1,2-dialkylcyclopropene-3-carboxylate esters (LXXVI) are converted to the dienoate esters (LXXVII).[110] It was proposed[110] that formation of (LXXVII) occurs via a vinylcarbene intermediate (LXXVIII), although the concerted mechanism proposed for copper compounds cannot be ruled out in this case.

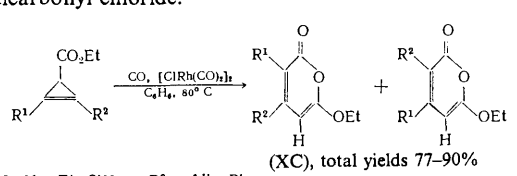


R^1, R^2 = H, Alk.

However, when chlorine or bromine at an α-position relative to the double bond is present in the side chain of a cyclopropene esters, ring-opening does not occur on treatment with $AgClO_4$ in MeOH but nucleophilic substitution takes place to give esters (LXXIX).[111,112]



It was recently demonstrated that α-pyrones can be obtained by carbonylation of cyclopropene-3-carboxylate esters in the presence of rhodium dicarbonyl chloride:[16]



R^1 = H, Me, Et, $SiMe_3$; R^2 = Alk, Ph.

In most cases the reaction is stereospecific, only isomer (XC) being formed, which makes this reaction valuable for preparative synthesis.

Other metal compounds—$Ni(COD)_2$, $MoCl_2-AlEt_3$, WCl_5-SnMe_4, a Ziegler–Natta catalyst—only cause cyclopropene esters (LX) to oligomerise.[70]

- - - o 0 o - - -

Thus, the material reviewed here demonstrates the availability of cyclopropene-3-carboxylate esters and their ability to undergo different chemical reactions with high conversion rates and selectivity. This makes it vital to carry out studies on the use of the reactions of cyclopropene-3-carboxylate esters and compounds derived from them in the directed organic synthesis of compounds with various useful properties.

References

1. I A D'yakonov, M M Komendantov *Vestn. Leningr. Univ., Fiz. Khim.*, 1956, **4**(22) 166
2. R Breslow, D Chipman *Chem. Ind. (London)*, 1960, 1105
3. R Breslow, R Winter, M Battiste *J. Org. Chem.*, 1959, **24** 415
4. R Breslow, J Lockhart, A Small *J. Am. Chem. Soc.*, 1962, **84** 2793
5. I E Dolgii, G P Okonnishnikova, O M Nefedov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1970, 197
6. O M Nefedov, I E Dolgii, G P Okonnishnikova, et al. *Angew. Chem.*, 1972, **84** 946
7. E A Shapiro, I E Dolgii, O M Nefedov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 2096
8. N Petiniot, A J Anciaux, A F Noels, et al. *Tetrahedron Lett.*, 1978, 1239
9. G L Closs *Advances in Alicyclic Chemistry* (Edited by H Hart, G L Karabatsos), Vol. 1, Academic Press, New York–London, 1966, p. 53
10. T V Mandel'shtam *Sovremmenye Problemy Organicheskoi Khimii* (Current Problems in Organic Chemistry) (Edited by K A Ogloblin), Izd. LGU, Leningrad, 1976, p. 87
11. N S Zefirov, N V Averina, A M Boganov, et al. *Zh. Org. Khim.*, 1981, **17** 1450
12. A Demonceau, A F Noels, A J Anciaux, et al. *Bull. Soc. Chim. Belg.*, 1984, **98** 949
13. I N Domnin, E F Zhuraveleva, N V Pronina *Zh. Org. Khim.*, 1978, **14** 2323
14. P Dowd, P Garner, R Schapper *J. Org. Chem.*, 1982, **47** 4240
15. E A Shapiro, T N Romanova, I E Dolgii, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 2535
16. S H Cho, L S Liebeskind *J. Org. Chem.*, 1987, **52** 2631
17. I A D'yakonov, M I Komendantov *Zh. Obshch. Khim.*, 1961, **31** 3881
18. I A D'yakonov, M I Komendantov, S P Korshunov *Zh. Obshch. Khim.*, 1962, **32** 923
19. I A D'yakonov, M I Komendantov *Zh. Obshch. Khim.*, 1963, **33** 2448
20. F L Carter, V L Frampton *Chem. Rev.*, 1964, **64** 497
21. M I Komendantov, I A D'yakonov, I Gokhmanova, et al. *Zh. Org. Khim.*, 1965, **1** 209

22. M Vidal, M Vincens, P Arnaud *Bull. Soc. Chim. Fr.*, 1972, 657
23. E A Shapiro, G V Lun'kova, I E Dolgii, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 2529
24. E A Shapiro, Candidate's Thesis in Chemical Sciences, Institute of Organic Chemistry, USSR Academy of Sciences, Moscow, 1977
25. USSR P. 566 830; *Byull. Izobret.*, 1977, (28)
26. I E Dolgii, G P Okonnishnikova, O M Nefedov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 822
27. G P Okonnishnikova, Candidate's Thesis in Chemical Sciences, Institute of Organic Chemistry, USSR Academy of Sciences, Moscow, 1978
28. E A Shapiro, G V Lun'kova, O M Nefedov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 2535
29. E A Shapiro, G V Lun'kova, I E Dolgii, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1316
30. H Lind, A J Deutschmann, Jr. *Z. Org. Chem.*, 1967, **32** 326
31. I A D'yakonov, M I Komendantov, I G Gokhmanova *Zh. Obshch. Biol. Khim.*, 1959, **29** 3848
32. W A Donaldson, R P Hughes *J. Am. Chem. Soc.*, 1982, **104** 4846
33. W Kirmse, L Horner *Liebigs Ann. Chem.*, 1958, **614** 1
34. H Reimlinger *Chem. Ber.*, 1959, **92** 970
35. M Frank-Neumann, C Buchecker *Tetrahedron Lett.*, 1972, 937
36. M Frank-Neumann, C Dietrich-Buchecker *Tetrahedron Lett.*, 1976, 2069
37. D P Cox, I R Gould, N P Hacker, et al. *Tetrahedron Lett*, 1983, **24** 5313
38. C D DeBoer *J Chem. Soc., Chem. Commun.*, 1972, 377
39. M T H Liu *The Chemistry of Diazonium and Diazo Groups* (Edited by S Patai), John Wiley and Sons, London, 1978, p. 127
40. M I Komendantov, I N Domnin, R M Kenbaeva, et al. *Zh. Org. Khim.*, 1973, **9** 1420
41. I N Domnin, E F Zhuravleva, M I Komendantov, et al. *Zh. Org. Khim.*, 1977, **13** 1789
42. M J Jorgenson *J. Am. Chem. Soc.*, 1969, **91** 6432
43. U-J Vogelbacher, P Eisenbarth, M Regitz *Angew. Chem.*, 1984, **96** 691
44. D M DeSimone, P J Desrosiers, R P Hughes *J. Am. Chem. Soc.*, 1982, **104** 4842
45. C E Chidsey, A W Donaldson, R P Hughes, et al. *J. Am. Chem. Soc.*, 1979, **101** 233
46. J L Williams, D S Sgoutas, *J. Org. Chem.*, 1971, **36** 3064
47. M Vidal, M Vincens, P Arnaud *Bull. Soc. Chim. Fr.*, 1969, 4543
48. M Vidal, M Vincens, P Arnaud *Bull. Soc. Chim. Fr.*, 1972. 665
49. W A Donaldson, R P Hughes *Synth. Commun.*, 1981, **11** 999
50. G Maiere, M Hoppe, H P Reisenauer, et al. *Angew. Chem.*, 1982, **94** 445
51. I N Domnin, C Dumont, M Vincens, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 1593
52. M Vidal, P Arnaud *Bull. Soc. Chim. Fr.*, 1972, 675
53. M Vincens, C Dumont, M Vidal *Tetrahedron*, 1983, **39** 4281
54. M Vincens, C Dumont, M Vidal *Tetrahedron*, 1981, **37** 2683
55. T N Grigorova *Sovremennye Problemy Organicheskoi Khimii* (Current Problems in Organic Chemistry) (Edited by K A Ogloblin), Izd. LGU, Leningrad, 1974, p. 100
56. T N Grigorova, M I Komendantov *Zh. Org. Khim.*, 1981, **17** 317
57. M Vincens, S Choubani, M Vidal *Tetrahedron Lett.*, 1981, **22** 4695
58. R Arnaud, S Choubani, R Subra, et al. *Can. J. Chem.*, 1985, **63** 2512
59. T N Grigorova, K A Ogloblin, M I Komendantov *Zh. Org. Khim.*, 1973, **9** 711
60. V R Kartashov, N V Gal'yanova, E V Skorobogatova, et al. *Zhur. Org. Khim.*, 1984, **20** 2623
61. V R Kartashov, N V Malisova, E V Skorobogatova, et al. *Zh. Org. Khim.*, 1986, **22** 867
62. R N Gymzina, I A D'yakonov, L P Danilkina *Zh. Org. Khim.*, 1970, **6** 2168
63. M Frank-Neumann, M Miesch *Tetrahedron Lett.*, 1982, 1409
64. Y Matsui, M Orchin *J. Organomet. Chem.*, 1983, **244** 369
65. T E Nalesnik, J G Fish, S W Hordon, et al. *J. Org. Chem.*, 1981, **46** 1987
66. W J Gensler, J J Langone, M B Floyd *J. Am. Chem. Soc.*, 1971, **93** 3828
67. I A D'yakonov, M I Komendantov *Zh. Obshch. Khim.*, 1963, **33** 2420
68. I A D'yakonov, V V Razin, M I Komendantov *Tetrahedron Lett.*, 1966, 1127
69. I A D'yakonov, V V Razin, M I Komendantov *Dokl. Akad. Nauk SSSR*, 1967, **177** 354
70. N Condé-Petiniot, A J Hubert, A F Noels, et al. *Bull. Soc. Chim. Belg.*, 1986, **95** 649
71. G V Lun'kova, Candidate's Thesis in Chemical Sciences, Institute of Organic Chemistry, USSR Academy of Sciences, Moscow, 1982
72. C D DeBoer, D H Wadsworth, W C Perkins *J. Am. Chem. Soc.*, 1973, **95** 861
73. S Farid, K A Brown *J. Chem. Soc., Chem. Commun.*, 1976, 564
74. K A Brown-Wensley, S L Mattes, S Farid *J. Am. Chem. Soc.*, 1978, **100** 4162
75. J A Pincock, A A Montsokapas *Can. J. Chem.*, 1977, **55** 979
76. A Padwa *Acc. Chem. Res.*, 1979, **12** 310
77. M J Bennett, J T Purdham, S Takada, et al. *J. Am. Chem. Soc.*, 1971, **93** 4063
78. M I Komendantov, I N Domnin *Zh. Org. Khim.*, 1973, **9** 939
79. M L Deem *Synthesis*, 1982, 701
80. C Guiboret, R Danion-Buogot, D Danion, et al. *Tetrahedron Lett.*, 1981, **22** 441
81. M I Komendantov, R R Bekmukhametov *Zh. Org. Khim.*, 1971, **7** 423
82. M I Komendantov, R R Bekmukhametov, V G Novinskii *Zh. Org. Khim.*, 1976, **12** 801
83. W E von Doering, M Pomerantz *Tetrahedron Lett.*, 1964, 961
84. M A Battiste *Tetrahedron Lett.*, 1964, 3795
85. M L Deem *Synthesis*, 1972, 675
86. I E Dolgii, G P Okonnishnikova, E A Baidzhigitova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 2592
87. H-D Martin, L Kaudy, D Stusche *Tetrahedron Lett.*, 1977, 3561
88. N A Ampilogova, I A D'yakonov, R R Kostikov *Zh. Org. Khim.*, 1966, **2** 1898
89. M Vincens, C Dumont, M Vidal *Bull. Soc. Chim. France*, 1974, 2811
90. M Vincens, C Dumont, M Vidal *C. R. Seances Acad. Sci.*, 1978, **286** 717
91. I N Domnin, I A D'yakonov, M I Komendantov *Zh. Org. Khim.*, 1967, **3** 2076
92. H Prinzbach, U Fischer *Helv. Chim. Acta*, 1967, **50** 1669

93. L E Friedrich, R A Cormies *Tetrahedron Lett.*, 1971, 4761
94. J K Grandall, W W Conover *J. Org. Chem.*, 1978, **43** 1323
95. A A Frimer, A Antebi *J. Org. Chem.*, 1980, **45**, 2334
96. L Schrader *Tetrahedron Lett.*, 1971, 2993
97. M N Protopopova, Candidate's Thesis in Chemical Sciences, Institute of Organic Chemistry, USSR Academy of Sciences, Moscow, 1986
98. E Wenkert, K J Chou, R P Hatch *Synth. Commun.*, 1977, **7** 375
99. I A D'yakonov, M I Komendantov, T S Smirnova *Zh. Org. Khim.*, 1969, **5** 1742
100. M I Komendantov, I N Domnin, E V Bulucheva *Tetrahedron*, 1975, **31** 2495
101. M Vincens, A Dussauge, M Vidal *Tetrahedron*, 1977, **33** 2936
102. I E Dolgii, Yu V Tomilov, O M Nefedeov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 700
103. Yu V Tomilov, E A Shapiro, M N Protopopova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 631
104. P Binger, J McMeeking *Angew. Chem*, 1974, **86** 518
105. Yu V Tomilov, V G Bordakov, N M Tsvetkova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 336
106. E A Shapiro, M N Protopova, O M Nefedov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 2153
107. M N Protopova, E A Shapiro, Yu V Tomilov, et al. *Izv. Akad Nauk SSSR, Ser. Khim.*, 1985, 2401
108. E A Shapiro, G V Lun'kova, M N Protopova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 2412
109. E A Shapiro, M N Protopopova, O M Nefedov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 237
110. J H Leftin, E Gil-Av *Tetrahedron Lett.*, 1972, 3367
111. M Vidal, A Dussauge, M Vincens *Tetrahedron Lett.*, 1977, 313
112. R Arnaud, A Dussauge, R Faucher, et al. *Tetrahedron Lett.*, 1984, **40** 315

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Carbene complexes in catalysis

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ABSTRACT. The methods for forming carbene complexes in catalysis are analysed in the case of the catalytic conversions of hydrocarbons, acids, carbonyl compounds, carbon monoxide, and methanol.

The bibliography includes 85 references.

Contents

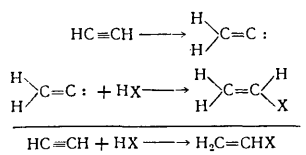
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I. Introduction

When the role of coordination compounds that contain carbene ligands is considered, most attention is usually given in catalysis[1–10] to the interaction between the carbene complex and substrate. Questions relating to the formation of such complexes have been examined to a considerably lesser extent. The present review is devoted mainly to examining those reactions, including model reactions, that result in the formation of carbene molecules and their complexes during the catalytic conversions of the main classes of organic compounds that are most frequently used in industrial and laboratory synthesis.

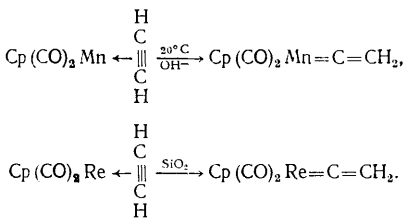
II. Alkynes

The idea that carbene molecules participate in the intermediate stages of catalytic processes was first suggested by Neff.[11] According to this hypothesis, addition reactions to acetylene such as those of hydrogen halides include the isomerisation of acetylene to the so-called "isoacetylene", which is free vinylidene, and reaction of the latter with hydrogen halides:



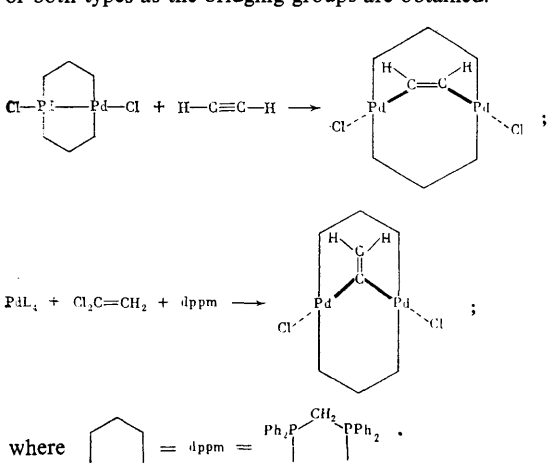
Neff did not elucidate the role of the catalyst, usually Hg^{2+} salts, in these reactions. This hypothesis was later contradicted by other ideas, according to which the reaction of acetylene with hydrogen halides takes place via an intermediate π-complex of Hg^{2+} with an acetylene molecule.[12,13] as well as a complex of a nucleophile with acetylene,[14] the so-called "reverse π-complex", in which bonding between the attacking reagent and the unsaturated ligand only occurs as a result of dative interaction.

However, it should be noted that when the central atom is a good electron donor, acetylene π-complexes and acetylides can be converted to vinylidene derivatives:[15–17]



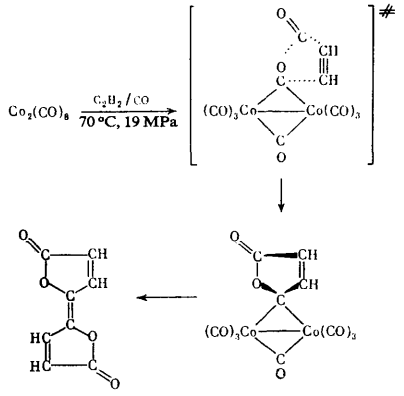
Thus as a result of the stabilisation of the vinylidene ligand in the internal coordination sphere of the transition metal complex, the reaction, which in the case of free acetylene and vinylidene requires the expenditure of about 167 kJ mol^{-1} of energy,[18] becomes possible. Quantum-chemical analysis of the interaction between the Cu^{1+} ion and acetylene and vinylidene indicates that there is stronger bonding of the latter with the central atom.[19] The relative stability of these types of complexes must depend to a considerable extent on the nature of the central atom. It cannot be ruled out that in time addition reactions to alkynes that take place with the involvement of carbene complexes as key intermediates will be discovered.

Reactions of alkynes in the presence of polynuclear systems are complicated by the possible formation of complexes with 1,2-vinylidene in addition to a symmetrical π-complex and a complex with a 1,1-vinylidene ligand.[20] Thus, for $Pd_2(\mu\text{-}Q)_2Cl_2$, where Q is bis(diphenylphosphino)methane, derivatives containing vinylidene ligands of both types as the bridging groups are obtained:[21]

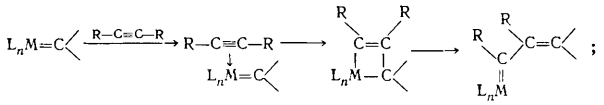


A number of cyclisation processes of alkynes which take place via intermediate complexes with bridging carbene ligands are known.[21]

Scheme 1



It is believed that the polymerisation of alkynes by carbene complexes of transition metals takes place via the cycloaddition of the alkyne to a carbene complex to form a metallocyclobutene followed by conversion of the latter to a complex with a new carbene ligand:[22]

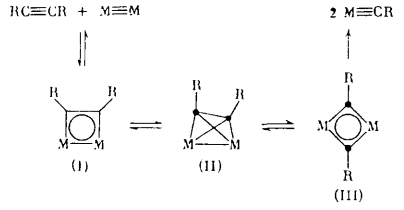


$L_nM = WCl_2[P(CH_3)_3]_2$.

Reaction of alkynes with ditungsten (3+) alkoxides that contain a W≡W bond gives carbyne complexes[23]

$$W_2(OBu\text{-}t)_6 + RC{\equiv}CR \rightarrow 2RC{\equiv}W(OBu\text{-}t)_3.$$

The W≡C bond is apparently so strong that the energy released on forming it compensates that expended on cleavage of the C≡C bond (~830 kJ mol^{-1}) and the reaction takes place in benzene at 25 °C. It is assumed that in this reaction the alkyne first adds on to the W≡W multiple bond to form the dimetallocyclobutadiene (I). The latter isomerises to complex (II), and both the electrons of the π-bonds of the initial ligand and the electrons of the π-bonds of the initial complex take part in formation of bonds between the metal atoms and the organic ligand. Isomerisation of this complex to the symmetrical dimetallocyclobutadiene (III) and dissociation of the latter result in formation of the observed and carbyne complex.

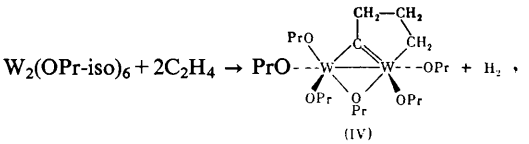


The isolated carbyne complexes catalyse the disproportionation of alkynes.

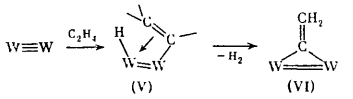
III. Alkenes

In the reaction of ditungsten hexa-alkoxides with alkynes the oxidation state of the metal atom increases as a result of oxidative addition. Oxidation of the metal is probably one of the driving forces for cleavage of the alkyne and formation of a carbyne complex. In the analogous reaction with an alkene the oxidation state of the metal would change to a lesser extent, which is evidently the explanation for the reaction of alkenes with ditungsten hexa-alkoxide not giving carbene analogues of the carbyne complexes.

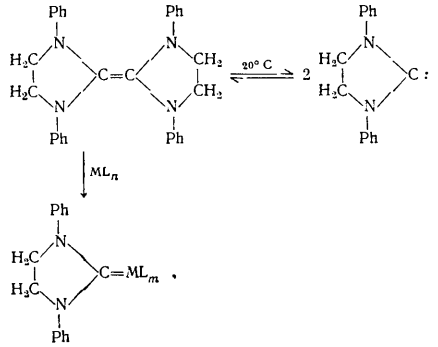
When $W_2(OPr\text{-}iso)_6$ is reacted with ethylene, complex (IV) containing a 5-membered metallocycle is formed:[24]



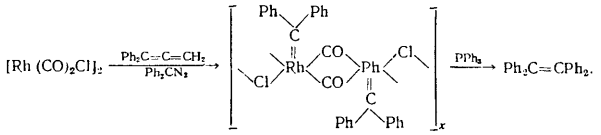
The driving force of this process is also oxidation of the metal atoms of the initial tungsten compound with the alkene. This process is believed to involve the intermediate formation of complexes with vinyl (V) and vinylidene (VI) ligands:



Cleavage of the C=C bond with formation of carbene complexes occurs comparatively rarely under mild conditions. Thus, it was possible to obtain a number of Pd(II), Pt(II), Au(I), Rh(I), Cr(0), and Re(0) complexes from electron-rich unsaturated compounds that can partially decompose to free carbenes even at 20 °C:[25-27]

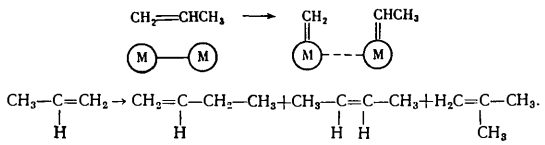


In the reaction of a Rh(I) complex with 1,1-diphenylallene (*o*-xylene, 4 h), which probably undergoes cleavage within the coordination sphere of the central atom to diphenylcarbene and vinylidene ligands, a polymeric complex of rhodium with diphenylcarbene was obtained. The same complex was synthesised by treating the initial rhodium complex with diphenyldiazomethane. Treatment of the carbene complex generated with PPh_3 gave tetraphenylethylene:[28]

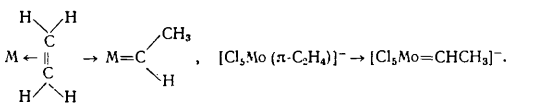


The cleavage of lower alkenes to give carbene complexes of transition metals appears to be a fairly general phenomenon only under relatively severe conditions. Thus, comparison of the

behaviour of CH_2N_2/H_2 and CO/H_2 mixtures, reaction of which with metals very probably leads to the formation of carbene intermediates, with the behaviour of a $CH_2=CHCH_3/H_2$ mixture showed that in all cases the distribution of products conforms to the same rule. This observation led to the conclusion that on Ru, Fe, Rh, and Os deposited on silica gel, alkenes dissociate at 1 atm and 250–300 °C to form carbene ligands, and the resulting complexes catalyse the homologisation of olefins:[29]

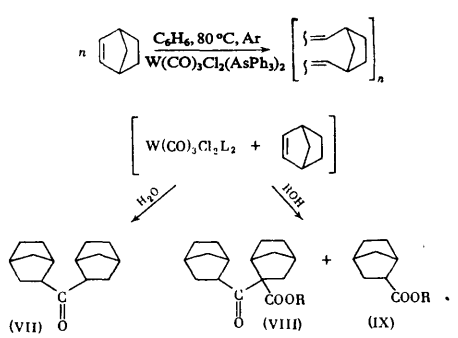


Another possible general method for the formation of carbene complexes from olefins assumes the internal isomerisation of a π-coordinated olefin to a carbene ligand. Quantum-chemical analysis showed that this type of isomerisation was energetically unfavourable for Pd(II) complexes but was practicable for Mo(IV) complexes:[30]

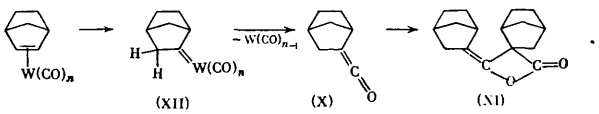


The theory concerning the mutual interconversion of alkyl- or dialkyl-carbene ⇄ alkene has been repeatedly discussed in the literature. Before the publication of the first X-ray diffraction studies devoted to an analysis of Zeise salt,[31] it was proposed[32] that this first known alkene π-complex was in fact a complex with methylcarbene. It transpired subsequently, however, that this view was incorrect and that even the isomerisation of alkenes in solutions of palladium and platinum salts takes place by routes that do not involve intermediate carbene complexes.[33] Nevertheless, it was not ruled out that in Mo(0) and W(0) carbonyl complexes the conversion of an alkene or alkadiene to a carbene ligand is possible. This is suggested by the results obtained from a study of the reaction between diphenylcarbenepentacarbonyltungsten and conjugated dienes.[34] Metathesis of lower olefins by contact with photoreduced molybdenum silicate catalysts that contain Mo(IV) ions is assumed to take place by a chain mechanism involving carbene intermediates that are generated by isomerisation of a π-coordinated alkene by means of an intramolecular 1,2-shift of an H atom.[35]

Chemical confirmation that such mechanisms occur was first obtained during a study of the reaction between norbornene and a tungsten(II) complex[36–38]

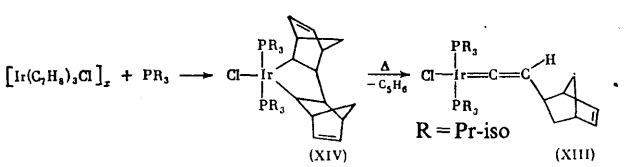


The composition of the observed products derived from alcoholysis and hydrolysis of the reaction mixture [compounds (VII), (VIII), and (IX)] clearly indicates that there is isomerisation of coordinated norbornene to the corresponding carbene ligand, which on reacting with coordinated CO is converted to ketene (X), giving the dimer (XI):[36–38]



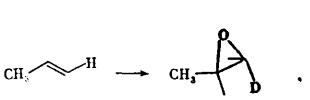
Ketone (VII) and ketocarboxylate ester (VII) are formed by the reaction of (XI) with water or alcohol, while the formation of (IX) results from the addition of alcohol to ketene (X). 2-Norbornylidene-phenylmethane was detected in the products resulting from interaction of the reaction mixture with benzaldehyde, which suggests that carbene complex (XII) is present in the mixture.

It is not ruled out that the 1,2-shift of an H atom, as detected by Bensze and Kraut-Vass,[38] which results in isomerisation of the π-coordinated alkene to the corresponding coordinated carbene is quite a general route for forming carbene intermediates. Another route which is apparently specific to norbornadiene occurred during a study of the behaviour of iridium complexes with this diene.[39] It was found that when polymeric tris(norbornadiene)iridium chloride was reacted with triisopropylphosphine in benzene at 50 °C, the square-planar vinylidene complex (XIII) was readily formed. At lower temperatures there is the formation of the polycyclic product (XIV), which is a precursor of the final vinylidene complex:



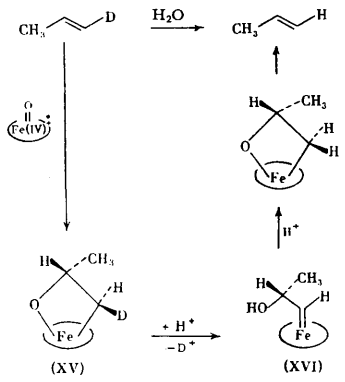
It is likely that in the first stage of this reaction during displacement of norbornadiene ligands by trialkylphosphine, the former undergo oxidative addition to the central atom, culminating in the formation of intermediate complex (XIV), which contains a substituted iridocyclopentane ring. This process is probably assisted by an increase in electron density on the iridium atom as a result of the initial addition of the strong donor ligand—triisopropylphosphine. Thermal elimination of cyclopentadiene from (XIV) should result in the formation of an intermediate with an iridocyclopentene residue. However, this intermediate probably isomerises to the more stable vinylidene complex (XIII) even as it is being formed.

In the epoxidation of propylene in D_2O containing cytochrome R-450, regiospecific and stereospecific substitution of the H atom situated *trans* to the CH_3 group occurs with replacement by a D atom:[40]



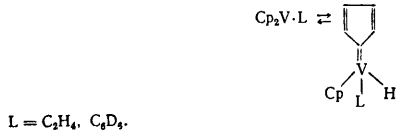
Under these conditions H/D exchange takes place between propylene and the solvent. It has been suggested that the reaction of the alkene with the active centre of cytochrome [$Fe^{4+}=O$] takes place

via the intermediate (XV) containing a four-membered metallocycle. Deprotonation of (XV) gives the carbene complex (XVI):



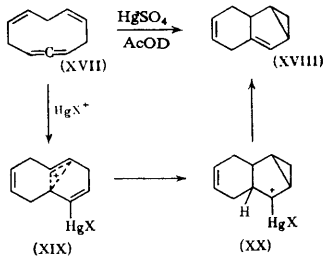
The process of protonation and deprotonation permits isotope exchange. The simultaneous cleavage of the Fe–O and Fe–C bonds in a complex of the type (XV), accompanied by elimination of epoxide, results in the formation of an alkene oxidation product.

Isotope exchange between ethylene and deuterobenzene in the presence of bis(cyclopentadienyl)vanadium occurs by a mechanism that involves the conversion of a cyclopentadienyl complex to a complex containing a cyclopentadienylidene ligand and hydride:[41]



The reversible insertion and elimination of ligand L on the V–H bond accounts for the observed deuterium exchange.

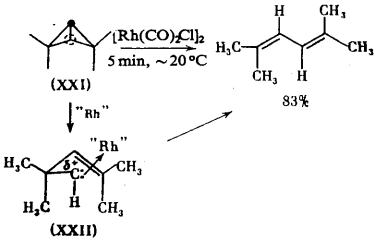
According to Thies et al.[42] cyclisation of the allene derivatives (XVII) to (XVIII) when treated with mercuric sulphate in acetic acid



involves attack by the mercury cation on the allene group. Then, after migration of the double bonds, the organomercury derivative (XIX) with delocalisation of the positive charge is formed. This non-classical cation is stabilised on being converted to carbene complex (XX), in which the C carbene atom has a positive charge. Elimination of the HgX^+ cation accompanied by a 1,2-shift of the H atom lead to the formation of the observed product (XVIII).[42]

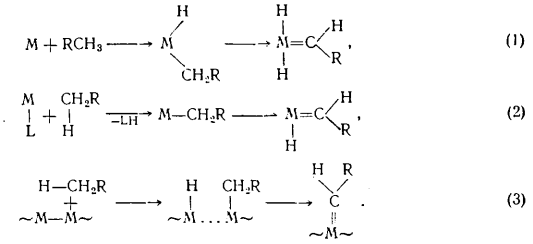
IV. Alkanes and their derivatives. Activation of C–H, C–C, and C–Cl bonds

The cleavage of C–C bonds in reactions of alkanes with metal complexes under mild conditions is a rare phenomenon. However, if the compound contains strained rings, cleavage of these bonds is considerably facilitated. Examples are known of the isomerisation of derivatives of cyclopropane, bicyclobutanes, and related hydrocarbons by treatment with silver, platinum, palladium, rhodium compounds, etc. It is thought that these reactions can take place via carbene intermediates. For example, 2,2,4,4-tetramethylbicyclo[1.1.0]butane (XXI) when treated with dimeric rhodium carbonyl chloride isomerises to 1,1,4,4-tetramethylbutadiene.



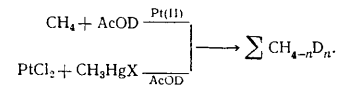
It appears that at the first stage oxidative addition of the initial hydrocarbon (XXI) to the Rh(I) atom takes place with cleavage of the weakest C–C bond (that common to both rings) and a compound containing two Rh–C σ-bonds is formed. As a result of the cleavage of one of the Rh–C bonds and one of the neighbouring C–C bonds, this complex is converted to a carbene–olefin complex (XXII, which isomerises to the final product.[43]

H/D exchange reactions of alkanes that are catalysed by metals or their coordinate compounds[44,45] are often represented by schemes involving oxidative addition of the alkane to a metal atom [reaction (1)] or replacement of ligand L by an alkyl within the coordination sphere of the complex [reaction (2)] followed by elimination of an α-hydrogen atom to form a carbene derivative:

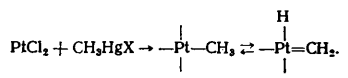


Oxidative addition of the alkane to a metal or polynuclear compound with cleavage of the metal–metal bond is probably much more energetically favourable than reaction (1) [reaction (3)].

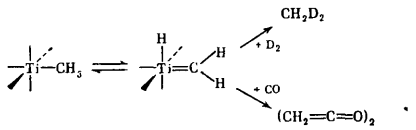
In the alkylation of $PtCl_2$ with methylmercury derivatives in the presence of deuteroacetic acid, the same series of deuteromethanes was detected[46] as in experiments on exchange between CH_4 and CH_3COOD in solutions containing Pt(II) chloride complexes:[46]



This phenomenon can be regarded as confirmation of the intermediate formation of methylplatinum complexes in H/D exchange between CH_4 and CH_3COOD. The simultaneous occurrence of not only monodeuterated products but also multiple exchange products in the reaction mixture indicates that there is an equilibrium between methyl and carbene

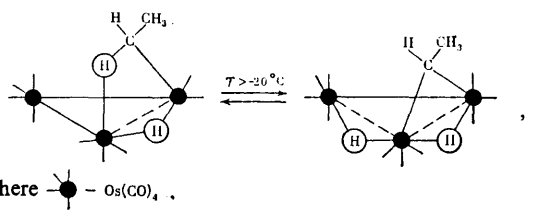


It appears that interconversions of alkyl and carbene hydride complexes occur quite widely in the chemistry of organic derivatives of transition metals. Thus, the simultaneous formation of all the deutero derivatives of methane with di- and tri-deuteromethanes predominating when the system $TiCl_4$ + $AlClMe_2$ is reacted with deuterium suggests[45] the following equilibrium is taking place:



Formaldehyde and ketene dimer were found amongst the products of the reaction between carbon monoxide and the $TiCl_4$ + $AlClMe_2$ mixture. The formation of ketene conforms well with the proposal that titanium carbene complexes are present during the experiments.[47]

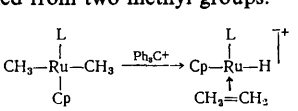
Not only methyl but also other alkyl derivatives display a tendency towards α-elimination of an H atom and formation of a complex containing both a carbene group and a coordinated hydride.[1-6,48] Analysis of PMR spectra of solutions of $HOs_3(CO)_{10}C_2H_5$ showed that above –20 °C this complex, which contains an ethyl group, is converted to a methylcarbene complex:[49]



where – Os(CO)$_4$.

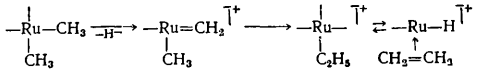
The process of α-elimination is assisted since in the initial complex one of the α-hydrogen atoms of the coordinated ethyl group converges with an Os atom as if ready for transposition to a bridging hydride ion.

The process in which a coordinated alkyl group is converted to a carbene ligand as a result of the elimination of a hydride ion is widely used in preparative work. Carbocations and other electrophiles are used as the H^- acceptor. Similar processes probably occur in catalysis, such as during oxidative dehydrogenation of hydrocarbons where a suitable oxidising agent can accept H^-. These types of processes may be responsible for the formation of new carbon–carbon bonds. A particular indication of this is given by the model reaction of a dimethylruthenium complex with triphenylcarbocation (hydride ion acceptor), as a result of which coordinated ethylene is formed from two methyl groups:[50]



Cp = η^5 cyclopentadienyl.

It appears that the complex formed after elimination of the hydride ion, containing both a coordinated methyl group and a carbene ligand, isomerises to a complex with an ethyl group as a result of insertion of coordinated carbene into the ruthenium–methyl bond. Elimination of a β-hydrogen atom from the ethyl group gives the observed final product:



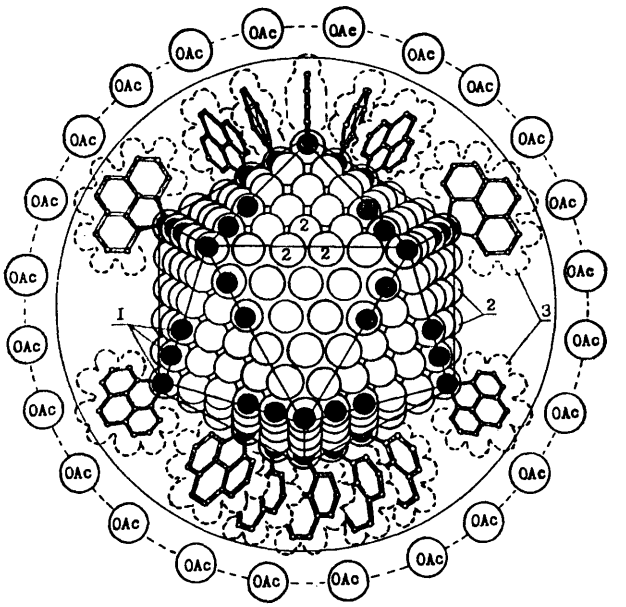
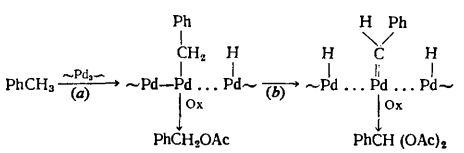


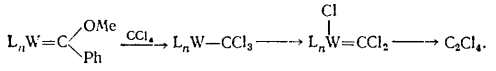
Figure 1. Hypothetical structural scheme of the very large cluster $Pd_{561}Phen_{60}(OAc)_{180}$: *1*, Pd atoms on the edges of the icosahedron that are available for coordination with phenanthroline molecules; *2*, Pd atoms that are available for coordination with substrate; *3*, coordinated phenanthroline molecules.[51,52]

Palladium clusters with the hypothetical formula $Pd_{561}Phen_mO_nX_l$ (m = 60, n = 0, X = OAc, l = 180; m = 80, n = 60, X = PF_6, l = 60) [51,52] catalyse the oxidative acetoxylation of alkenes and arylalkanes. Analysis of molecular models (Fig. 1) shows that out of 252 palladium atoms of the external layer of the compact metal core of these compounds only 30–40 are sterically accessible to substrate molecules. The results of determining the number of active sites in the cluster by an inhibition method [53] are consistent with this conclusion. It follows also from molecular models that the active sites of such clusters contain three palladium atoms. This makes it possible to simplify the discussion of the mechanism of the interaction between substrate and cluster by considering only three out of all the palladium atoms. In the acetoxylation of toluene appreciable quantities of benzylidene diacetate are formed together with benzyl acetate.[54] Since benzyl acetate is not oxidised to benzylidene diacetate under the experimental conditions, this indicates that when the route responsible for the formation of benzylidene diacetate occurs, a toluene molecule does not leave the surface of the cluster until two hydrogen atoms have separated from it. This condition is met by a scheme involving the oxidative addition of toluene to a group of three palladium atoms [stage (*a*)] and also elimination of an H atom from a coordinated phenylmethyl group to give a coordinated phenylcarbene [stage (*b*)].



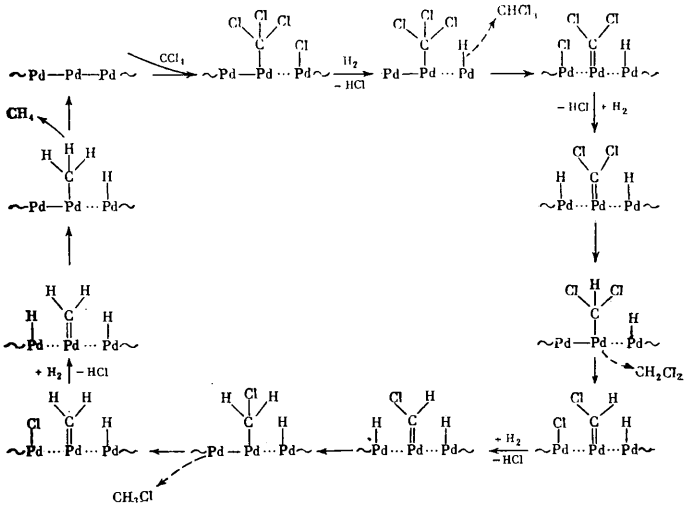
The reaction products, as in the acetoxylation of alkenes, are formed by transfer of electrons from the coordinated organic ligands and H atoms to the oxidising agent (Ox).

Processes related to α-elimination apparently occur during the conversion of haloalkanes using transition metal compounds. Thus, tetrachloroethylene is amongst the products from the reaction between CCl_4 and pentacarbonylphenylmethoxycarbenotungsten, in addition to CO, HCl, CH_2Cl_2, and $CHCl_3$. The occurrence of tetrachloroethylene may be due to the formation of a trichloromethyltungsten derivative and its conversion by α-elimination of a chlorine atom from the CCl_3 group to a dichlorocarbene complex.[55] The latter is the source of tetrachloroethylene:

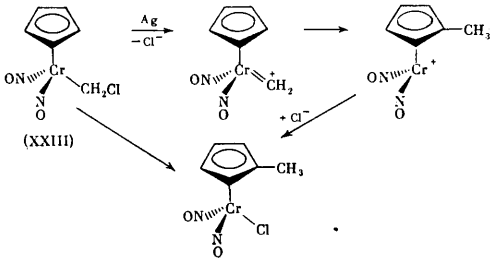


In the reactions of CCl_4 with hydrogen on palladium catalysts obtained by reduction of palladium(II) compounds in the presence of alcohols, $CHCl_3$, CH_3Cl, and CH_4 are all formed at the same time.[56] The simultaneous formation of these products indicates that a substrate molecule can, without leaving the surface of the catalysts, replace more than one Cl atom with H. In the same way as for the oxidative acetoxylation of toluene, these phenomena can be accounted for by a scheme that involves the oxidative addition of CCl_4 to two atoms of the "triplet" of Pd atoms with alternating stages for replacement of Cl atoms on palladium by H atoms and α-elimination of Cl atoms to form a carbene ligand. Addition of H atoms to the latter results in regeneration of a coordinated halomethyl group. According to this scheme, the observed reaction products are formed by reductive elimination of a methyl or halomethyl radical and H or Cl atoms. The yield of reaction products is determined by the ratio of rates for reductive elimination and α-elimination:

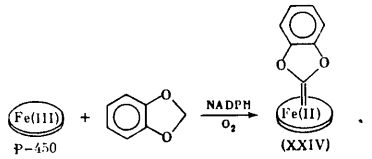
Scheme 2



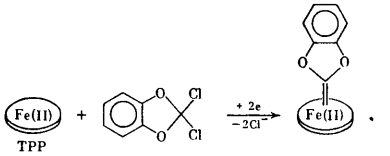
Elimination of the Cl^- ion from the chloromethyl group bonded to the chromium atom and formation of an intermediate chromium carbene complex are responsible for the silver-catalysed migration of the CH_2 group in the chloromethyl residue to the cyclopentadienyl ring of complex (XXIII):[57]



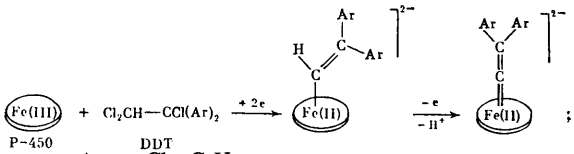
The formation of carbene complexes from compounds containing C–H and C–Hal bonds plays an important part in redox processes which take place in living organisms.[58] Thus, it is thought that during oxidative metabolism of 1,3-benzodioxole, a powerful insecticide synergist, a complex is formed in which the iron atom of cytochrome P-450 is bonded to a carbene ligand that is generated after the removal of two H atoms from the methylene group of 1,3-benzodioxole:[58]



An analogue of complex (XXIV) was obtained from tetraphenylporphyrin (TPP) and 2,2-dichloro-1,3-benzodioxole:



It is thought that carbene complexes also occur during the reductive metabolism of a number of inhalation anaesthetics by cytochrome P-450. When the insecticide 2,2-bis(*p*-chlorophenyl)-1,1,2-trichloroethane (DDT) is reacted with the cytochrome P-450 analogue, iron(II) tetraphenylporphyrinate, a very stable arylvinylidene complex is obtained:[58]



Results which suggest that σ-alkyl and carbene complexes of iron undergo interconversion during the oxidation or reduction of a number of substrates with cytochrome P-450 have been obtained.[59–61]

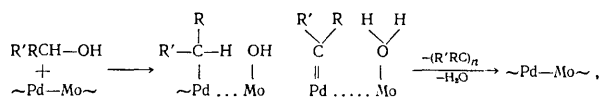
V. Alcohols

In recent years the reactions of methanol on high-temperature zeolite catalysts of the type ZSM-5 have stimulated considerable interest.[62] At 300–500 °C a mixture of hydrocarbons—alkanes, alkenes, arenes, etc.—is formed from methanol. In practical terms

those reactions of the greatest interest are selective conversions of methanol, such as:

$$2CH_3OH \longrightarrow CH_2{=}CH_2 + 2H_2O,$$
$$3CH_3OH \longrightarrow CH_3CH{=}CH_2 + 3H_2O,$$
$$3CH_3OH \longrightarrow CH_2 - CH_2 + 3H_2O,$$
$$\quad\quad\quad

diethyl ether nor ethylene is formed. This suggests that the elimination of water is not catalysed by either protons or Lewis acids. In the dehydration of benzyl alcohol, approximately equal quantities of *trans*-stilbene and water are formed. These findings may be interpreted by assuming that an H atom and hydroxyl radical are eliminated from the same carbon atom of the alcohol molecule to form a carbene ligand that is stabilised through coordination. It should be noted that homonuclear palladium clusters such as $Pd_4(CO)_4(OAc)_4$ and mononuclear molybdenum carbonyl complexes do not catalyse this reaction. It is probable that the Pd–Mo bond which occurs in complex (XXV) is absolutely essential for catalysis. It is possible that the alcohol, when introduced on to this bond in the Pd_4Mo_4 group, alkylates the Pd atom and oxidises the Mo atom, to which a hydroxyl group is added. After transfer of a proton from the coordinated alkyl to the coordinated hydroxyl on the reaction site, an H_2O molecule bonded to the Mo atom and a carbene ligand coordinated with the Pd atom are formed.



$$PhCH_2OH \xrightarrow[80^\circ C]{«Pd_4Mo_4»} PhCH{=}CHPh + 2H_2O.$$

Elimination of these ligands and restoration of the palladium–molybdenum bond complete the catalytic cycle.

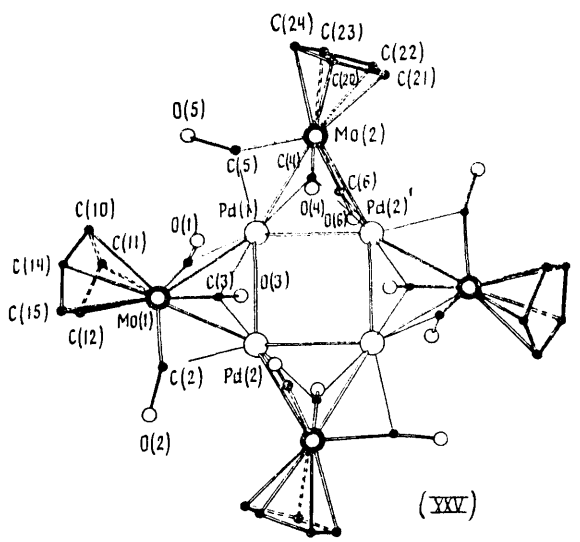


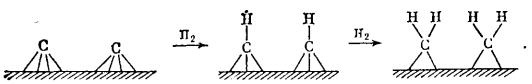
Figure 2. Structure of the anion of the palladium–molybdenum cluster with the composition $Na_2\{Pd_4[CpMo(CO)_3]_4\}.2THF$.[70]

VI. Carbon monoxide

The theory concerning the formation of intermediate carbene complexes has been widely applied in discussions of the mechanism of the hydrogenation of carbon monoxide (Fischer–Tropsch reaction) on both solid catalysts and in solution.[75] It is thought that both coordinated (adsorbed) carbonyl groups and carbide carbon, i.e. C atoms actually coordinated, participate in reduction processes. Thus, for the most general case the reduction of CO is based on the reaction:

$$M(CO)_n + M^1 \xrightarrow[-M^1O]{} (CO)_{n-1}MC.$$

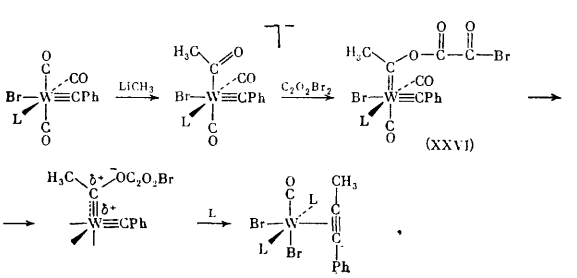
It may be assumed that M^1O subsequently reacts with CO or H_2, resulting in regeneration of the catalyst. Depending on the nature of the catalyst, it appears that routes involving hydrogen and $M(CO)_n$ or $(CO)_{n-1}MC$ or both compounds together take place. It is thought, however, that intermediate carbene species are formed in all these reactions. Thus, carbene complexes play a key role in the initiation of this process, which has the kinetic characteristics of a chain process (primary reactions of coordinated carbonyl, conversions of the carbide atom to carbyne and carbene groups), in chain growth, in reactions of metal acyl derivatives, and others.[73] For example, reduction of carbide complexes by heterogeneous catalysis is depicted by a scheme that involves the formation of intermediate carbyne and carbene compounds (without specifying the nature of the groups bonded to the C atom)



Carbene complexes constitute a source of alkenes and alkanes. It would appear that alkynes could be formed from carbyne complexes, but the synthesis of acetylene in the gas phase according to the reaction

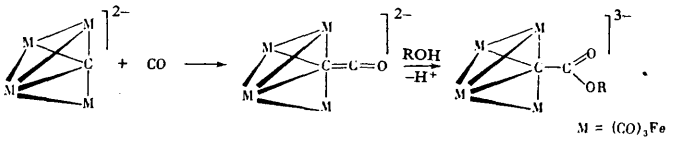
$$2CO + 3H_2 = HC{\equiv}CH + 2H_2O$$

is fairly improbable thermodynamically (ΔG^0_{298} = + 26.5 kJ mol^{-1}) and is not feasible under mild conditions. There has only been one report[76] about the synthesis of acetylene from CO and H_2 at 1 atm and 100 °C in the presence of graphite intercalation compounds with $FeCl_3$ (composition C_9FeCl_3) activated with potassium naphthalide. The nature of the processes taking place in this system is unclear. It should be noted, however, that the synthesis of acetylene from CO to H_2 will probably occur if it is interlinked with any exoergic process. Thus, for example, in the model reaction in which LiMe serves as the reducing agent instead of H_2 while one of the oxygen atoms of a carbonyl group is removed using oxalyl bromide, the carbyne group PhC≡ is included in the composition of the final alkyne PhC≡CMe:[77]



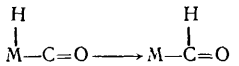
In this case not only is phenylacetylene formed but an exoergic process also takes place—the partial hydrolysis of oxalyl bromide. It is of considerable importance that this synthesis takes place via an intermediate carbene-carbyne complex (XXVI).

Another route for converting carbide complexes assumes the formation of intermediate ketenides—analogues of transition metal vinylidene derivatives—by a scheme[78] such as

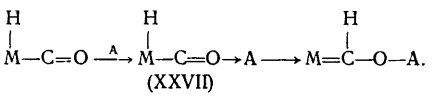


M = $(CO)_3Fe$

Hydroxycarbene groups play a key role during the reduction of coordinated CO groups. Migration of a coordinated H atom to coordinated CO

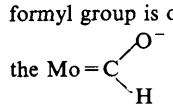


is somewhat unfavourable thermodynamically and difficult kinetically.[79] For this process $\Delta G^0_{298} > 0$ and $E_\alpha > 167$ kJ mol^{-1}. Analysis[79] of the experimental data indicated that in all cases isomerisation of the carbonyl hydride complex to a formyl derivative only takes place when there is a proton or aprotic acid A in the system which is capable of forming an adduct with the carbonyl hydride complex (XXVII):



(XXVII)

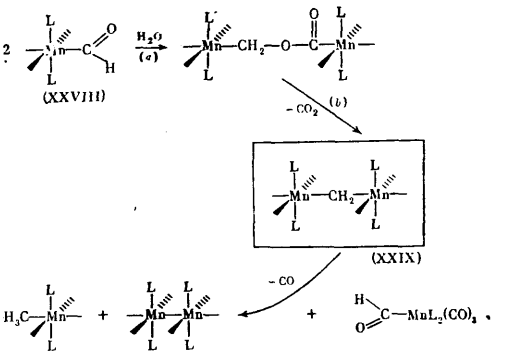
Apart from a proton, cations of alkali and alkaline earth metals as well as complexes of virtually all transition metals can act as electrophile A. It appears that because of the increase in effective positive charge on the carbon atom of the carbonyl group in adduct (XXVII), transfer of the coordinated hydride from the metal to carbon is facilitated. The final product is hydroxycarbene complex in which the H atom has been replaced by electrophile A. It is probable that the higher the stability of such a hydroxycarbene complex, the stronger is the influence of thermodynamic factors that assist this transfer of the H atom. Addition of two hydrogen atoms to this hydroxycarbene complex results in the formation of a complex with a hydroxymethyl ligand MCH_2OH, which on reaction with synthesis gas can give methanol, oxygenated products with a longer chain, and other products.

It should be noted that in the formyl derivative of molybdenum $C_5Me_5(CO)_2(PPh)_3MoCHO$, the vibration frequently ν_{CO} of the formyl group is only 1602 cm^{-1}, which suggests that a structure with the  bond predominates. In fact, this and related complexes are readily protonated or methylated to form cationic hydroxycarbene complexes with the composition

$$[(\eta^5\text{-}C_5Me_5)(CO)_2(PPh_3)Mo{=}C(H)OR^-]^+X^-,$$

R = H or Me, $X^- + CF_3COO^-$ or PF_6^- (Ref.80).

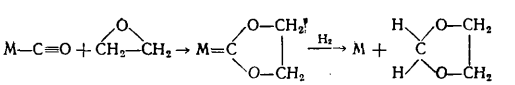
However, there are examples which suggest that conversion of the CHO group to CH_3 can occur by a more complex route[81] than that discussed above:



(XXVIII) (XXIX)

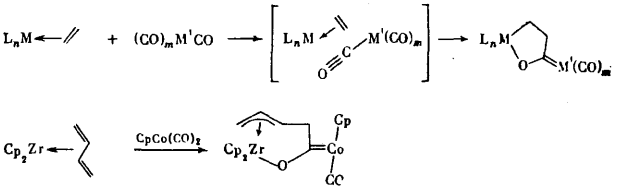
In fact, reduction of the manganese formyl complex (XXVIII) incorporates a redox disproportionation involving a water molecule [stage (*a*)], elimination of CO_2 from the complex with a bridging ester group [stage (*b*)] and finally the formation of a binuclear complex (XXIX) with a bridging carbene. Reduction of this methylene derivative with a third molecule of formyl complex (XXVIII) gives a methyl derivative and a dimeric derivative with a Mn–Mn bond.

In the schemes reviewed in the literature, the reactions of carbonyl complexes with reagents which are present in the system other than H_2 and hydride complexes are not usually taken into account. It is possible that the inclusion of oxygenated compounds as potential reagents would considerably extend our ideas about possible routes for reducing CO. Thus, it was shown[82] that carbonyl complexes of Fe, Ru, Mn, and Re can react with ethylene oxide to form dioxocarbene complexes that are potential sources of cyclic formaldehyde acetal:



M = $CpFe(CO)_2^+$, $CpRu(CO)_2$, $CpMn(CO)(NO)^-$, $Re(CO)_4Cl$, $Ru_3(CO)_{11}$, $Re_2(CO)_9$.

In a similar manner the condensation of a π-coordinated alkene or diene with a coordinated carbonyl leads to carbene complexes[83] which can be hydrogenated to obtain oxygenated compounds in a Fischer–Tropsch synthesis:



Reactions of this type are to be expected for Group IV elements, which can apparently form fairly strong bonds with the oxygen atom of the coordinated carbonyl group. Probably this "double" coordination of CO assists the cycloaddition of carbon monoxide and the coordinated alkene or alkadiene as depicted in the scheme shown here.

VII. Carbonyl compounds and carboxylic acids

Information about reactions in which a carbonyl compound acts as a donor of a carbene ligand is extremely limited. This is not surprising if we consider the strength of the C=O bond and the need to use a very powerful reducing agent to bond to the O atom being removed from this group. Amongst reactions of this type, in which the formation of intermediate carbene complexes may be presumed, should be included the reduction of benzophenone to tetraphenylethylene:[84]

$$2Ph_2C{=}O \xrightarrow[97\%]{\text{Red, } TiCl_3/THF} Ph_2C{=}CPh_2,$$

Red = Zn, $LiAlH_4$, Li, K.

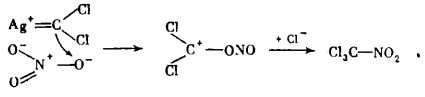
The titanium complex present in the system evidently has different functions compared to the reducing agents used. It cannot be excluded that the Ti atom first coordinates ketone molecules and then—after the removal of O atoms on treatment with the reducing agent—forms a complex with diphenylcarbene, which undergoes conversions to give tetraphenylethylene:

$$Ph_2C{=}O \xrightarrow{\text{Red, } TiX_n} Ph_2C{=}TiX_n \xrightarrow[-TiX_n]{} Ph_2C{=}CPh_2.$$

The thermolysis of anions of trihalo-substituted carboxylic acids is one of the oldest methods for generating carbenes.[85] However, the effect of transition metals on this process and on the reactions of dihalocarbenes formed in the system has hardly been studied at all. One of the few known reactions is the synthesis of chloropicrin[85] by thermolysis of trichloroacetate in the presence of silver nitrate:

$$Cl_3CC(O^-)=O \xrightarrow{AgNO_2} Cl_3C{-}NO_2.$$

It cannot be excluded that the dichlorocarbene formed in the system is stabilised by coordinating with the silver ion, and then acting as a fairly strong electrophile it attacks the nitrate ion according to the scheme



From the examples given in this review it follows that in principle the generation of carbene complexes is to be expected from elements of virtually all Groups of the Period Table in their reactions with the most important examples of organic substrates. It is probable that structural factors which enhance the strength of the metal–ligand bond must assist the formation of intermediate carbene complexes. Identification of these factors constitutes a problem of theoretical chemistry and undoubtedly plays an important part in determining the mechanism of many catalytic processes and predicting the activity of catalyst complexes. It would not be an exaggeration to say that carbenes and coordinated compounds that contain them as ligands should be regarded as just as important and as widely occurring intermediates as carbocations and *C*-centred free radicals were traditionally considered to be. The genetic bond which exists between these intermediate species and their complexes is responsible for the interconversions of these intermediates.

References

1. B A Dolgoplosk *Kinet. Katal.*, 1977, **18** 1146
2. B A Dolgoplosk *Kinet. Katal.*, 1981, **22** 807
3. B A Dolgoplosk *Kinetika i Kataliz* (Kinetics and Catalysis), Vol. 13 (Results in Science and Technology), Moscow, VINITI, 1984, p. 70
4. B A Dolgoplosk, K L Makovetskii, Yu V Korshak, et al *Vysokomol. Soedin.*, 1977, **19** 2464
5. K L Makovetskii, B A Dolgoplosk, Yu V Korshak, et al. *Zh. Vses. Khim. Ova. im D. I Mendeleeva*, 1979, **24** 513
6. B A Dolgoplosk, I A Oreshkin, E I Tinyakova *Kinet. Katal.*, 1984, **25** 306
7. M Regits, G Maas *Diazo Compounds: Properties and Synthesis*, Academic Press, New York, 1986, 75 pp
8. M P Doyle *Chem. Rev.*, 1986, **86** 919
9. M Brookhart, W B Studabaker *Chem. Rev.*, 1987, **87** 411
10. R Taube, K Sayfert *Rev. Inorg. Chem.*, 1986, **8** 31
11. J A Nieuwland, R R Vogt *The Chemistry of Acetylene* (Translated into Russian), Izd. Inostr. Lit., Moscow, 1947, 325 pp
12. R M Flid, I I Moiseev, E M Kalmykova *Zh. Fiz. Khim.*, 1957, **31** 904
13. I I Moiseev, Candidate's Thesis in Chemical Sciences, Lomonosov Institute of Fine Chemical Technology, Moscow, 1958
14. E A Shilov *Problemy Mekhanizma Organicheskikh Reaktsii* (Problems Concerning the Mechanism of Organic Reactions), Izd. AN UKrSSR, 1954, p. 14
15. A B Antonova, N E Kolobova, P V Petrovsky, et al. *J. Organomet. Chem.*, 1977, **137** 55
16. N E Kolobova, L L Ivanov, O S Zhvanko, et al. *J. Organomet. Chem.*, 1984, **265** 271
17. A Hohn, H Otto, M Dziallas, H Wernen *J. Chem. Soc., Chem. Commun.*, 1987, 852
18. C Dykstra, H F Shaefer *J. Am. Chem. Soc.*, 1978, **100** 1378
19. N M Vitkovskaja, V G Bernshtein, F K Schmidt *React. Kinet. Catal. Lett.*, 1986, **31** 167
20. B L Shaw *J. Chem. Soc., Chem. Commun.*, 1986, 1629
21. R S Dickson, P J Frazer *Adv. Organomet. Chem.*, 1974, **12** 812
22. A Mayr, K S Lee, M A Kjelsberg, D V Engen *J. Am. Chem. Soc.*, 1986, **108** 6079
23. M L Listemann, R R Schrock *Organometallics*, 1985, **4** 74
24. M H Chisholm, M Hampden-Smith *J. Am. Chem. Soc.*, 1987, **109** 5871
25. D J Cardin, M J Doyle, M F Lappert *J. Chem. Soc., Chem. Commun.*, 1975, 907
26. B Cetinkaya, P Dixneuf, M F Lappert *J. Chem. Soc., Chem. Commun.*, 1973, 206
27. D J Cardin, B Cetinkaya, M F Lappert *J. Chem. Soc., Dalton Trans.*, 1973, 515
28. P Hong, N Nishii, K Sonogashira, N Nagihara *J. Chem. Soc., Chem. Commun.*, 1972, 993
29. M Leconte, A Theoller, D Rojas, J M Basset *J. Am. Chem. Soc.*, 1984, **106** 1141
30. O V Gritsenko, M I Mitkov, A A Bagatur'yants, V B Kazanskii *IV Mezhdunarodnyi Simpozium po Gomogennomy Katalizy: Tezisy Dokladov* (Abstracts of Reports at the IVth International Symposium on Homogeneous Catalysis), Vol. 1, Chernogolovka, 1984, p. 78
31. G B Bokii, G A Kukina *Kristallografiya* (Crystallography), Vol. 2, Izd. Nauka, Moscow, p. 400
32. J Chatt *Cationic Polymerisation and Related Complexes* (Edited by P H Plesh), Heffer, Cambridge, 1953, p. 40

33. I I Moiseev *π-Kompleksy v Zhidkofaznom Okislenii Olefinov* (π-Complexes in the Liquid-phase Oxidation of Olefins), Izd. Nauka, Moscow, 1970, 240 pp
34. S P Kolesnikov, N I Okhrimenko, O M Nefedov *Dokl. Akad. Nauk SSSR*, 1978, **243** 1193
35. I V Elev, B N Shelemov, V B Kazanskii *Kinet. Katal.*, 1987, **28** 409
36. L Bensze, A Kraut-Vass, L Prokai *J. Chem. Soc., Chem. Commun.*, 1985, 911
37. L Bensze, L Prokai *J. Organomet. Chem.*, 1985, **294** C5
38. L Bensze, V Kraust-Vass *J. Organomet. Chem.*, 1985, **280** C14
39. M Dziallas, H Werner *J. Organomet. Chem.*, 1987, **333** C29
40. J T Groves, G V Avaria-Neisser, K M Fish, et al. *J. Am. Chem. Soc.*, 1986, **108** 3837
41. E A Grigoryan *Usp. Khim.*, 1984, **53**(2) 347 [English translation in *Russ. Chem. Rev.*, 1984(2)]
42. R W Thies, P K Hong, R Buswell *J. Chem. Soc., Chem. Commun.*, 1972, 1091
43. P G Gassman, T J Atkins, F J Williams *J. Am. Chem. Soc.*, 1971, **93** 1812
44. N F Gol'dshleger, M B Tyabin, A E Shilov, A A Shteinman *Zh. Fiz. Khim.*, 1969, **43** 2174
45. A E Shilov, A A Shteinman *Kinet. Kataliz.*, 1977, **18** 1129
46. E A Grigoryan, Kh R Gyulumyan, F S D'yakovskii, I R Mullagaliev *Kompleksnye Metalloorganicheskie Katalizatory Polimerizatsii Olefinov* (Organometallic Complex Catalysts for the Polymerisation of Olefins), Vol. 4, Chernogolovka, 1977, p. 6
47. E A Grigoryan, Kh R Gyulumyan *Kompleksnyeni Metalloorganicheskie Katalizatory Polimerizatsii Olefinov* (Organometallic Complex Catalysts for the Polymerisation of Olefins), Vol. 8, Chernogolovka, 1980, p. 74
48. V A Yakovlev, I A Oreshkin, B A Dolgoplosk *Zh. Metalloorg. Khim.*, 1989, **2** 93
49. M Gree-Uchijima, J R Shapley, G M St. George *J. Am. Chem. Soc.*, 1986, **108** 1316
50. H Kletzin, H Werner, O Serhadli, M L Ziegler *Angew. Chem.*, 1983, **95** 49
51. M N Vargaftik, V P Zagorodnikov, I P Stolyarov, et al. *Dokl. Akad. Nauk SSSR*, 1985, **284** 896
52. M N Vargaftik, V P Zagorodnikov, I P Stolarov, et al. *J. Chem. Soc., Chem. Commun.*, 1985, 937
53. V P Zagorodnikov, M N Vargaftik *Kinet. Katal.*, 1986, **27** 851
54. M K Starchevskii, M N Vargaftik, O M Nefetov, I I Moiseev *Izv. Akad. Nauk, SSSR, Ser. Khim.*, 1980, 2427
55. S P Kolesnikov, T L Mitenina, O M Nefedov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 2303
56. G S Dosaeva, S M Velichko, Yu A Treger, I I Moiseev *IV Vsesoyuznaya Konferentsiya "Sovremennoe Sostoyanie i Perspektivy Razvitiya Teoreticheskikh Osnov Proizvodstva Khlororganicheskikh Productov" Tezisy Dokladov* (Abstracts of Reports at the IVth All-Union Conference "The Present State and Future Prospects for the Development of Theoretical Principles for the Production of Organochlorine Products"), Part 1, Baku, 1985, p. 179
57. J L Hubbard, W R McVicar *J. Am. Chem. Soc.*, 1986, **108** 6422
58. J-I Setsune, D Dolphin *Can. J. Chem.*, 1987, **65** 459
59. D Mansuy *Pure Appl. Chem.*, 1987, **59** 759
60. P J Brothers, J P Collman *Acc. Chem. Res.*, 1986, **19** 209
61. I Artand, N Gregoire, J-PBattioni, D Dupre, D Mansuy *J. Am. Chem. Soc.*, 1986, **110** 8714
62. Kh M Minachev, D A Kondrat'ev *Usp. Khim.*, 1983, **52**(12) 1921 [English translation in *Russ. Chem. Rev.*, 1983(12)]
63. V B Kazanskii *Kinet. Katal.*, 1987, **27** 47
64. V I Kondrat'ev (Editor) *Energii Razryva Khimicheskikh Svyazei. Potentsialy Ionizatsii i Srodstvo k Elektronu: Spravochnik* (Chemical Bond Energies. Ionisation Potentials and Electron Affinity: Handbook), Izd. Nauka, Moscow, 1974, 351 pp
65. G A Olah *J. Chem. Soc., Chem. Commun.*, 1986, 9
66. J Sommer *J. Chem. Soc., Chem. Commun.*, 1986, 1497
67. R A Olofson, S W Walinsky, J P Marino, J L Jernow *J. Am. Chem. Soc.*, 1968, **90** 6554
68. J Rooney, J K A Clarke, R Darcy, et al. *J. Chem. Soc., Chem. Commun.*, 1986, 425
69. R Hunter, G J Hutchings, W Pickl *J. Chem. Soc., Chem. Commun.*, 1987, 843
70. R Hunter, G J Hutchings, W Pickl *J. Chem. Soc., Chem. Commun.*, 1987, 1369
71. S D Hellring, K D Schwitt, C D Chang *J. Chem. Soc., Chem. Commun.*, 1987, 1320
72. R M Dessau *J. Catal.*, 1986, **99** 111
73. T A Stromnova, I N Busygina, S B Katser, et al. *Dokl. Akad. Nauk SSSR*, 1987, **295** 890
74. T A Stromnova, I N Busygina, S B Katser, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1435
75. V Chime (Editor) *Catalysis in C_1 Chemistry* (Translated into Russian from English) (Edited by I I Moiseev), Izd. Khimiya, Leningrad, 1987
76. W Jones, R Schlogl, J M Thomas *J. Chem. Soc., Chem. Commun.*, 1984, 464
77. G A McDermott, A Mayr *J Am. Chem. Soc.*, 1987, **109** 580
78. M A Beno, J M Williams, M Tachikawa, E L Muetterties *J. Am. Chem. Soc.*, 1981, **103** 1485
79. I I Moiseev *Zh. Vses. Khim. Ova im D. I. Mendeleeva* 1982, **27** 309
80. A Asdar, C Lapinte *J. Organomet. Chem.*, 1987, **327** C33
81. H Berke, G Weller *Angew. Chem.*, 1982, **94** 135
82. G L Missler, S Kim, R G Angelici, R A Jacobson *Inorg. Chem.*, 1987, **26** 1690
83. G Erker, R Lecht, J L Petersen, H Bönnemann *Organometallics*, 1987, **6** 1962
84. H M Colquhour et al. (Editors) *New Pathways for Organic Synthesis*, Pergamon, New York–London, 1985, 431 pp
85. V Kirmse *The Chemistry of Carbenes* (Translated into Russian), Izd. Mir, Moscow, 1966, 320 pp

Translated from *Uspekhi Khimii* **58** 1197–1230 (1989) U.D.C. 547.1'13

Transition metal complexes of unsaturated carbenes: synthesis, structure, and reactivity

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ABSTRACT. The methods of synthesis, structure, physicochemical properties, and reactivity of transition metal complexes containing unsaturated carbene ligands (vinylidenes, allenylidenes, and heterocumulenylidenes) are examined. Attention is concentrated on heterometallic compounds. The prospects for the development of the chemistry of unsaturated carbene complexes and their use in organic and organometallic synthesis are discussed.

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I. Introduction

The chemistry of unsaturated carbene complexes (UCC) is a new field which has arisen at the junction between organometallic, coordination, and organic chemistry and has been developing vigorously during the last decade. Unsaturated carbenes include unsaturated species with an unshared electron pair at an *sp*-hybridised carbon atom C_α and a $C_\alpha=C_\beta$ double bond: vinylidene (ethenylidene) $:C=CH_2$ and its homologues $:C=CHR$ and $:C=CRR'$, allenylidenes (propadienylidenes) $:C=C=CR_2$, ketenylidene $:C=C=O$, and other heterocumulenylidenes $:C=C=S$, $:C=C=C=O$. The involvement of unsaturated carbenes in organic reactions has been described in Stang's reviews.[1–3]

Unsaturated carbenes, which are unstable in a free state, can be stabilised by coordination to Group V–VIII transition metal atoms in low oxidation states. The first structurally characterised complex $(CO)_8Fe_2(\mu\text{-}C=CPh_2)$ was obtained in 1966 by Pauson and Bagga[4] in 3% yield by the interaction of diphenylketen with iron carbonyl. After the discovery in 1974–1978 of the possibility of the formation of UCC from acetylenes and metal carbonyl complexes[5–7] and also from π-acetylenic[8] and σ-alkynyl[9] complexes, simple general methods of synthesis were developed, which made UCC quite readily available. This stimulated a rapid development of their chemistry.

According to the review of Bruce and Swincer,[10] about 150 stable UCC were known in 1983; in their molecules the vinylidene, allenylidene, and heterocumulenylidene ligands were bound to one or several identical or different metal atoms: Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, and Ni. During the last 6 years, the number of such complexes has trebled. The first UCC containing Pt,[11–13] Pd,[14] Ir,[15] and Ta[16] have been synthesised. A new type of bonding of unsaturated carbenes in dinuclear complexes—lateral bridge-type η^1, η^2-coordination—has been discovered.[17–19]

The heterometallic UCC, the first representative of which—$Cp_2(CO)_4MnRe(\mu\text{-}C=CHPh)$—was obtained in 1978,[20] are of special interest. Exotic cluster UCC, such as $CpNiRu_3.(\mu_4\text{-}C=CHR)(\mu\text{-}H)(CO)_9$,[21,22] $CpWOs_3(\mu\text{-}C=CHC_6H_4Me)(\mu\text{-}H).(\mu\text{-}O)(CO)_9$,[23] and $(Ph_3P)_2Au_2Ru_3(\mu_3\text{-}C=CHBu^t)(CO)_9$ [24] have been synthesised by various methods. A general approach to the synthesis of dinuclear and polynuclear complexes, in which mononuclear and dinuclear UCC are used as "building blocks", has been recently discovered on the basis of the application of Hoffmann's isolobal principle[25] (see Section IV, subsection 2). This makes it possible to obtain compounds containing the atoms of two and three different transition metals, including platinum metals, in specified combinations and proportions. Heterometallic UCC can be applied in homogeneous and heterogeneous catalysis. Their employment for the creation of new polymetallic materials (powders, coatings, etc.), necessary for different branches of modern engineering, is promising.

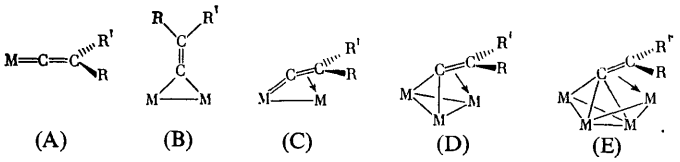
At the present time UCC have been segregated as a special class of organometallic compounds with unusual electronic structures and reactivities. The ease of the formation of UCC from a wide variety of sources and the multiplicity of their reactions suggest that they can be active intermediates in many catalytic reactions involving transition metal atoms. The first examples of the direct use of UCC as catalysts of organic synthetic processes and stoichiometric reactions, leading to valuable organic substances which are difficult to obtain otherwise, have appeared.

In the present review, attention is concentrated on studies performed during the last five years; references to investigations published up to 1982 are given in another exhaustive review.[10]

II. Types of coordination of unsaturated carbenes to metal atoms. The structural and spectroscopic characteristics of the complexes

In contrast to the carbenes $:CR_2$ and :CRX (R = H, alkyl, aryl; X = halogen, OR, NR_2, etc.), which form bonds with only one or

two metal atoms,[26–30] five types of coordination are known for vinylidenes:

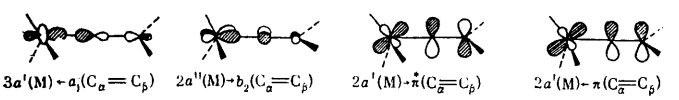


(A) (B) (C) (D) (E)

Coordinations of types (A)–(D) are now known for cumulenylidene complexes.

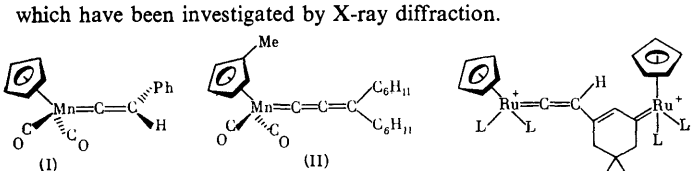
A detailed analysis of the nature of the bonding of unsaturated carbenes to metal atoms has been carried out only for the simplest of such species—vinylidene :C=CH$_2$. The occupied a_1 and π Mo and the unoccupied b_2 and π^* MO of vinylidene participate in the formation of bonds with the metal.[31–33] The character of the bonding of other unsaturated carbenes, isolobal with vinylidene, to metal atoms is apparently similar.

Vinylidene complexes and allenylidene complexes of type (A) contain a linear metallallene M=C=C or metallacumulene M=C=C=C system. Their M–C$_\alpha$ σ-bond is formed as a result of the overlap of the a_1 HOMO of the ligand with $3a'$ LUMO of the metallic fragment. The π-component of the M–C$_\alpha$ bond is formed as a result of the reverse transfer of electron density from the occupied $2a''$ and $2a'$ orbitals of the metal to the unoccupied b_2 and π^* MO of the ligand. Ultimately, the M–C$_\alpha$ bond should have a character intermediate between that of a double and triple bond.

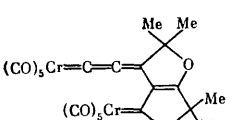


$3a'(M) \leftarrow a_1(C_\alpha{=}C_\beta)$ $2a''(M) \rightarrow b_2(C_\alpha{=}C_\beta)$ $2a'(M) \rightarrow \pi^*(C_\alpha{=}C_\beta)$ $2a'(M) \leftarrow \pi(C_\alpha{=}C_\beta)$

Indeed, very short M–C$_\alpha$ distances have been found in the molecules of vinylidene complexes[10,15,34–48] and allenylidene complexes,[49–53] which have been investigated by X-ray diffraction.



(I) (II) (III), L = PPh$_3$



(IV)

The Mn=C$_\alpha$ bond lengths in the vinylidene derivatives of cymantrene [1.68(2) Å in the complex (I),[6,34] 1.79(2) Å in $(C_5H_4Me)(CO)_2Mn{=}C{=}CMe_2$,[54] and 1.75(2) Å in $Cp(CO)_2Mn{=}C{=}CHC_6H_4CBr{=}CH_2$ [45]] and in the allenylidene complex (II) (1.806 Å [51]) are smaller than in the dimethylcarbene compound $Cp(CO)_2Mn{=}CMe_2$ (1.872 Å [55]) and approach the length of the Mn≡C triple bond (1.665 Å) in the carbyne complex $[Cp(CO)_2Mn{\equiv}C{-}CH{=}CPh_2]^+$.[56] The Ru=C distance in $Cp(PMe_3)_2Ru{=}C{=}C{=}CPh_2$ [1.884(5) Å [52]] and the Ru=C (vinylidene) distance (1.83 Å) in the bimetallic complex (III)[48] are shorter than the Ru=C (carbene) distance in compound (III) (1.93 Å). The Cr=C (allenylidene) and Cr=C (carbene) distances in the furofurandiylidene complex (IV) are respectively 1.913(7) and 9.73(6) Å.[50]

According to MO calculations,[31,32] the horizontal conformation of vinylidene and the vertical conformation of allenylidene are more favourable in type (A) complexes. Such conformations have in fact been established by X-ray diffraction for the majority of the complexes, for example, in (I) and (II). However, the barrier to rotation about the M–C$_\alpha$ bond is low (~4 kcal mol^{-1}).[32] In the NMR spectra of type A complexes with a $=CR_2$ (R = H or alkyl) terminal group, magnetic equivalence of the substituents R is therefore frequently observed.[8,57,58] The vertical conformation of phenylvinylidene has been observed in the crystal structure of $Cp[P(OMe)_3](Br)Mo{=}C{=}CHPh$.[36]

Owing to the presence of two unoccupied orbitals available for bonding to the metal, vinylidenes are some of the strongest π acceptors. Analysis of the IR spectra of the complexes $Cp(CO)_2MnL$ established the series based on the diminution of the electron-accepting properties of L:

$$SO_2 > CS > \boxed{C{=}CHPh} > AsF_3 > CO > PF_3 > \eta^3\text{-}PhC{\equiv}CPh > CPh_2 > PPh_3.$$

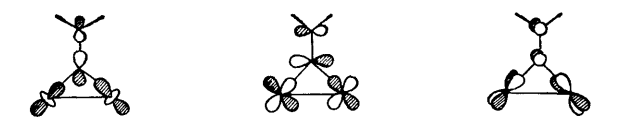
According to this series, the vinylidene ligand C=CHPh is greatly superior to carbenes and π-acetylenes in its electron-accepting capacity.[7]

In the vinylidene complexes, the LUMO is mainly concentrated on the C$_\alpha$ atom, while the HOMO is concentrated on the C$_\beta$ atom.[32] Accordingly, in the vinylidene complexes the attack by the nucleophile is directed to the C$_\alpha$ atom and that by electrophiles is directed to the C$_\beta$ atom. In the allenylidene complexes, there are two electrophilic centres (C$_\alpha$ and C$_\gamma$) and one nucleophilic centre (C$_\beta$). By virtue of the presence of the electrophilic centre, the electrochemical reduction of the complex (I) is much easier ($E_{1/2}$ = –1.99 V)[59] than the reduction of the isoelectronic complexes $Cp(CO)_2MnL$ (L = CO: $E_{1/2}$ = –2.70 V; $L = \eta^2$-HC≡CPh: $E_{1/2}$ = –2.38 V).[60]

The presence in the ^{13}C NMR spectra of type (A) complexes of a signal at very low field is consistent with reduced electron density at the C$_\alpha$ atom: δ = 320–390 p.p.m. for vinylidene complexes (Fig. 1), δ = 250–380 p.p.m. for allenylidene complexes, and even δ = 440.6 p.p.m. in the spectrum of $(CO)_5Cr{=}C{=}C{=}C{=}O$.[61] The C$_\beta$ chemical shifts are in the range δ = 100–145 p.p.m. for vinylidene complexes and 140–190 p.p.m. for allenylidene complexes.

The C$_\alpha$=C$_\beta$ bond length in type (A) vinylidene complexes (1.30–1.38 Å) differs little from the C=C bond length in alkenes, whereas in allenylidene complexes it is somewhat shorter (~1.25 Å). The ν(C=C) frequencies in the IR spectra of vinylidene ligands are in the range 1590–1690 cm^{-1}, while the ν(C=C=C) frequencies of the allenylidene ligands are in the range 1900–1940 cm^{-1}.[62]

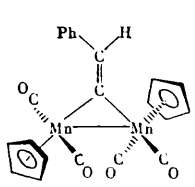
In the type (B) complexes, where the unsaturated carbene bridging ligand is linked symmetrically to two metal atoms, there are two M–C$_\alpha$ σ-bonds, which are formed as a result of the overlap of the a_1 and b_2 MO of the ligand with the MO of the metallic fragments, consisting mainly of the d_{z^2} and d_{xz} AO of the metal atoms.

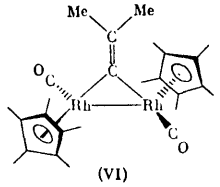


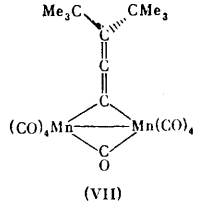
$d_{z^2}(M) \leftarrow a_1(C_\alpha{=}C_\beta)$ $d_{xz}(M) \rightarrow b_2(C_\alpha{=}C_\beta)$ $d_{yz}(M) \leftarrow \pi(C_\alpha{=}C_\beta)$

The optimum overlap is achieved when the b_2 MO of the ligand is arranged parallel to the metal–metal bond axis. This leads to the formation of the planar methylene dimetallacyclopropane system in the μ-vinylidene complexes. The coplanarity of the metallocycle and the =CRR′ fragment has been established in X-ray diffraction studies of a large number of vinylidene complexes of type (B),[10,12,13,23,63–76] for example, in the complexes (V)[6,76] and (VI).[65]

In the μ-allenylidene complexes $[(CO)_5W]_2(\mu\text{-}C=C=CPh_2)$ [77] and (VII),[78] the substituents at the C_γ atom are in a plane perpendicular to that of the metallocycle.


(V)


(VI)

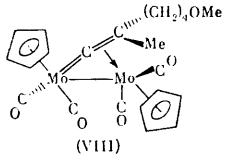

(VII)

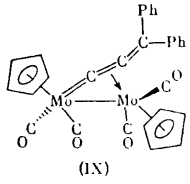
In type (B) complexes there is a possibility of the partial conjugation of the M–C_α and $C_\alpha=C_\beta$ bonds as a result of the overlap of the π and π* MO of the ligand with the MO, having a suitable symmetry, of the metal-containing fragments, the degree of which should depend on the donor–acceptor characteristics of the latter. Indeed, the M–C_α bonds in μ-vinylidene complexes are appreciably stronger[79] than in the related compounds with the μ-CR_2 or μ-CRX ligands, for which such conjugation is impossible.[28,80,81]

In type (B) UCC, there is apparently a higher electron density at the C_α atom than at the C_α atom in mononuclear type (A) compounds. This is indicated by the appreciable upfield shift of the C_α signal in the ^{13}C NMR spectra of type (B) complexes (δ = 240–290 p.p.m.) (see Table 1). The results of a polarographic study indicate a decrease in the electrophilicity of the bridging carbon atom in the complex (V) compared with the C_α atom of the terminal vinylidene ligand in the complex (I): the first stage in the reduction of compound (V) (2*e*, $E_{1/2}$ = –1.81 V) corresponds to the homolytic cleavage of the Mn–Mn bond and one of the Mn–C_α bonds is cleaved only in the second stage (1*e*, $E_{1/2}$ = –2.23 V).[59]

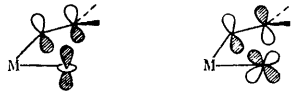
In contrast to the UCC of types (A) and (B), where the ligand supplies two electrons to the metal atoms, in complexes of types (C)–(E), the unshared electron pair of the C_α atom and the π-system of the $C_\alpha=C_\beta$ bond particpate in the bonding to the metal atoms and the unsaturated carbene thus becomes a donor of four electrons.

In the recently synthesised type (C) compounds with the lateral η^1, η^2-coordination of the unsaturated carbene,[17–19] for example in the complexes (VIII) and (IX)


(VIII)


(IX)

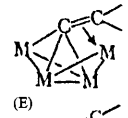
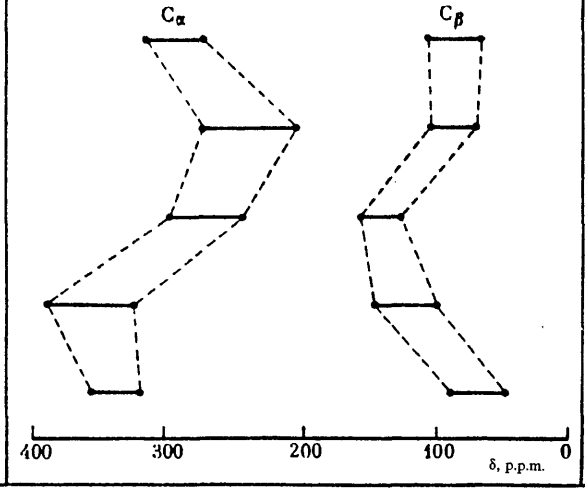
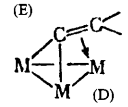
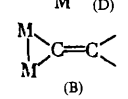
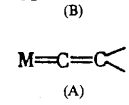
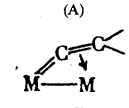
the C_α atom is linked to one of the metal atoms by a double bond similar to the M=C_α bond in mononuclear type (A) UCC. The bond between the unsaturated carbene and the second metal atom is formed as a result of the overlap of the π and π* MO of the $C_\alpha=C_\beta$ bond with the *d* orbitals of the metal.



The ^{13}C NMR spectroscopic data for type (C) complexes agree well with this bonding pattern: the C_α chemical shift is at very low field (δ = 320–340 p.p.m.), while the C_β chemical shift has undergone an upfield shift (δ = 45–85 p.p.m.) as a consequence of electron transfer from the second M atom to the π* MO of the $C_\alpha=C_\beta$ bond, compared with compounds of types (A) and (B) (Fig. 1). Thus the difference between the chemical shifts of the C_α and C_β signals in the type (C) complexes reaches ~300 p.p.m.

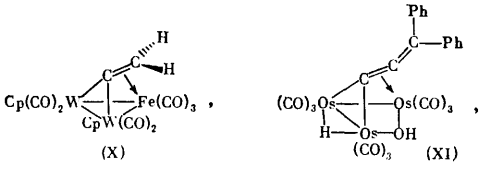
The η^2-coordination of the $C_\alpha=C_\beta$ bond to the metal lengthens it slightly [to 1.380 Å in the complex (VIII)[18] and to 1.336 Å in the complex (IX) [19]] and bends the metallacumulene chain [the

Table 1. Characteristics of the vinylidene ligands.

Type of complex	^{13}C NMR spectrum	C=C bond length, Å
 (E)		1.41–1.45
 (D)		1.37–1.43
 (B)		1.29–1.38
 (A)		1.29–1.34
 (C)		1.38

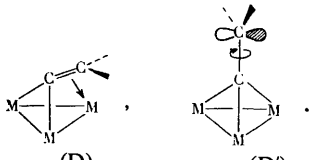
Mo–C_α–C_β valence angle is 168.5° in compound (VIII) and 167.2° in compound (IX), while the C_α–C_β–C_γ angle in compound (IX) is 144.5°].

Type (D) coordination combines elements characteristic of types (B) and (C). In the μ_3-vinylidene and μ_3-allenylidene complexes, examples of which are compounds (X)[82] and (XI),[83] i.e.



(X) (XI)

the unsaturated carbene forms two C_α–M σ-bonds with two metal atoms and a π-bond with the third metal atom:

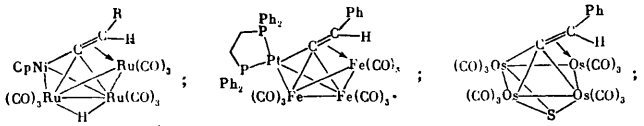


(D) (D′)

According to X-ray diffraction data,[10,24,82–88] the M–C_β distances in all type (D) compounds are appreciably longer than the M–C_α distances, while the $C_\alpha=C_\beta$ bonds are significantly extended (1.37–1.43 Å). The frequencies ν(C=C) in the IR spectra of complexes of this type are also displaced to the region below 1400 cm^{-1}.[89] According to MO calculations for $[(CO)_9Co_3(\mu_3\text{-}C=CH_2)]^+$,[90,91] the lateral μ_3,η^2-coordination of the vinylidene ligand (D) is more favourable than the centrosymmetrical μ_3-coordination (D′), but the difference between their energies is small. The stereochemical non-rigidity of the μ_3-vinylidene complexes, observed in the NMR spectra, is probably caused by the presence in these compounds of a weak M–C_β bond and the possibility of the transition of the molecules in solutions to the (D′) configuration.

By virtue of the transfer of electron density from the three M atoms to the C_α atom, the latter can apparently acquire nucleophilic properties. This is especially characteristic of μ_3-ketenylidene complexes,[92,96] for example, $[(CO)_9Fe_3(\mu_3\text{-}C=C=O)]^{2-}$.[96] The reduction of the electrophilicity of the C_α atom in type (D) vinylidene complexes is apparently indicated by the appreciable upfield shift of the C_α signal in their ^{13}C NMR spectra (δ = 200–280 p.p.m.) compared with types (A)–(C) (see Table 1).

In the μ_4-vinylidene complexes of type (E),[21,22,97–104] for example, in the complexes (XII),[22] (XIII),[104] and (XIV),[101] the unsaturated carbene is linked by C_α–M σ-bonds to three metal atoms and the $C_\alpha=C_\beta$ fragment is π-coordinated to the fourth metal atom:



(XIIa): R = Bu^t
(XIIb): R = Pr^i (XIII) (XIV)

X-Ray diffraction analysis has shown that the M–C_α bonds in type (E) complexes are stronger than the M–C_β bonds and that the C_α–C_β distance (1.41–1.45 Å) approaches the length of a C_{sp^2}–C_{sp^2} single bond (1.46 Å). The downfield shift of the C_α signal in the ^{13}C NMR spectra (δ = 270–310 p.p.m.) suggests an electrophilic character of this atom in type (E) compounds, whose chemical properties have not yet been investigated.

It is noteworthy that the positions of the C_α and C_β signals in the ^{13}C NMR spectra of the complexes examined are greatly influenced not only by the mode of coordination of the unsaturated carbene[105] but also by the nature of the metal atoms and their surrounding ligands, which is reflected in the wide ranges of the chemical shifts illustrated in Table 1. At the same time, the difference Δδ between the C_α and C_β chemical shifts for the majority of types of UCC is more individual than the positions of the C_α and C_β signals themselves. This makes it possible to establish reliably the type of coordination of the unsaturated carbene ligand on the basis of the ^{13}C NMR spectra for many UCC with a known number of metal atoms.

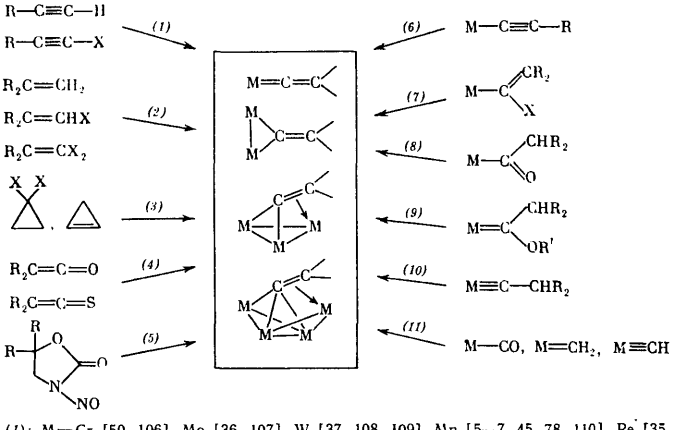
III. The synthesis of unsaturated carbene complexes

The sources and methods of formation of unsaturated carbenes in the coordination spheres of transition metal atoms are much more varied than in organic chemistry.[1] Unsaturated carbene ligands are formed both from organic molecules (alkynes, alkenes, cyclopropanes, cyclopropenes, ketens, *N*-nitrosooxazolidinones) and from the organic ligands forming part of the composition of the complexes (acetylide, vinyl, acyl, carbene, carbyne) (Scheme 1). The formation of vinylidene ligands at metallic centres also from single-carbon fragments (CO, CH_2, CH) is known.

Since it is impossible to give an exhaustive survey of all the methods of synthesis of UCC within the framework of a general publication, in this Section we shall consider only the most general or especially interesting methods of preparation of these compounds.

Scheme 1

Sources of unsaturated carbene ligands



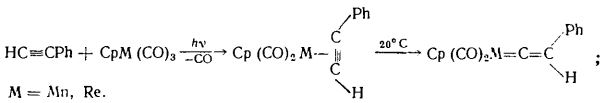
(*1*): M=Cr [50, 106], Mo [36, 107], W [37, 108, 109], Mn [5–7, 45, 78, 110], Re [35, 39, 78, 111], Fe [53, 58, 112], Ru [43, 48, 58, 64, 84, 109, 113–116], Os [46, 101–103], Co [84, 109, 113, 117], Rh [15, 38, 118–120], Ir [15], Pt [121].
(*2*): M=Ta [16], Fe [67, 68, 122], Ru [123], Os [123–125], Co [66, 126], Pd [14].
(*3*): M=Mo [87], Fe [127], Os [128].
(*4*): M=Fe [4, 40, 129].
(*5*): M=Co, Rh [65, 69].
(*6*): M=W [130, 131], Fe [58, 132], Ru [9, 21, 22, 24, 41, 42, 44, 47, 83, 100, 116, 133], Os [85, 134–136], Pt [13].
(*7*): M=Mo, W [137], Fe, Co [138], Os [139–142], Rh [142].
(*8*): M=Fe [143].
(*9*): M=Cr, W [49], W, Pt [12].
(*10*): M=Mo [144, 145], W [12, 72, 82], Fe [82, 86, 146–152], Ru [64, 153, 154], Os [72, 155], Ir [156], Pt [12].
(*11*): M=Mn [143], Fe [147–149, 157–164], Ru [153, 164–167], Co [74].

Note. Here the numerals in square brackets denote references (Ed. of Translation).

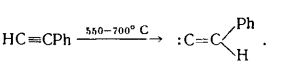
1. Generation of unsaturated carbene ligands from organic molecules

(a) The acetylene–vinylidene rearrangement

The most general method of synthesis of complexes with monosubstituted vinylidenes involves the acetylene–vinylidene rearrangement (AVR) at metallic centres. AVR was first observed for Mn and Re complexes:[5–7,35]



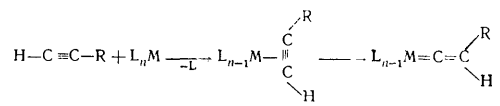
The isomerisation of free acetylenes to vinylidenes is known[1] to occur under severe conditions:



According to calculations,[33] the energy of acetylene is lower by 44 kcal mol^{-1} than that of vinylidene and the activation energy for the AVR is 76 kcal mol^{-1}. On coordination to the metal, the thermodynamic stabilities of acetylene and vinylidene are reversed: $Cp(CO)_2Mn=C=CH_2$ has an energy lower by 32 kcal mol^{-1} than the π-acetylene isomer. This is responsible for the easier occurrence of the AVR at a metallic centre at 5–65 °C.

The principle features of the AVR, its mechanism, and its driving force can be elucidated only now as a result of the accumulation of information about the conditions governing the occurrence of the reaction for a large number of metals (see Scheme 1 and the bibliography quoted in it as well as the review of Bruce and Swincer[10]) with different ligand environments.

In all cases, the synthesis of unsaturated carbenes from acetylenes proceeds via the intermediate formation of π-acetylene complexes:



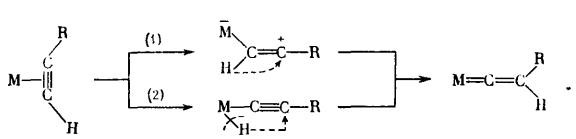
R = H, Alk, Ar, C(OH)R$_2$, COOR etc.

However, they frequently cannot be detected because of the high rate of the AVR, for example, in the formation of $Cl(dppe)_2Re=C=CHPh$ from HC≡CPh and $Cl(dppe)_2Re(N_2)$.[39]

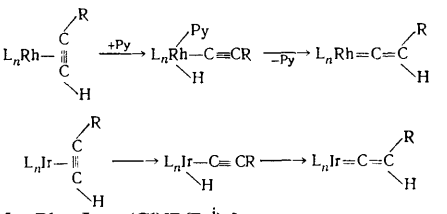
Two alternative mechanisms of the conversion of a π-alkyne complex into a vinylidene complex are most probable:

(1) a two-stage process involving the conversion of the alkyne into a metal-stabilised vinyl cation and the subsequent 1,2-shift of an H atom;[33]

(2) oxidative addition of the alkyne to the metal with formation of a hydride–acetylide intermediate with subsequent dissociation of the M–H bond and protonation (intra- or inter-molecular) of the C_β atom:[7,33]



According to calculations,[33] the mechanism (1) is energetically more favourable but it does not take into account the active role of the metallic centre in the reaction. Although the oxidative addition of alkynes to a metal[168] and the protonation reactions of σ-alkynyl complexes with formation of vinylidene complexes (see below) have been thoroughly investigated, experimental confirmation of the mechanism (2) has been obtained only recently. It has been shown[15] that the reactions involving the conversion of the π-acetylene complexes of rhodium and iridium into the vinylidene complexes proceed via intermediate hydride-acetylide compounds:



R = H, Me, Ph; $L_n = (Cl)[P(Pr^i)_3]_2$.

The ease of the AVR increases with increasing basicity of the metallic centre. The spontaneous isomerisation of π-acetylene complexes to vinylidene is observed more often for sixth-Period transition metals (W, Re, Os, Ir) than for their lighter analogues. The rearrangement is promoted by the presence of donor ligands in the coordination sphere of the metal atom. When the basicity of the metallic centre is insufficient, the presence of bases is required for the occurrence of the AVR.

Thus the isomerisation of the π-complexes of iridium quoted above takes place spontaneously, but the rearrangement of the analogous rhodium complexes requires the presence of pyridine, which participates in the formation of the hydride-acetylide intermediate.[15] The vinylidene complexes $[(C_5Me_5)(PPh_3)(CO)Os=C=CHR]^+$ are obtained in quantitative yields in the reactions of the alkynes HC≡CR (R = Bu^t, Ph) with $(C_5Me_5)(PPh_3)(CO)OsI$ in the presence of $AgBF_4$ (CH_2Cl_2, 22 °C), but a vinylidene complex is not formed under these conditions from $(C_5Me_5)(CO)_2OsI$.[46] The complex $Cp(CO)_2Re(\eta^2\text{-}HC\equiv CPh)$ is converted into $Cp(CO)_2Re=C=CHPh$ in a neutral medium,[35] while the isomerisation of $Cp(CO)_2Mn(\eta^2\text{-}HC\equiv CPh)$ to $Cp(CO)_2Mn=C=CHPh$ takes place either on a column with Al_2O_3 at pH 9–10 [7] or in the presence of catalytic amounts of hexamethylenetetramine.[110] On passing to alkynes HC≡CR with substituents R having more pronounced electron-accepting properties than Ph, the rearrangement of the π-complexes of Mn requires stronger bases: PhLi (for $HC\equiv C\text{–}C_6H_4\text{–}C\equiv CH$-4) and Bu^{t}Li or KOH (for HC≡CCOOMe).[10,45] The role of the bases in these reactions apparently consists in increasing the basicity of the metallic centre, which can be achieved by their interaction either directly with the metal atom or with the CO ligands.

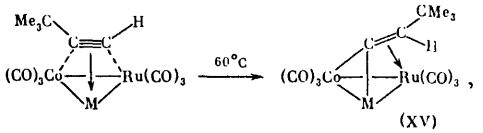
The rearrangement to vinylidene complexes is unknown for π-acetylene complexes of transition metals at the beginning of the Period, in which the metal atom has an unfilled 16-electron shell, for example, $Cp(CO)Nb(\eta^2\text{-}PhC\equiv CEPh_3)_2$ (E = Si, Ge, Sn)[169] or $Br_2(PPh_3)_2M(\eta^2\text{-}HC\equiv CR)$ (M = Mo, W; R = Bu, Ph).[170] On the other hand, the 18-electron complex $(dppe)(CO)_3W(\eta^2\text{-}HC\equiv CPh)$ isomerises spontaneously to the vinylidene complex at 20 °C.[108] The spontaneous conversion of the 18-electron Mn,[7] Re,[111] and Ru[114,115] complexes with the η^2-ligands $PhC\equiv CEPh_3$ (E = Si, Ge, Sn) or $RC\equiv CSiMe_3$ (R = H, Ph) into compounds with the vinylidene groups C=CHR is preceded by the elimination of the EPh_3 or $SiMe_3$ substituents; the solvent serves as the source of the H atom in such cases.

On the basis of the foregoing, one can postulate that the endeavour of the electron-rich metal atom to reduce its electron density is in fact responsible for the rearrangement of the η^2-alkyne to the vinylidene with more marked electron-accepting properties.

Apart from the energy gain, the AVR is also favourable for steric reasons, since the vinylidene incorporated in the metallallene system creates a much smaller steric hindrance in the ligand environment of the metal than the η^2-coordinated alkyne.

The AVR has been less thoroughly investigated for polynuclear systems than for mononuclear systems. The conversion of the halogenoalkynes RC≡CX (R = Bu, Ph, Br, I; X = Cl, Br, I) in reactions with dinuclear cobalt complexes into the vinylidene ligands μ_2-C=CXR as a result of a 1,2-shift of the halogen atom has been reported.[117]

The ready isomerisation of the μ_3-alkyne clusters $RuCO_2$,[84,88,113] MoRuCo,[171] and WRuCo [109] into the μ_3-vinylidene clusters has been observed:

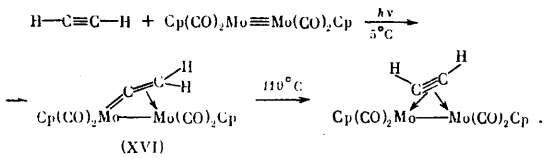


(XV)

where M = $Co(CO)_3$, $Mo(CO)_2Cp$ (XV), or $W(CO)_2Cp$.

The phenylvinylidene clusters (XIV),[101] $Os_6(CO)_{20}(\mu_3$-C=CHPh), and $Os_5(CO)_{15}(\mu_4$-C=CHPh) have been obtained by the interaction of PhC≡CH with $Os_4(CO)_{12}(\mu_3$-S) and $Os_6(CO)_{20}$(MeCN).[102]

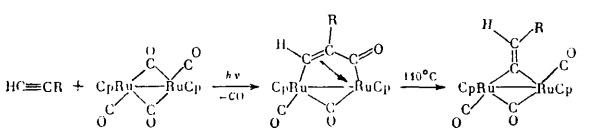
The first type (C) complex with the lateral coordination of vinylidene has been obtained by the photochemical reaction of acetylene with an unsaturated Mo_2 complex:[17]



(XVI)

The reverse isomerisation of the vinylidene to the alkyne is possible for the complexes (XV) and (XVI) with the η^2-coordination of the C=C fragment to the metal: on treatment with the $Cp(CO)_3Mo^-$ anion in boiling tetrahydrofuran (THF)[171] for compound (XV) and on boiling in toluene for compound (XVI).[17]

The reaction



R = H, Ph

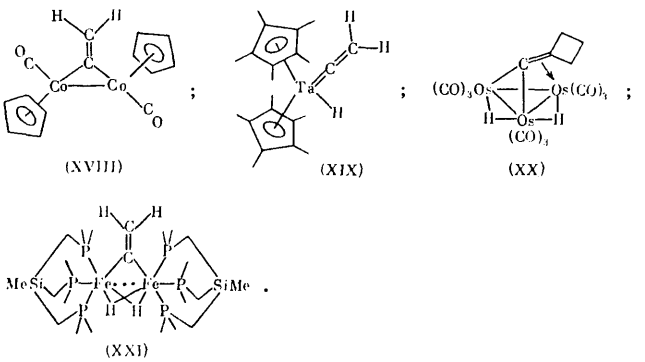
(XVIIa): R=H,
(XVIIb): R=Ph,

as a result of which the alkyne is initially inserted into the Ru–CO bond and the intermediate then isomerises with formation of the complex (XVII),[64,172,173] is a special case of the conversion of an alkyne into a vinylidene.

(b) The synthesis of vinylidene complexes from alkenes

Not only 1,1-dihalogenoalkenes and vinyl halides—the traditional precursors of vinylidene species,[1] but also ethylene and its homologues can serve as sources of the vinylidene ligands.

The complexes $Cp_2(CO)_3Fe_2[\mu$-C=C$(CN)_2]$[10,122] and $Cp_2(CO)_2$.$Co_2[\mu$-C=$CH_2]$ (XVIII),[66,126] have been obtained by the reaction of 1,1-dihalogenoalkenes with carbonylmetallate anions. An example of the dehalogenation of 1,1-dihalogenoalkenes by neutral complexes involving the transfer of Cl atoms to the metal is provided by the formation of $Cl_2(\mu$-dppm$)_2Pd_2(\mu$-C=$CH_2)$ from $H_2C=CCl_2$ and $Pd(PPh_3)_4$ in the presence of dppm:[14]

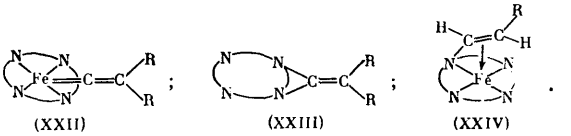


(XVIII) (XIX) (XX) (XXI)

The migration of the vinyl hydrogen atom to the metal during the reaction of $H_2C=CHMgBr$ with $(C_5Me_5)_2TaCl_2$ leads to the complex (XIX).[16]

Processes involving the transfer of two alkene hydrogen atoms to the metallic centre are characteristic of polynuclear systems. A series of complexes $H_2(CO)_9M_3(\mu_3$-C=CRR′) (M = Ru, Os) of type (D) have been obtained by reactions of $H_2C=CRR'$ with $M_3(CO)_{12}$.[10,123] The cluster (XX) has been synthesised recently from methylenecyclobutane and $Os_3(CO)_{12}$ by a similar procedure.[124,125] The unusual complex (XXI) has been obtained by treating (tmps)Fe(μ^4-C_6H_6) [tmps = $MeSi(CH_2PMe_2)_3$; 7 atm, 50 °C] or $[(tmps)_2Fe_2Cl_2]^+$ (1.5 atm, Na/Hg, 20 °C) with $H_2C=CH_2$.[67,68] The formation of the μ-vinylidene and μ-hydride ligands from $H_2C=CH_2$ can be regarded as a model of the first stage in the chemisorption of ethylene on the surfaces of metals.

The report by Mansuy[174,175] that the products of the reactions of $Cl_3CCH(C_6H_4Cl$-4$)_2$ (the insecticide DDT) with Fe-porphyrins (*in vitro*) and with cytochrome P-450 (*in vivo*) are vinylidene complexes of the type (TPP)Fe=C=CR_2 (XXII) aroused much interest:[10]



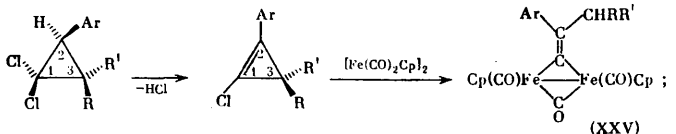
(XXII) (XXIII) (XXIV)

Similar products have been obtained by the reaction of $M_3(CO)_{12}$ (M = Fe, Ru) with *NN′*-vinylideneporphin (XXIII).[176] Later Castro and Wade[177] concluded from the results of an NMR spectroscopic study of the reactions of DDT with Fe-porphyrins that the compounds formed are not the vinylidene complexes (XXII) but the π-alkene complexes (XXIV). However, a recent X-ray diffraction study[178] of the tetraphenylporphyrin derivative of DDT, i.e. the complex (TPP)Fe=C=$C(C_6H_4Cl$-4$)_2$, confirmed that Mansuy's original hypothesis[174,175] was correct.

(c) The synthesis of vinylidene complexes from cyclopropanes and cyclopropenes

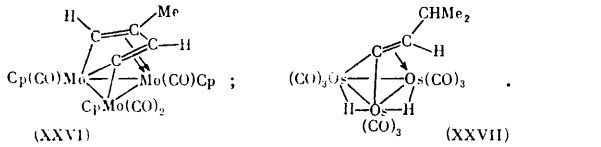
The vinylidene complexes (XXV) are readily formed in heterophase reactions of 2-aryl-1,1-dichlorocyclopropanes with $[Cp(CO)_2$.$Fe]_2$ (NaOH, $NBu_4^+HSO_4^-$, THF/H_2O, 20 °C).[127] The cycloalkanes are dehydrochlorinated in the first stage in these reactions, with

formation of chlorocyclopropenes, which then react with the bimetallic centre, this being accompanied by the selective cleavage of the C(1)–C(3) bond:



Ar = Ph, C_6H_4Me-4, C_6H_4OMe-4; R = H, Me; R' = H, Me, Ph.

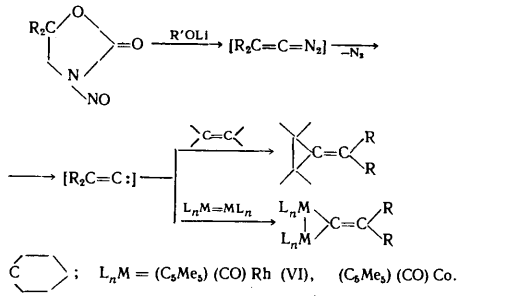
3,3-Dimethylcyclopropene adds at 20 °C with ring opening to the complexes $Cp_2Mo_2(CO)_4$ and $H_2Os_3(CO)_{10}$ containing multiple metal–metal bonds; thermolysis of the adducts leads to the μ_3-vinylidene clusters (XXVI)[87] and (XXVII)[128] respectively:



(XXVI) (XXVII)

(d) The synthesis of vinylidene complexes from *NN'*-nitrosooxazolidinones

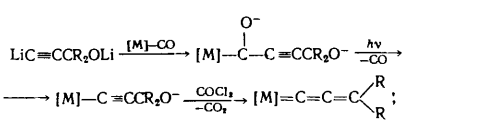
The successful use of the isolobal analogy between the C=C and M=M double bonds enabled Herrmann et al.[65,69] to develop a novel method of synthesis of vinylidene complexes with the aid of diazo-compounds formed when cyclic *N*-nitrosourethanes are treated with Bu^tOLi:



CR_2 = CMe_2, C; L_nM = $(C_5Me_5)(CO)Rh$ (VI), $(C_5Me_5)(CO)Co$.

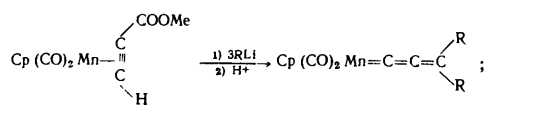
(e) The synthesis of cumulenylidene complexes

t-Propargyl alcohols and their dilithio-derivatives are widely used for the synthesis of the allenylidene complexes of Cr, W, Mn, Re, Fe, and Ru:[10,48,50,53,77,106]



R = Alk, Ar.

The salts and esters of propiolic acid are also used for this purpose:[8,10,57]



R = Bu^t (II), C_6H_{11}, CH_2Ph, Ph.

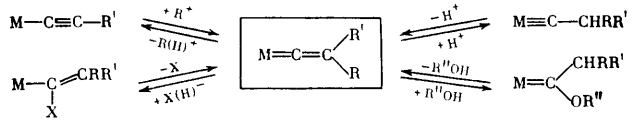
Together with simple dialkyl- or diaryl-allenylidene complexes, more complex products, for example compound (IV), are formed in these reactions.[50]

The oxapropatrienylidene complex $(CO)_5Cr=C=C=C=O$ has been obtained from $[ICr(CO)_5]^-$ and $AgC\equiv CCOONa$ in the presence of $AgBF_4$ and $CSCl_2$.[61]

2. The synthesis of unsaturated carbene complexes from complexes with σ-organic ligands

The general approach to the synthesis of vinylidene complexes from complexes with σ-alkynyl, vinyl, carbyne, and carbene ligands (Scheme 2) is based on the conversion of these ligands into vinylidenes on treatment with acid and bases. Scheme 2 also illustrates the possibility of the interconversion of complexes of these types proceeding via vinylidene complexes and determining the chemical behaviour of the latter (see Section IV):

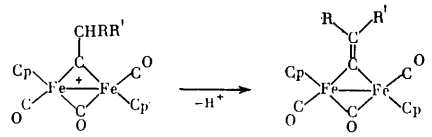
Scheme 2



R = H, Alk; X = H, Hal; R'' = Me, Et.

The addition of cations to the nucleophilic C_β atom in complexes with the M–C≡CR group is a general method of synthesis of mononuclear vinylidene complexes of W, Fe, Ru, and Os. The acetylide complexes can be protonated by acids[9,10,116] and alkylated with the aid of R_3O^+ (R = Me, Et),[9,131] $MeSO_3F$,[130,132] or RX (R = Me, Et, Ph, CH_2; X = halogen).[44,58,131] Tropylium[41] and arenediazonium[41,133] cations and halogen atoms[42,47] add to the C_β atom. On treatment of $H(CO)_9Os_3(\mu_3\text{-}C\equiv CCPh_2OH)$ with CF_3COOH, the OH group migrates from the C_γ atom to the Os_3 ring, which results in the formation of the μ_3-allenylidene cluster (XI).[83]

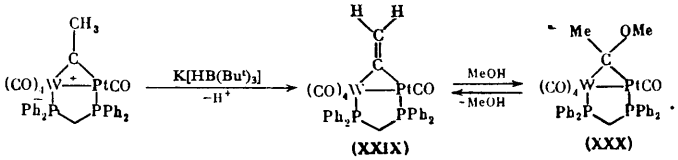
A second general method of synthesis of vinylidene complexes consists in the deprotonation of carbyne complexes, which proceeds under mild conditions on treatment with a wide variety of reagents. A proton is eliminated from $Cp[P(OMe)_3]_2Mo\equiv C\text{–}CH_2Bu^t$ in the reactions with BuLi, CF_3I, and PhN_2^+.[144,145] The methylcarbyne complex $[Cp_2(CO)_2(\mu\text{-}CMe_2)Ru_2(\mu\text{-}CCMe)]^+$ is converted into $Cp_2(CO)_2(\mu\text{-}CMe_2)Ru_2(\mu\text{-}C=CH_2)$ in the presence of water.[153] A series of vinylidene complexes (XXVIII) have been obtained by treating μ-carbyneiron cationic complexes with MeLi, NH_4OH, or $NaHCO_3/H_2O$:[146–149]



(XXVIII)

R and R' = H, Alk, $-(CH_2)_n-$; n = 4, 5.

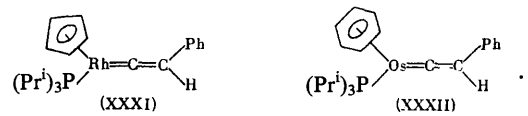
The heterometallic vinylidene complex (XXIX) has been obtained by a similar procedure:[12]



(XXIX) (XXX)

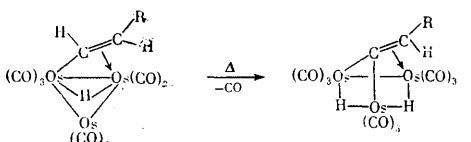
It has also been synthesised from the μ-carbene complex (XXX) as a result of the elimination of MeOH on Al_2O_3 at pH 9–10; the last reaction is reversible.[12]

The allenylidene compounds $(CO)_5M=C=C=C(Ph)(NEt_2)$ are formed as a result of the elimination of EtOH on treatment of the carbene complexes $(CO)_5M=C(OEt)CH=C(Ph)(NEt_2)$ (M = Cr, W) with BF_3 or $AlEt_3$.[49] The vinylidenerhodium complex (XXXI) and the vinylideneosmium complex (XXXII) have been obtained by eliminating HCl in reactions of $L_n(Cl)M-CH=CHR$ with NEt_3 and Bu^tLi respectively:[142]



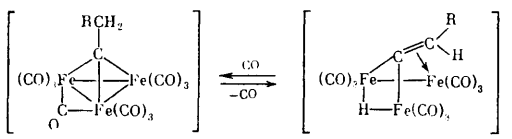
(XXXI) (XXXII)

In the synthesis of type (D) vinylidene complexes from carbonyl clusters with μ-vinyl ligands [compounds (XXXIII)][10,139–141] or μ-carbyne ligands [compounds (XXXV)],[150–152] a hydrogen atom migrates from the ligand to the metallocycle, which precedes the elimination of a CO group from the metal:



(XXXIII) (XXXIV)

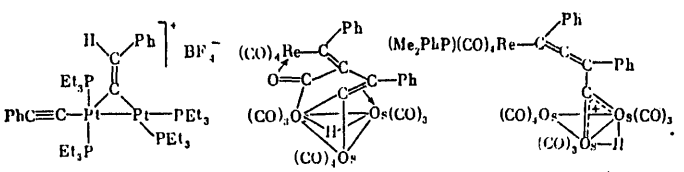
R = H, Alk, Ph, C_5H_4FeCp;



(XXXV) (XXXVI)

R = H, Pr, Ph, C(O)Me, COOMe.

A series of polynuclear vinylidene complexes have been synthesised by adding metal-containing fragments or molecules to σ-alkynyl complexes. Thus the complex (XXXVII) has been synthesised by the interaction of $(PEt_3)_2Pt(C\equiv CPh)_2$ with $[HPt(PEt_3)_2.(Me_2CO)]BF_4$.[13] The combination of alkynyl ligands in $(CO)_5.Re-C\equiv CPh$ and $H(CO)_{10}Os_3(\mu-C\equiv CPh)$ led to the unusual μ_3-vinylidene complex (XXXVIII), which rearranges to the complex (XXXIX) with an allenyl-substituted μ_2-carbyne ligand on treatment with PMe_3Ph:[85,135,136]



(XXXVII) (XXXVIII) (XXXIX)

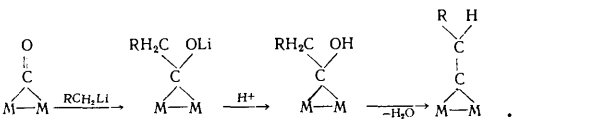
Heating of the complex $H(CO)_9Ru_3(\mu_3-C\equiv CR)$ (R = Pr^i, Bu^t) with $[CpNiCO]_2$ in the presence of H_2 leads to the complexes (XII).[21,22] The pentanuclear vinylidene cluster $(Ph_3P)_2Au_2Ru_3(\mu_3-C=CHBu^t).(CO)_9$ is formed in the reaction of $[(CO)_9Ru_3(\mu_3-C\equiv CBu^t)]^-$ with $[(Ph_3PAu)_3O]BF_4$.[24]

The heteronuclear vinylidene complex (X) has been obtained by the reaction of the two carbyne complexes $Cp(CO)_2W\equiv CMe$ and $CpWFe_2(\mu_3-CC_6H_4Me\text{-}4)(CO)_9$ at 80 °C.[82]

3. The formation of vinylidene ligands from CO, CH_2, and CH

In view of the growing interest in the synthesis of organic products from CO and H_2,[179] the possibility of the formation of unsaturated carbenes as a result of the reduction of CO at metallic centres merits special attention.

The conversion of CO groups into $C=CH_2$ was first noted in the reaction of $Ru_3(CO)_{12}$ with $NaBH_4$.[10,166] Stone and co-workers[157] developed a preparative method of synthesis of $Cp_2(CO)_3Fe_2.(\mu-C=CH_2)$ (XXVIII) (yield 80%) by the successive treatment of $Cp_2(CO)_2Fe_2(\mu-CO)_2$ with MeLi and CF_3COOH at –60–0 °C. The synthesis of compound (XVII) and of its FeRu analogue has been achieved similarly.[153,164,165] It has been shown for $(CO)_8(\mu_4-PPh)_2.Co(\mu-CO)_2$ that complexes with monosubstituted vinylidene can be obtained by this method: using BuLi as the alkylating agent, $(CO)_8(\mu_4-PPh)_2(\mu-CO)Co_4(\mu_2-C=CHPr)$ has been synthesised.[74] It is suggested that the process proceeds via the formation of a μ-methyl-(hydroxy)carbene intermediate, whose dehydration leads to the vinylidene complex:

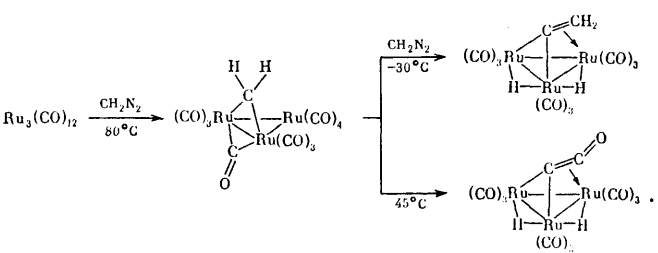


The conversion of the terminal CO group into $C=CH_2$ takes place in the reaction[143]

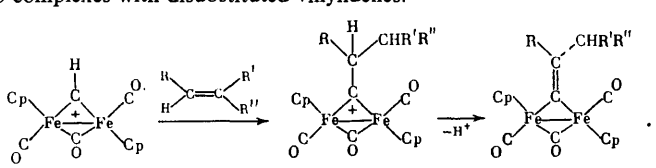
$$CpMn(CO)_3 \xrightarrow[2)(CF_3SO_2)_2O]{1)\,MeLi} [Cp(CO)_2Mn{=}C{=}CH_2] \longrightarrow [Cp(CO)_2Mn]_2(\mu\text{-}C{=}CH_2).$$

The formation of the complex $Cp_2(CO)_2Fe_2(\mu-C=CH_2)_2$ on treatment of $Cp_2(CO)_2Fe_2(\mu-CO)_2$ with the Wittig reagent $Ph_3P=CH_2$ has been reported.[158]

Ruthenium and osmium clusters with the μ-methylene ligand, which readily combines with CO or with a second CH_2 fragment with transfer of two H atoms to the metallocycle and the formation of new C–C bonds, may be key compounds in the synthesis of UCC:[167]



The μ-methylidyne complex $[Cp_2(CO)_3Fe_2(\mu-CH)]^+$ readily combines with alkenes, including cycloalkenes, via the C–H bond, being converted into compounds with more complex μ-carbyne ligands, whose deprotonation on treatment with $NaHCO_3/H_2O$ leads to complexes with disubstituted vinylidenes:[147–149,159–163]



Processes involving the growth of the carbon chain with formation of C=C double bonds, similar to the reactions illustrated above, can probably occur in the surface reduction of metal-containing catalysts with CO.

IV. The reactivity of the complexes

The complexes of unsaturated carbenes are usually crystalline brightly coloured substances, many of which are stable in air at 20 °C. Their thermal stability increases with increase in the number of metal atoms in the molecule on passing from type (A) to type (E). Neutral UCC are soluble in aliphatic hydrocarbons, while the ionic complexes are soluble in polar organic solvents. In solutions, the UCC as a rule gradually decompose.

The UCC exhibit a high and varied reactivity due to the presence of several reaction centres in their molecules. Reactions involving the cleavage of the M–C_α, C=C, and C–H bonds are known for the type (A), (B), and (D) complexes. Cyclo-addition reactions via the electron-rich M=C and C=C bonds and reactions involving insertion in a C–H bond are characteristic of the type (A) complexes. By virtue of the clear-cut charge distribution in the metallacumulene chains $M=\overset{+}{C}_\alpha=\overline{C}$ and $M=\overset{+}{C}_\alpha=\overline{C}_\beta=\overset{+}{C}_\gamma$ (see Section II), the reactions of type (A) UCC with electrophiles and nucleophiles are distinguished by a high regioselectivity.

1. The cleavage of the M–C_α and $C_\alpha=C_\beta$ bonds

The study of the mass spectra of the carbonyl complexes $[(CO)_4Fe]_2(\mu\text{-}C=CPh_2)$,[4] $[Cp(CO)_2M]_n(C=CHPh)$ (M = Mn, Re; n = 1, 2),[180] and $Cp(CO)_2Mn=C=C=CR_2$ (R = Bu^t, C_6H_{11})[8,57] indicates a greater strength of the M–C_α bonds compared with M=CO. The $[C=CPh_2]^+$ fragments recombine with formation of the butatriene $[C_4Ph_4]^+$ and the radialene $[C_6Ph_6]^+$,[4] while the $[C=C=CR_2]^+$ fragments recombine into the hexapentaene $[C_6R_4]^+$.[8,57]

The high strength of the M–C_α bonds in the UCC prevents the use of the latter as the sources of unsaturated carbenes. The formation of the hexapentaenes $R_2C=C=C=C=C=CR_2$ (R = Bu^t, C_6H_{11}, CH_2Ph) on thermolysis of the complexes $Cp(CO)_2Mn=C=C=CR_2$ is known.[8,57] The complex $(CO)_5Cr=C=C=C=O$ eliminates the C_2 species in hexane at 0 °C and is converted into $Cr(CO)_6$, whose treatment with Me_2SO/MeOH leads to dimethyl malonate.[61]

Ethylene is evolved on hydrolysis and methanolysis of $(C_5Me_5)_2.(H)Ta=C=CH_2$ (XIX).[16] Treatment of $Cp_2(CO)_3Fe_2(\mu\text{-}C=CH_2)$ (XXVIII) with H_2 lead to the evolution of ethane.[146] Cp_2Fe, $Cp_2Fe_2(CO)_4$, and $Cp_3(\mu\text{-}CO)_3Fe_3(\mu_3\text{-}CMe)$ are formed when compound (XXVIII) is refluxed in Bu_2O.[99]

The cleavage of the C=C bond on photolysis of compound (XVII) leads to $Cp_2(CO)_3Ru_2(\mu\text{-}CH_2)$.[165,173] Treatment of $[(\eta^5\text{-}C_9H_7)(PPh_3)_2Ru=C=CHPh]^+$ with O_2 affords $[(\eta^5\text{-}C_9H_7).(PPh_3)_2Ru\text{–}CO]^+$,[43] while after the oxidation of $[Cp(PPh_3)(L)Ru=C=CHPh]^+$ (L = PPh_3, CO) (CH_2Cl_2, 25 °C), PhCHO and PhCOOH were isolated in addition to the carbonyl complexes.[181]

The possibility of the involvement of type (E) vinylidene complexes in metathetical reactions of alkenes has been demonstrated: when the complex (XII) was heated with $D_2C=CD_2$ (toluene, 70 °C), the formation of $D_2C=CHBu^t$ was detected.[182]

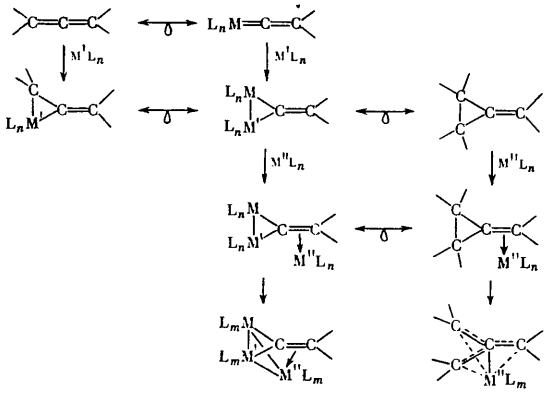
The cleavage of the ketenylidene ligand into C and CO takes place in the reaction of $H_2(CO)_9Os_3(\mu_3\text{-}C=C=O)$ with $(C_2H_4)_2PtL$ [L = $P(C_6H_{11})_3$] in toluene at 20 °C, which leads to the carbonyl-carbide clusters $H_2(CO)_9Os_3Pt(\mu_4\text{-}C)(CO)L$ and $H_2(CO)_9Os_3Pt_2.(\mu_5\text{-}C)(\mu\text{-}CO)L_2$.[183]

2. Addition to the M=C_α, C=C, and C–H bonds

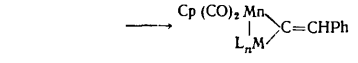
(a) Metallation of the M=C=C system

The metallallene system-containing type (A) complexes $L_nM=C=CR_2$, the character of the bond in which was examined in Section II, are isolobal with the organic allenes $R_2C=C=CR_2$, because the L_nM and R_2C fragments are in isolobal correspondence with one another.[25] The ability of allenes to coordinate transition metal atoms with formation of π-complexes is widely known. The fact that the type (A) complexes are isolobal with allenes is manifested by their ability to combine with coordinatively unsaturated and electron-unsaturated species $[L_nM]$ at the M=C_α bond. The type (A) complexes are then converted into type (B) compounds with bridging unsaturated carbenes (Scheme 3):

Scheme 3



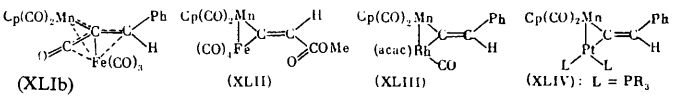
The possibility of the metallation of the M=C=C system was first demonstrated in relation to reactions of a vinylidene derivative of cymantrene (I):[7,20,184]



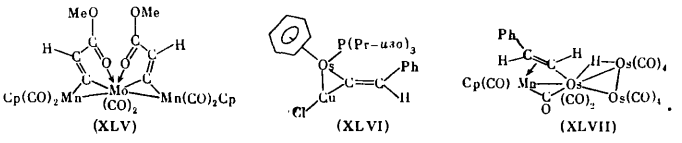
ML_n = Mn $(CO)_2$ Cp (V),
Re $(CO)_2$ Cp (XL),
Fe $(CO)_4$ (XLIa).

By virtue of the tendency of certain neutral type (A) vinylidene and allenylidene complexes to be converted into a more stable type (B) compound, such reactions sometimes proceed spontaneously.[7,53,57,77,118,143]

A series of dinuclear vinylidene complexes with Mn–Mo,[71,185] Mn–W,[71,185] Mn–Mn,[7,186] Mn–Re (XL),[20] Mn–Fe (XLII),[63,187] Mn–Rh (XLIII),[75] and Mn–Pt (XLIV),[11,79,188] bonds as well as the trinuclear bisvinylidene complex (XLV)[71] have been obtained from $Cp(CO)_2Mn=C=CHR$ [R = Ph (I) or COOMe]. The unusual dinuclear complex (XLIb) with an organometallic ligand of the trimethylene-methane type is formed as a result of the isomerisation of compound (XLIa) via the intramolecular carbonylation of the C_α atom:[184]



(XLIb) (XLII) (XLIII) (XLIV): L = PR_3

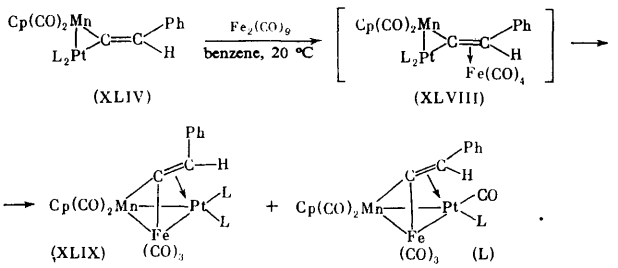


(XLV) (XLVI) (XLVII)

μ-Vinylidene compounds with Rh–Cr, Rh–Mn, Rh–Fe, and Rh–Cu bonds[70,189] have been obtained by the metallation of the Rh=C=C system in compound (XXXI), while the addition of CuCl to compound (XXXII) led to the synthesis of the complex (XLVI) with an Os–Cu bond.[142] The possibility of the addition of unsaturated cluster molecules to type (A) vinylidene complexes has been demonstrated in the formation of compound (XLVII) from the complex (I) and $H_2Os_3(CO)_{10}$.[190,191]

The allenylidene complexes $L_nM=C=C=CR_2$ combine with the $[M'L_n]$ fragment at the $M=C_\alpha$ bond with formation of type (B) μ-allenylidene compounds; compounds with W–W,[77] Mn–Mn,[62,63] Fe–Fe,[53] and Mn–Fe[63] bonds have been obtained in this way.

The type (B) complexes, incorporating the planar $\overline{MM'}(\mu\text{-}C=CR_2)$ system (see Section II), are isolobal with methylenecyclopropanes and, like the latter, can combine with yet another metal-containing fragment (see Section 3). The reaction of compound (XLIV) [L = PPh_3 or $P(OR)_3$] with $Fe_2(CO)_9$ results in the formation of the type (D) complexes (XLIX) and (L), whose molecules contain Mn, Pt, and Fe atoms:[104,192,193]



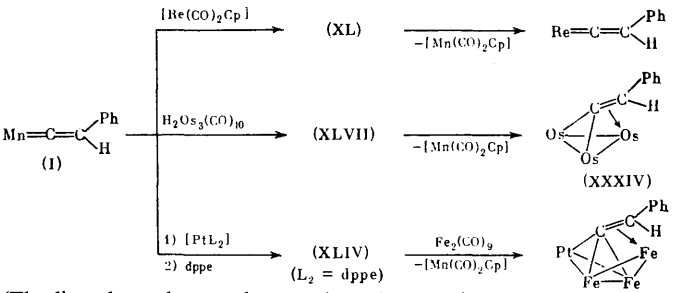
The metallation of type (B) vinylidene complexes with the aid of transition metal carbonyl hydrides involves the hydrogenation of the C_β atom of the vinylidene and the formation of μ_3-carbyne complexes. The cluster $Cp_2(CO)_6MnFe_2(\mu_3\text{-}CMe)$ has been obtained by treating the complex (XXVIII) with $H_2Mn_3(CO)_{12}$.[98,99] The trinuclear clusters $Cp_3(CO)_3MoCo_2(\mu_3\text{-}CMe)$ and $Cp_2(CO)_5MnCo_2(\mu_3\text{-}CMe)$ are formed in the reactions of $HMo(CO)_3Cp$ and $HMn(CO)_5$ respectively with $Cp_2(CO)_2Co_2(\mu\text{-}C=CH_2)$ (XVIII).[66,126]

An example of the metallation of type (D) μ_3-vinylidene clusters is the synthesis of $H(CO)_{11}Fe_3Rh(\mu_4\text{-}C=CHR)$ (R = H, Ph) from $[H(CO)_9Fe_3(\mu_3\text{-}C=CHR)]^-$ and $[ClRhCO]_2$ in the presence of $TlBF_4$.[194]

In a number of instances, the stabilisation of heterometallic intermediates similar to compound (XLVIII) is achieved as a result of the elimination of one of the metallic fragments and its substitution by new groups $[M'L_n]$. The reaction of a vinylidene complex of type (XLIV), where L_2 = dppe, with $Fe_2(CO)_9$ results in the formation of $(dppe)PtFe_3(\mu_4\text{-}C=CHPh)(CO)_9$ (XIII).[104] The tetranuclear complex $Cp(CO)_9FeCo_3(\mu_4\text{-}C=CH_2)$ has been obtained by heating compound (XXVIII) with $Co_2(CO)_8$ or $Co_4(CO)_{12}$.[98,99] The interaction of $(CO)_9Co_2Ru(\mu_3\text{-}C=CHBu^t)$ with $NaMo(CO)_3Cp$ leads to the formation of the complex (XV) as a result of the exchange of one of the $Co(CO)_3$ groups for $Mo(CO)_2Cp$.[109,171]

The possibility of the transfer of an unsaturated carbyne from one metal atom to another is of special interest. In the transfer of the C=CHPh ligand from the Mn to the Re atom,[20] to the Os_3 metallocycle,[190,191] and to the "butterfly" type cluster $PtFe_3$ [104] (Scheme 4), the cleavage of the $Mn=C_\alpha$ bond is preceded by the stage involving the formation of new metal–carbon and metal–metal bonds:

Scheme 4

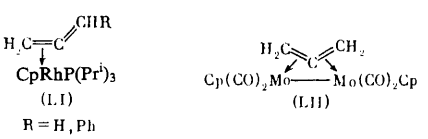


(The ligands at the metal atoms have been omitted.)

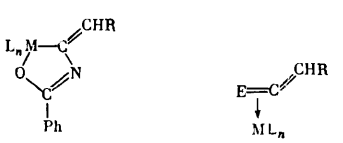
The transmetallation reactions can be used to synthesise UCC for which convenient direct methods of synthesis are not available.

(b) The addition of unsaturated organic compounds

The type (A) compounds (XXXI) and the type (C) compounds (XVI) combine with methylene at the electron-rich $M=C_\alpha$ bond, being converted into the corresponding allene π-complexes (LI) [195] and (LII):[17]

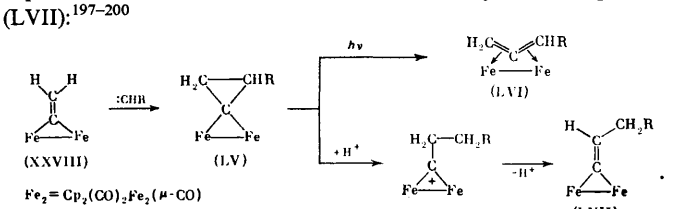


The [2 + 3]cycloaddition of benzoylnitrene to the $M=C_\alpha$ bond, which occurs in the reactions of compounds (XXXI) and (XXXII) with benzoyl azide at –78 °C, affords in 70–80% yield the complexes (LIII) with five-membered heterocycles, whose acidification leads to the corresponding immonium salts.[196] The π-complexes of thio-, seleno-, and telluro-ketens (LIV) have been obtained in the reactions of compound (XXXI) and (XXXII) with chalcogens:[119,120,142]



$L_nM = Cp[P(Pr^i)_3]Rh$, $(\eta^6\text{-}C_6H_6)[P(Pr^i)_3]Os$;
R = H, Ph; E = S, Se, Te.

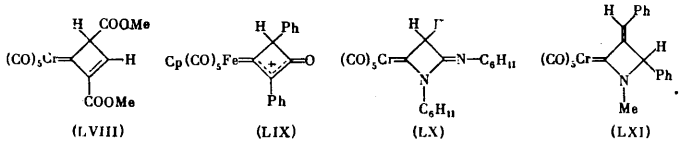
The carbenes :CHR (R = H, COOEt) add to the type (B) complex (XXVIII) at the $C_\alpha=C_\beta$ bond with formation of the cyclopropylidene compounds (LV), which isomerise on UV irradiation to the π-allene complexes (LVI) and the subsequent protonation and deprotonation reactions convert them into the vinylidene complexes (LVII):[197–200]



The structures of compounds (LV) and (LVI) have been confirmed by X-ray diffraction.[197,199]

The photochemical reaction of $Cp_2(CO)_3Ru_2(\mu\text{-}C{=}CH_2)$ (XVIIa) with ethylene leads to the μ-carbene complex $Cp_2(CO)_3Ru_2[\mu\text{-}C(Me).CH{=}CH_2]$.[165,173]

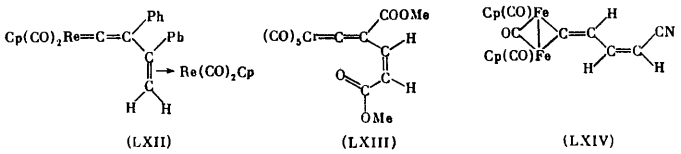
A wide variety of complexes with cyclic carbenes have been obtained by the [2 + 2]cycloaddition to the vinylidene ligand of alkynes, σ-acetylide complexes, carbodiimides, and imines—for example, compounds (LVIII),[106] (LIX),[201] (LX),[202] (LXI),[203] and others:[10]



(LVIII) (LIX) (LX) (LXI)

The complex (III) is formed as a result of the [3 + 3]cycloaddition of $Cp(PPh_3)_2Ru^+{=}C{=}CHC(Me){=}CH_2$ to $Cp(PPh_3)_2.Ru^+{=}C{=}C{=}CMe_2$.[48]

The insertion of alkynes in the C–H bond of the C=CHR ligands led to the butadienylidene complexes (LXII),[35] (LXIII),[106] and (LXIV):[204]



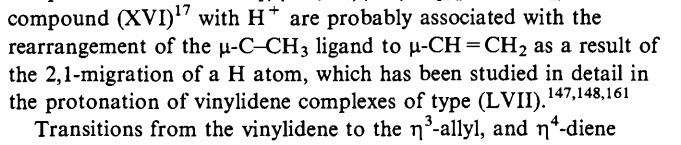
(LXII) (LXIII) (LXIV)

3. The reactions of unsaturated carbene complexes with electrophiles and nucleophiles

(a) The addition of electrophiles to the C_β atom in type (A) and (B) complexes

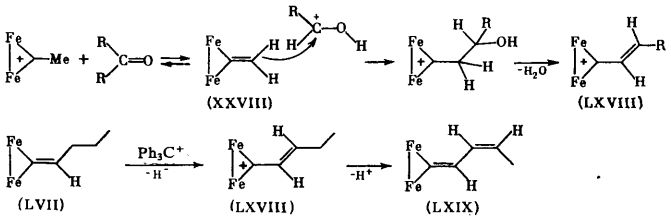
In conformity with the nucleophilic character of the C_β atom in type (A) and (B) UCC (see Section II), the protonation of these compounds leads to mononuclear[36,37,56,108,130,205] and dinuclear[10,12,56,64,66,126,146,147,149,160–163,204] carbyne complexes respectively (see Scheme 2). The instances of the formation of σ,π-vinyl complexes on treatment of $[(\eta^5\text{-}C_9H_7)(CO)Rh]_2(\mu\text{-}C{=}CH_2)$[118] and compound (XVI)[17] with H^+ are probably associated with the rearrangement of the μ-C–CH_3 ligand to μ-CH=CH_2 as a result of the 2,1-migration of a H atom, which has been studied in detail in the protonation of vinylidene complexes of type (LVII).[147,148,161]

Transitions from the vinylidene to the η^3-allyl, and η^4-diene complexes of molybdenum have been achieved by adding carbonium ions to the C_β atom and by subsequent reactions of the carbyne ligands.[144] The complexes (LXV) (M = Fe, R = H;[206] M = Ru, R = Me[73,207]), (LXVI),[73] and (LXVII)[207] with highly unsaturated bridges have been obtained by the electrophilic addition of $[Cp_2(CO)_3M_2(\mu\text{-}CR)]^+$ (M = Fe, Ru; R = H, Me) to the complexes (XXVIII) with R = R′ = H and (XVIIa) with subsequent shifts of the H atom along the chain or the loss of H_2:



(LXV) (LXVI) (LXVII)

The condensation of the μ-methylcarbyne with the aldehydes RCHO (R = Bu^t, C_6H_4Me-4, CH=CHPh), leading to the vinylcarbynes (LXVIII), proceeds via the intermediate formation of compound (XXVIII) and the electrophilic attack by the protonated aldehydes on its C_β atom:[208]



(XXVIII) (LXVIII)

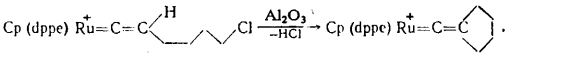
(LVII) (LXVIII) (LXIX)

On the other hand, treatment of a vinylidene complex of type (LVII) with Ph_3C^+ induces the dehydrogenation of the vinylidene side chain, which makes it possible to achieve a conversion to the vinylvinylidenes (LXIX) via the vinylcarbynes (LXVIII).[15]

(b) Deprotonation of the vinylidene ligand

A general reaction of type (A) complexes with the C=CHR ligands is deprotonation on treatment with various bases, which leads to σ-acetylide compounds[10,43,46,58,107,116,143] (see Scheme 2).

In a number of instances, the deprotonation is accompanied by the simultaneous elimination of a substitutent from the vinylidene side chain, for example:[58]



The dehydration of the γ-vinylidene alcohols $L_nM{=}C{=}CHC.(OH)R_2$ is a general method of synthesis of the allenylidene complexes $L_nM{=}C{=}C{=}CR_2$ (M = Mn,[109,110] Fe, Ru [48,52]).

The formation of the η^2-keten ligand $CH_2{=}C{=}O$ from $\mu\text{-}C{=}CH_2$ at a diruthenium centre, which occurs on hydrolysis of the product of the deprotonation of the vinylidene complex (XVII) on Al_2O_3, is of interest.[209]

(c) The reactions of vinylidene ligands at polynuclear centres

In contrast to the type (A) and (D) UCC, the metallic centre is actively involved in the reactions of type (D) vinylidene complexes and the mode of their reactions with electrophiles and nucleophiles depends on the charge on the cluster.

The neutral complex (XXXIV) (R = H) reacts with CF_2COOD, combining with D^+ at the Os–Os bond and being converted into $[(\mu\text{-}H)_2(\mu\text{-}D)(CO)_9Os_3(\mu_3\text{-}C{=}CH_2)]^+$;[210] the analogous reaction of compound (XXXIV) (R = C_5H_4FeCp) proceeds via the intermediate formation at −30 °C of the unstable σ,π-vinyl complex $(\mu\text{-}H)_2(CO)_8(\mu\text{-}CO)(CF_3COO)Os_3(\mu\text{-}CD{=}CHR)$.[140]

Treatment of the anionic complex (XXXVI) (R = H) with D^+ in the presence of H_2 leads to $(\mu\text{-}H)_3(CO)_9Fe_3(\mu_3\text{-}C\text{–}CH_2D)$, whereupon the H_2 molecule adds to the metallic core with formation of hydride bridges.[211] On the other hand, the cation $[(C_5Me_5)_3(\mu\text{-}CO)_3Ru_3.(\mu_3\text{-}C{=}CH_2)]^+$ is converted into the μ_3-carbyne clusters $(C_5Me_5)_3.(\mu\text{-}CO)_3Ru_3(\mu_3\text{-}C\text{–}CH_2R)$ (R = H, Me) on treatment with $NaBH_4$ or MeLi.[154]

The reactions of the vinylidene complexes (XV) [171] and (XXXIV)[105,212] with H_2 (60–100 °C) entail the selective addition of one H atom to the C_β atom and of the other to the metal–metal bond. It has been shown recently[100] that the hydrogenation of $(CO)_{13}(\mu\text{-}PPh_2)Ru_5(\mu_5\text{-}C{\equiv}CPPh_2)$ (1 atm, 80 °C), leading to the cleavage of the C≡C bond, takes place stepwise with absorption of

three H_2 molecules and the successive formation of clusters with μ_4-vinylidene, μ_4-carbyne, and μ_5-carbide ligands and at each stage of this process one H atom adds to the C_β atom of the ligand, while the other becomes a bridge at the Ru–Ru bond:

$$[M](C{\equiv}CPPh_2) \xrightarrow{H_2} [HM](C{=}CHPPh_2) \xrightarrow{H_2} \longrightarrow [H_2M](C{-}CH_2PPh_2) \xrightarrow[-2CO]{H_2} [H_3M'](\mu_5\text{-}C)(CH_3PPh_2),$$

$[M] = (CO)_{13}(\mu\text{-}PPh_2)Ru_5$, $[M'] = (CO)_{11}(\mu\text{-}PPh_2)Ru_5$.

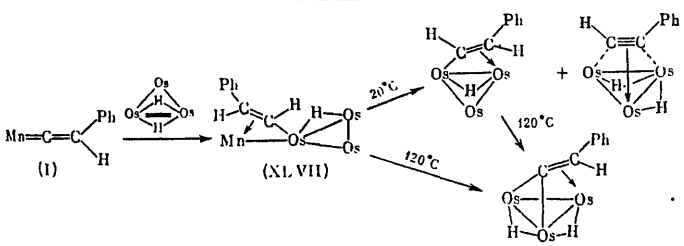
There is no doubt that in the interconversions of the vinylidene, carbyne, and other ligands at polynuclear centres, the metallic core of the cluster functions as a "hydrogen sponge", combining with hydrogen from outside and then transferring it to the ligand and also participating in processes involving H transfer from one part of the molecule to the other.

The migration of an H atom from the metallic core to the C_β atom of vinylidene has been observed in the conversion of the vinylidene complexes (XXXVI) into the carbyne complexes (XXXV) on treatment with CO at 20 °C[150–152] (see above).

The formation of the formylcarbyne cluster $(\mu\text{-}H)_3(CO)_9Os_3.(\mu_3\text{-}C\text{–}CHO)$ in the reaction of $[(\mu\text{-}H)_2(CO)_9Os_3(\mu_3\text{-}C{\equiv}CH)]^+$ with H_2O at 0 °C proceeds via a stage involving the isomerisation of the unstable hydroxyvinylidene complex $(\mu\text{-}H)_2(CO)_9Os_3[\mu_3\text{-}C{=}CH(OH)]$ via the intramolecular transfer of a H atom from the hydroxyl to the Os_3 ring.[134]

An example illustrating the migration of a H atom from the Os_3 ring to the organic ligand and in the reverse direction is provided by the reactions of phenylvinylidene in the presence of the $MnOs_3$ system illustrated in the scheme below:[190,191]

Scheme 5



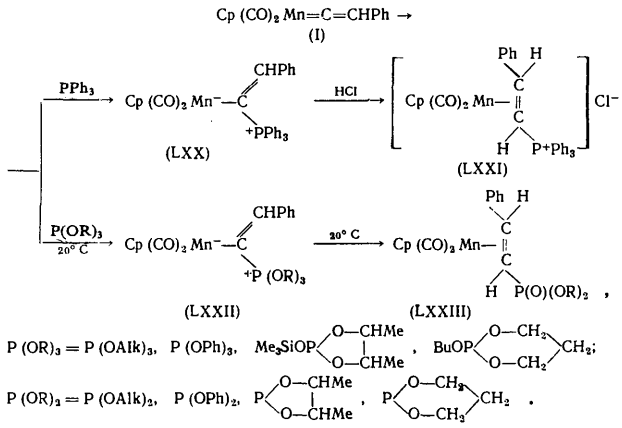
(I) (XLVII)

(d) The addition of nucleophiles to the C_α atom

Reactions involving the addition of nucleophiles are most characteristic of the type (A) UCC $L_nM{=}C{=}CRR'$, which have a very markedly electrophilic C_α centre (see section II). The hydrogenation of vinylidene complexes leads to σ-vinyl complexes (see Scheme 2).[10] When vinylidene complexes are acted upon by alcohols, thiols, ammonia, and primary and secondary amines, the nucleophilic species (OR^-, SR^-, NH_2^-, NHR^-, NR_2^-) adds selectively to the C_α atom, while a hydrogen atom adds to a C_β atom and Fischer carbene complexes are formed.[10,12,116,143,213] A direct method of synthesis of alkoxycarbene complexes from $W(CO)_6$, alkynes, and alcohols via vinylidene intermediates has been proposed recently:[214]

$$W(CO)_6 \xrightarrow{RC{\equiv}CH} (CO)_5W(HC{\equiv}CR) \longrightarrow \longrightarrow (CO)_5W{=}C{=}CHR \xrightarrow{R'OH} (CO)_5W{=}C\begin{matrix}CH_2R\\OR'\end{matrix}.$$

Pyridine[143] and tertiary phosphines,[10,45,215–217] none of which contain an active H atom, add to the C_α atom of the vinylidene complexes of Mn, Re, and Fe with formation of zwitter-ionic complexes, for example, (LXX):[215]



(I) (LXX) (LXXI) (LXXII) (LXXIII)

$P(OR)_3 = P(OAlk)_3$, $P(OPh)_3$, Me_2SiO, BuO; $P(OR)_2 = P(OAlk)_2$, $P(OPh)_2$, P.

The ionic π-alkene complex (LXXI) is formed from compound (LXX) on treatment with HCl.[218] The products of the addition of phosphites to compound (I)—the zwitter-ionic complexes (LXXII)—are spontaneously converted into the neutral vinylphosphonate π-complexes (LXXIII) as a result of the Arbuzov reaction.[219–221]

The allenylidene complexes $L_nM{=}C{=}C{=}CR_2$, having two electrophilic centres, combine with electrophiles (OR^-, SR^-, NR_2^-, PR_3) at either the C_α atom or the Cγ atom depending on their electron-donating capacity.[10,51,106,216]

V. Prospects for the utilisation of unsaturated carbene complexes

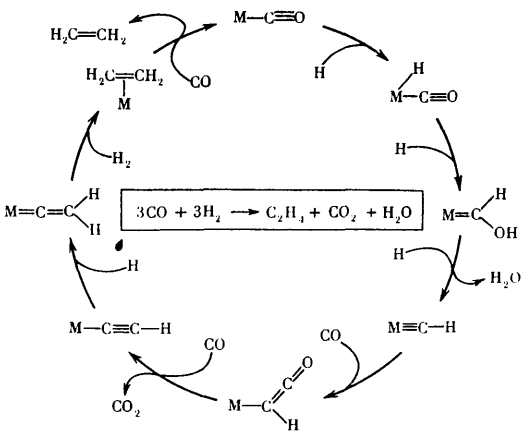
The vigorous development of the chemistry of the UCC during the last decade has led to a better understanding of the rules governing the formation, structure, and chemical behaviour of compounds of this new class. By virtue of the development of convenient preparative methods of synthesis (see Section III), not only individual UCC but also a series of related complexes have become available. Reactions involving the successive metallation of unsaturated carbenes, in which mono-, di-, and tri-nuclear UCC are used as "building blocks" as well as transmetallation reactions have led to the possibility of the specific synthesis of compounds whose molecules incorporate the atoms of several transition metals in definite combinations and proportions, for example, MnFe, MnRh, MnPt, RhCu, OsCu, $MoCo_2$, $MnCo_2$, Co_2Ru, MoCoRu, MnFePt, $MnOs_3$, $FeCo_3$, Fe_3Rh, Fe_3Pt, etc. There is no doubt that such compounds can find applications both directly (in catalysis) and for the preparation on their basis of new polymetallic materials (powders, coatings, films, ceramics, etc.).

The examples of the formation of unsaturated carbene ligands from a wide variety of sources, including single-carbon sources, presented in Section III, permit the conclusion that the UCC or the unsaturated carbene species present on the surface of the catalyst can participate in many catalytic processes. The ketenylidene Fe, Ru, and Os clusters are regarded as model compounds in the study of the reactions of CO on the surfaces of metals. It has been reported[222] that the synthesis of methyl acetate from CO, H_2, and

MeOH in the presence of $[Fe_6(CO)_{16}C]^{2-}$ proceeds via the intermediate $[(CO)_{12}Fe_4(\mu_4\text{-}C{=}C{=}O)]^{2-}$. The observed proportions of linear and branched hydrocarbons in Fischer–Tropsch processes have been explained by the formation of surface vinylidene species and their subsequent reactions.[223]

On the basis of the latest advances in the chemistry of organic compounds of transition metals, a model has been proposed for the mechanism of the catalytic synthesis of alkenes from CO and H_2 at a metallic centre, including vinylidene intermediates (Scheme 6).[224] The known reactions of complexes of Group VI–VIII transition metals, occurring with high degrees of conversion under mild conditions, serve as prototypes of each stage in this cycle.

Scheme 6

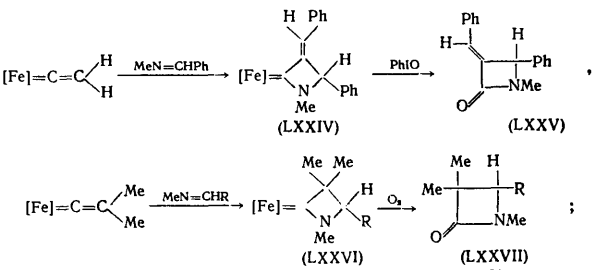


The selective formation of the butatriene *trans*-$(Bu^t)HC{=}C{=}C{=}CH(Bu^t)$ in the catalytic dimerisation of $HC{\equiv}CBu^t$ in the presence of the complex $H_2Ru(CO)(PPh_3)_3$ (50 cycles per Ru atom) proceeds via the AVR stage and the subsequent combination of two butylvinylidene species in the coordination sphere of Ru.[225]

The "small-scale chemistry"—the synthesis of organic substances necessary for modern medicine, agriculture, the special polymer industry, the food and perfume industry, etc.—have nowadays assumed increasing current interest. The new approaches to the synthesis of these substances should satisfy criteria such as high selectivity, productivity, low cost, low energy consumption by the processes, and their ecological safety.[226,227]

The reactions of unsaturated carbenes at metallic centres, examined in Section IV, include processes involving the hydrogenation, dehydrogenation, carbonylation, phosphorylation, and isomerisation of unsaturated organic groups, the growth of the carbon chain, and the formation of C_3–C_6 carbocyclic and heterocyclic compounds. As a rule, these processes proceed at 20–60 °C and atmospheric pressure. The high regioselectivity and stereoselectivity of the majority of the reactions are striking. Many organometallic compounds are formed in nearly quantitative yields. These complexes contain as the ligand an organic molecule capable of existing in a free state (alkene, allene, keten) or an organic group which constitutes a synthon prepared for further processes. The removal of the metal-containing fragment and the isolation of the organic product from these complexes do not usually present special difficulties. All these factors make the synthesis of a wide variety of organic substances with the aid of UCC extremely attractive.

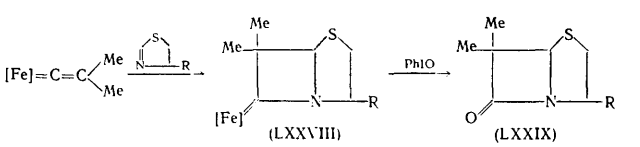
The synthesis of a series of β-lactams (LXXV) and (LXXVII) from imines and the available vinylidene iron complexes via [2 + 2]cycloaddition stages (–78–+25 °C) with formation of the azetidinylidene complexes (LXXIV) and (LXXVI) and their subsequent oxidation can serve as an example:[228]



[Fe] = Cp (CO) (PPh_3) Fe^+; R = Ph, C_6H_4Me-3, C_6H_4Me-4, CH=CHPh.

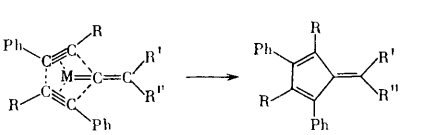
α-Benzylidene-β-lactam (LXXV) has been obtained similarly from the chromium complex (LXI).[203]

The interaction of the complex $\{Cp(CO)[P(OMe)_3].Fe{=}C{=}CMe_2\}^+$ and 2-thiazoline derivatives with subsequent oxidation of the carbene intermediate (LXXVIII) leads to bicyclic β-lactams with the penicillin structure (LXXIX):[229]



[Fe] = Cp (CO) $[P(OMe)_3]$ Fe^+; R = H, COOEt.

The possibility of obtaining unsaturated cyclic compounds involving vinylidene complexes is illustrated by the "assembly" of fulvenes from two alkyne molecules and a vinylidene ligand in the coordination spheres of palladium[230] and molybdenum:[231]



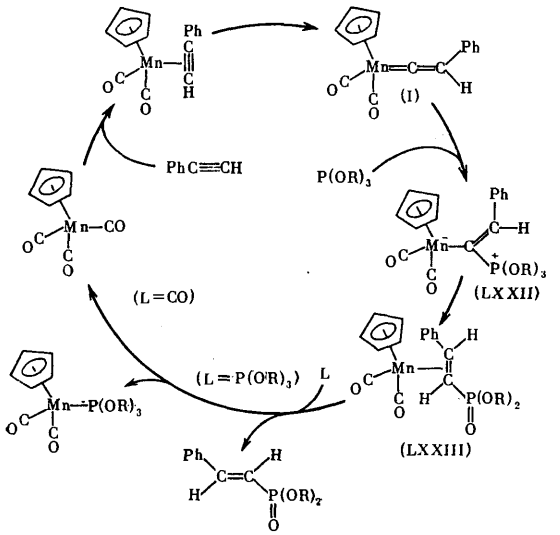
M = Pd, R = R'' = H, R' = Ph; M = Mo, R = Ph, R' = R'' = CN.

A fundamentally new approach to the synthesis of vinylphosphonic acid esters (usually obtained by the esterification of the chlorides of phosphonic acids or by the reactions of alkyl phosphites with alkynes or halogenoalkenes at 150–170 °C) is based on the interaction of phosphites with an unsaturated carbene in the coordination sphere of a transition metal atom.[219–221, 232]

The cyclic Scheme 7 illustrates the successive stoichiometric reactions: the formation of $Cp(CO)_2Mn{=}C{=}CHPh$ (I) from $CpMn(CO)_3$ and $PhC{\equiv}CH$, the conversion of the complex (I) into

the phosphonium complex (LXXII) and the styrylphosphonate complex (LXXIII), and the isolation from the latter of a phosphorus-containing alkene on treatment with $P(OR)_3$ or CO.

Scheme 7



In practice, styrylphosphonates are synthesised in one stage, without the isolation of the intermediate complexes (LXXII) and (LXXIII), in aliphatic or aromatic hydrocarbons:

$$Cp(CO)_2Mn{=}C{=}CHPh + 2P(OR)_3 \xrightarrow[4\text{–}6\ h]{20\text{–}60^\circ C} \longrightarrow \begin{matrix} Ph \\ H \end{matrix}\!\!>\!C{=}C\!<\!\begin{matrix} H \\ P(O)(OR)_2 \end{matrix} + Cp(CO)_2MnP(OR)_3.$$

The reaction is rigorously stereoselective and the styrylphosphonates formed in quantitative yields have exclusively the trans-configuration.[221,232] With the aid of this method, it is possible to obtain not only dialkyl but also the diaryl and cyclic esters of styrylphosphonic acids which are otherwise difficult to obtain.

It is to be expected that the number of examples of the use of UCC in the syntheses of organic compounds will increase. Since many UCC are prochiral or incorporate a chiral metallic centre, they will probably find applications in the asymmetric synthesis of biologically active substances and preparations.

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The enhancement of interest in the chemistry of UCC and the expansion of studies on these lines in many countries have been reflected in a sharp increase in the number of publications during the last 2–3 years†. Information has been published about the improvement of the methods of synthesis and the discovery of new useful properties of these compounds, and new possible applications of such substances are being vigorously sought. All these factors permit an optimistic prediction of the development of the chemistry of UCC and of the realisation of its potential practical possibilities in the immediate future.

†During the preparation of the review for the press, new communications appeared on this topic.[233–280]

References

1. P J Stang *Chem. Rev.*, 1978, **78** 383
2. P J Stang *Acc. Chem. Res.*, 1978, **11** 107
3. P J Stang *Acc. Chem. Res.*, 1982, **15** 348
4. O S Mills, A D Redhouse *J. Chem. Soc., Chem. Commun.*, 1966, 444
5. A N Nesmeyanov, A B Antonova, N E Kolobova, K N Anisimov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 2873
6. A N Nesmeyanov, G G Aleksandrov, A B Antonova, et al. *J. Organomet. Chem.*, 1976, **110** C36
7. A B Antonova, N E Kolobova, P V Petrovsky, et al. *J. Organomet. Chem.*, 1977, **137** 55
8. H Berke *Angew. Chem., Int. Ed. Engl.*, 1976, **15** 624
9. M I Bruce, R C Wallis *J. Organomet. Chem.*, 1978, **161** C1
10. M I Bruce, A G Swincer *Adv. Organomet. Chem.*, 1983, **22** 59
11. A B Antonova, S P Gubin, S V Kovalenko *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 953
12. M R Awang, J C Jeffery, F G A Stone *J. Chem. Soc., Dalton Trans.*, 1983, 2091
13. D Afzal, P G Lenhert, C M Lukehart *J. Am. Chem. Soc.*, 1984, **106** 3050
14. S J Higgins, B L Shaw *J. Chem. Soc., Chem. Commun.*, 1986, 1629
15. F J Garcia Alonso, A Höhn, J Wolf, et al. *Angew. Chem.*, 1985, **97** 401
16. A van Asselt, B J Burger, V C Gibson, J E Bercaw *J. Am. Chem. Soc.*, 1986, **108** 5347
17. N M Doherty, C Elschenbroich, H-J Kneuper, S A R Knox *J. Chem. Soc., Chem. Commun.*, 1985, 170
18. R J Mercer, M Green, A G Orpen *J. Chem. Soc., Chem. Commun.*, 1986, 567
19. S F T Froom, M Green, R J Mercer, et al. *J. Chem. Soc., Chem. Commun.*, 1986, 1666
20. N E Kolobova, A B Antonova, O M Khitrova *J. Organomet. Chem.*, 1978, **146** C17
21. E Sappa, A Tiripicchio, M Tiripicchio Camellini *J. Chem. Soc., Chem. Commun.*, 1979, 254
22. A J Carty, N J Taylor, E Sappa, A Tiripicchio *Inorg. Chem.*, 1983, **22** 1871
23. M R Churchill, Y-J Li *J. Organomet. Chem.*, 1985, **294** 367
24. M I Bruce, E Horn, O B Shawkataly, M R Snow *J. Organomet. Chem.*, 1985, **280** 289
25. R Hoffmann *Angew. Chem., Int. Ed. Engl.*, 1982, **21** 711
26. E O Fischer *Angew. Chem.*, 1974, **86** 651
27. R R Schrock *Acc. Chem. Res.*, 1979, **12** 98
28. W A Herrmann *Adv. Organomet. Chem.*, 1982, **20** 159
29. F G A Stone *Inorg. Chim. Acta*, 1981, **50** 33
30. F G A Stone *Angew. Chem., Int. Ed. Engl.*, 1984, **23** 89
31. B E R Schilling, R Hoffmann, D L Lichtenberger *J. Am. Chem. Soc.*, 1979, **101** 585
32. N M Kostić, R F Fenske *Organometallics*, 1982, 1 974
33. J Silvestre, R Hoffmann *Helv. Chim. Acta*, 1985, **68** 1461
34. G G Aleksandrov, A B Antonova, N E Kolobova, Yu T Struchkov *Koord. Khim.*, 1976, **2** 1684
35. N E Kolobova, A B Antonova, O M Khitrova, et al. *J. Organomet. Chem.*, 1977, **137** 69
36. R G Beevor, M Green, A G Orpen, I D Williams *J. Chem. Soc., Chem. Commun.*, 1983, 673
37. K R Birdwhistell, S J N Burgmayer, J L Templeton *J. Am. Chem. Soc.*, 1983, **105** 7789

38. J Wolf, H Werner, O Serhadli, M L Ziegler *Angew. Chem., Int. Ed. Engl.*, 1983, **22** 414
39. A J L Pombeiro, J C Jeffery, C J Pickett, R L Richards *J. Organomet. Chem.*, 1984, **277** C7
40. H Umland, U Behrens *J. Organomet. Chem.*, 1984, **273** 39
41. M I Bruce, C Dean, D N Duffy, et al. *J. Organomet. Chem.*, 1985, **295** C40
42. M I Bruce, M G Humphrey, G A Koutsantonis, B K Nicholson *J. Organomet. Chem.*, 1985, **296** C47
43. L A Oro, M A Ciriano, M Campo, et al. *J. Organomet. Chem.*, 1985, **289** 117
44. M I Bruce, M G Humphrey, M R Snow, E R T Tiekink *J. Organomet. Chem.*, 1986, **314** 213
45. N E Kolobova, O S Zhvanko, L L Ivanov, et al. *J. Organomet. Chem.*, 1986, **302** 235
46. D B Pourreau, G L Geoffroy, A L Rheingold, S J Geib *Organometallics*, 1986, **5** 1337
47. M I Bruce, G A Koutsantonis, M J Liddell, B K Nicholson *J. Organomet. Chem.*, 1987, **320** 217
48. J P Selegue *J. Am. Chem. Soc.*, 1983, **105** 5921
49. E O Fischer, H-J Kalder, A Frank, et al. *Angew. Chem.*, 1976, **88** 683
50. H Berke, P Härter, G Huttner, J von Seyerl *J. Organomet. Chem.*, 1981, **219** 317
51. H Berke, G Huttner, J von Seyerl *Z. Naturforsch. B*, 1981, **36** 1277
52. J P Selegue *Organometallics*, 1982, **1** 217
53. H Berke, U Größmann, G Huttner, L Zsolnai *Chem. Ber.*, **1984, 117** 3432
54. H Berke, G Huttner, J von Seyerl *J. Organomet. Chem.*, 1981, **218** 193
55. P Friedrich, G Besl, E O Fischer *J. Organomet. Chem.*, 1977, **139** C68
56. N E Kolobova, L L Ivanov, O S Zhvanko, et al. *J. Organomet. Chem.*, 1984, **262** 39
57. H Berke *Chem. Ber.*, 1980, **113** 1370
58. S Abbott, S G Davies, P Warner *J. Organomet. Chem.*, 1983, **246** C65
59. A A Ioganson, A B Antonova, V A Trukhacheva, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 56
60. V A Trukhacheva, G V Burmakina, G R Gul'bis, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 200
61. H Berke, P Härter *Angew. Chem.*, 1980, **92** 224
62. H Berke *J. Organomet. Chem.*, 1980, **185** 75
63. N E Kolobova, L L Ivanov, O S Zhvanko, et al. *J. Organomet. Chem.*, 1982, **228** 265
64. R E Colborn, D L Davies, A F Dyke, et al. *J. Chem. Soc., Dalton Trans.*, 1983, 2661
65. W A Herrmann, C Weber, M L Ziegler, O Serhadli *J. Organomet. Chem.*, 1985, **297** 245
66. E N Jacobsen, R G Bergman *J. Am. Chem. Soc.*, 1985, **107** 2023
67. J M Boncella, M L H Green, D O'Hare *J. Chem. Soc., Chem. Commun.*, 1986, 618
68. J M Boncella, M L H Green *J. Organomet. Chem.*, 1987, **325** 217
69. W A Herrmann, C Weber *J. Organomet. Chem.*, 1985, **282** C31
70. H Werner, F J Garcia Alonso, H Otto, et al. *J. Organomet. Chem.*, 1985, **289** C5
71. N E Kolobova, L L Ivanov, O S Zhvanko, et al. *J. Organomet. Chem.*, 1985, **279** 419
72. J R Shapley, J T Park, M R Churchill, et al. *J. Am. Chem. Soc.*, 1984, **106** 1144
73. C P Casey, M S Konings, K J Haller *J. Organomet. Chem.*, 1986, **301** C55
74. M G Richmond, J K Kochi *Organometallics*, 1987, **6** 777
75. A B Antonova, A A Ioganson, S V Kovalenko, et al. *Zh. Obshch. Khim.*, 1988, **58** 1173
76. G G Aleksandrov, A V Antonova, N E Kolobova, Yu T Struchkov *Koord. Khim.*, 1976, **2** 1561
77. H Berke, P Härter, G Huttner, L Zsolnai *Chem. Ber.*, 1982, **115** 695
78. H Berke, P Härter, G Huttner, L Zsolnai *Chem. Ber.*, 1984, **117** 3423
79. A B Antonova, S v Kovalenko, E D Korniyets, et al. *Inorg. Chim. Acta*, 1985, **105** 153
80. P Hofmann *Angew. Chem., Int. Ed. Engl.*, 1979, **18** 554
81. D C Calabro, D L Lichtenberger, W A Herrmann *J. Am. Chem. Soc.*, 1981, **103** 6852
82. E Delgado, J C Jeffery, F G A Stone *J. Chem. Soc., Dalton Trans.*, 1986, 2105
83. S Aime, A J Deeming, M B Hursthouse, J D J Backer-Dirks *J. Chem. Soc., Dalton Trans.*, 1982, 1625
84. W Bernhardt, H Vahrenkamp *Angew. Chem., Int. Ed. Engl.*, 1984, **23** 141
85. A A Koridze, O A Kizas, N E Kolobova, et al. *J. Chem. Soc., Chem. Commun.*, 1984, 1158
86. R Aumann, H Heinen, C Krüger, R Goddard *Chem. Ber.*, 1986, **119** 401
87. W E Carroll, M Green, A G Orpen, et al. *J. Chem. Soc., Dalton Trans.*, 1986, 1021
88. E Roland, W Bernhardt, H Vahrenkamp *Chem. Ber.*, 1985, **118** 2858
89. J Evans, G S McNulty *J. Chem. Soc., Dalton Trans.*, 1983, 639
90. B E R Schilling, R Hoffmann *J. Am. Chem. Soc.*, 1978, **100** 6274
91. B E R Schilling, R Hoffmann *J. Am. Chem. Soc.*, 1979, **101** 3456
92. J W Kolis, E M Holt, M Drezdzon, et al. *J. Am. Chem. Soc.*, 1982, **104** 6134
93. M J Sallor, D F Shriver *Organometallics*, 1985, **4** 1476
94. J R Shapley, D S Strickland, G M St George, et al. *Organometallics*, 1983, **2** 185
95. A M Crespi, D F Shriver *Organometallics*, 1986, **5** 1750
96. J W Kolis, E M Holt, D F Shriver *J. Am. Chem. Soc.*, 1983, **105** 7307
97. A J Carty, S A MacLaughlin, N J Taylor *J. Chem. Soc., Chem. Commun.*, 1981, 476
98. P Brun, G M Dawkins, M Green, et al. *J. Chem. Soc., Chem. Commun.*, 1981, 966
99. P Brun, G M Dawkins, M Green, et al. *J. Chem. Soc., Dalton Trans.*, 1983, 1357
100. M I Bruce, B W Skelton, A H White, M L Williams *J. Chem. Soc., Chem. Commun.*, 1985, 744
101. R D Adams, S Wang *Organometallics*, 1985, **4** 1902
102. J G Jeffrey, B F G Johnson, J Lewis, et al. *J. Chem. Soc., Chem. Commun.*, 1986, 318
103. E Sappa, A Tiripicchio, M Tiripicchio Camellini *J. Organomet. Chem.*, 1983, **246** 287
104. S V Kovalenko, A B Antonova, N A Deikhina, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 2870
105. J Evans, G S McNulty *J. Chem. Soc., Dalton Trans.*, 1984, 79
106. H Berke, P Härter, G Huttner, L Zsolnai *Z. Naturforsch. B*, 1981, **36** 929

107. J S Adams, M Cunningham, M W Whiteley *J. Organomet. Chem.*, 1985, **293** C13
108. K R Birdwhistell, T L Tonker, J L Templeton *J. Am. Chem. Soc.*, 1985, **107** 4474
109. C von Schnering, T Albiez, W Bernhardt, H Vahrenkamp *Angew. Chem.*, 1986, **98** 474
110. USSR P. 1 113 383; *Byul. Izobret.*, 1984(34), 63
111. N E Kolobova, O M Khitrova, A B Antonova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 1124
112. G Consiglio, F Bangerter, C Daurpin, et al. *Organometallics*, 1984, **3** 1446
113. E Roland, H Vahrenkamp *J. Mol. Catal.*, 1983, **21** 233
114. P M Treichel, D A Komar *Inorg. Chim. Acta*, 1980, **42** 277
115. K Ouzzine, H LeBozec, P H Dixneuf *J. Organomet. Chem.*, 1986, **317** C25
116. G Consiglio, F Morandini, G F Ciani, A Sironi *Organometallics*, 1986, **5** 1976
117. I T Horváth, G Pályi, L Markó, G Andreetti *J. Chem. Soc., Chem. Commun.*, 1979, 1054
118. Y N Al-Obaidy, M Green, N D White, G E Taylor *J. Chem. Soc., Dalton Trans.*, 1982, 319
119. H Werner *Angew. Chem. Int. Ed. Engl.*, 1983, **22** 927
120. H Werner, J Wolf, R Zolk, U Schubert *Angew. Chem. Int. Ed. Engl.*, 1983, **22** 981
121. M Rashidi, R J Puddephat *J. Am. Chem. Soc.*, 1986, **108** 7111
122. R B King, M S Saran *J. Am. Chem. Soc.*, 1973, **95** 1811
123. J Lewis, B F G Johnson *Pure Appl. Chem.*, 1975, **44** 43
124. A A Koridze, O A Kizas, N E Kolobova, et al. *J. Organomet. Chem.*, 1984, **265** C33
125. A S Batsanov, V G Andrianov, Yu T Struchkov, et al. *J. Organomet. Chem.*, 1987, **329** 401
126. E N Jacobsen, R G Bergman *Organometallics*, 1984, **3** 329
127. D F Marten, E V Dehmlow, D J Hanlon, et al. *J. Am. Chem. Soc.*, 1981, **103** 4940
128. M Green, A G Orpen, C J Schaverien *J. Chem. Soc., Chem. Commun.*, 1984, 37
129. I Bkouche-Waksman, J S Ricci, T F Koetzle, et al. *Inorg. Chem.*, 1985, **24** 1492
130. A Mayr, K C Schaefer, E Y Huang *J. Am. Chem. Soc.*, 1984, **106** 1517
131. K R Birdwhistell, J L Templeton *Organometallics*, 1985, **4** 2062
132. D L Reger, C A Swift *Organometallics*, 1984, **3** 876
133. M I Bruce, M G Humphrey, M J Liddell *J. Organomet. Chem.*, 1987, **321** 91
134. E Boyar, A J Deeming, S E Kabir *J. Chem. Soc, Chem. Commun.*, 1986, 577
135. A A Koridze, O A Kizas, N E Kolobova, P V Petrovskii *J. Organomet. Chem.*, 1986, **302** 413
136. A A Koridze, O A Kizas, N E Kolobova, P V Petrovskii *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1630
137. R B King, M S Saran *J. Am. Chem. Soc.*, 1973, **95** 1817
138. J Ros, R Mathieu *Organometallics*, 1983, **2** 771
139. A J Deeming, S Hasso, M Underhill *J. Chem. Soc., Dalton Trans.*, 1975, 1614
140. A A Koridze, O A Kizas, P V Petrovskii, et al. *Dokl. Akad. Nauk SSSR*, 1987, **293** 117
141. C J Cooksey, A J Deeming, I P Rothwell *J. Chem. Soc., Dalton Trans.*, 1981, 1718 1528
142. R Weinand, H Werner *J. Chem. Soc., Chem. Commun.*, 1985, 1145
143. B E Boland-Lussier, M R Churchill, R P Hughes, A L Rheingold *Organometallics*, 1982, **1** 628
144. R G Beevor, M J Freeman, M Green, et al. *J. Chem. Soc., Chem. Commun.*, 1985, 68
145. M Green *J. Organomet. Chem.*, 1986, **300** 93
146. S C Kao, P P Y Lu, R Pettit *Organometallics*, 1982, **1** 911
147. C P Casey, P J Fagan, W H Miles, S R Marder *J. Mol. Catal.*, 1983, **21** 173
148. C P Casey, S R Marder, P J Fagan *J. Am. Chem. Soc.*, 1983, **105** 7197
149. C P Casey, M W Meszaros, S R Marder, P J Fagan *J. Am. Chem. Soc.*, 1984, **106** 3680
150. M Lourdichi, R Mathieu *Nouv. J. Chim.*, 1982, **6** 231
151. M Lourdichi, R Mathieu *Organometallics*, 1986, **5** 2067
152. J Suades, R Mathieu *J. Organometal. Chem.*, 1986, **312** 335
153. M Cooke, D L Davies, J E Guerchais, et al. *J. Chem. Soc., Chem. Commun.*, 1981, 862
154. N G Connelly, N J Forrow, S A R Knox, et al. *J. Chem. Soc., Chem. Commun.*, 1985, 16
155. W R Roper, J M Waters, L J Wright, F van Meurs *J. Organomet. Chem.*, 1980, **201** C27
156. A Höhn, H Werner *Angew. Chem.*, 1986, **98** 474
157. G M Dawkins, M Green, J C Jeffery, C Sambale, G F A Stone *J. Chem. Soc., Dalton Trans.*, 1983, 499
158. R Korswagen, R Alt, D Speth, M Ziegler *Angew. Chem., Int. Ed. Engl.*, 1981, **20** 1049
159. C P Casey, S R Marder *Organometallics*, 1985, **4** 411
160. C P Casey, M W Meszaros, P J Fagan, et al. *J. Am. Chem. Soc.*, 1986, **108** 4043
161. C P Casey, M W Meszaros, S R Marder, et al. *Organometallics*, 1986, **5** 1873
162. C P Casey, M A Gohdes, M W Meszaros *Organometallics*, 1986, **5** 196
163. C P Casey, M W Meszaros, P J Fagan, et al. *J. Am. Chem. Soc.*, 1986, **108** 4053
164. B P Gracey, S A R Knox, K A Macpherson, et al. *J. Organomet. Chem.*, 1984, **272** C45
165. N J Forrow, S A R Knox *J. Chem. Soc., Chem. Commun.*, 1984, 679
166. C R Eady, B F G Johnson, J Lewis *J. Chem. Soc., Dalton Trans.*, 1977, 477
167. J S Hokmgren, J R Shapley *Organometallics*, 1985, **4** 793
168. L P Yur'eva *Tipy Metalloorganicheskikh Soedinenii Perekhodnykh Metallov* (The Types of Organometallic Compounds of Transition Metals) (Edited by A N Nesmeyanov, K A Kocheshkov), Izd. Nauka, Moscow, 1975, vol. 1, p. 384 [Methods of Organoelemental Chemistry (Translated into Russian)]
169. A N Nesmeyanov, N E Kolobova, A B Antonova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 859
170. P B Winston, S J N Burgmayer, T L Tonker, J L Templeton *Organometallics*, 1986, **5** 1707
171. W Bernhardt, C von Schnering, H Vahrenkamp *Angew. Chem.*, 1986, **98** 285
172. D L Davies, A F Dyke, A Endesfelder, et al. *J. Organomet. Chem.*, 1980, **198** C43
173. S A R Knox *Pure Appl. Chem.*, 1984, **56** 81
174. D Mansuy, M Lange, J-C Chottard *J. Am. Chem. Soc.*, 1978, **100** 3213
175. D Mansuy *Pure Appl. Chem.*, 1980, **52** 681

176. Y W Chan, M W Renner, A L Balch *Organometallics*, 1983, **2** 1888
177. C E Castro, R S Wade *J. Org. Chem.*, 1985, **50** 5342
178. D Mansuy, J-P Battioni, D K Lavallee, et al. *Inorg. Chem.*, 1988, **27** 1052
179. G Henrici-Olive, S Olive *The Chemistry of the Catalysed Hydrogenation of Carbon Monoxide* (Translated into Russian), Izd. Mir, Moscow, 1987, 248 pp
180. V F Sizoi, Yu S Nekrasov, Yu N Sukharev, et al. *J. Organomet. Chem.*, 1978, **162** 171
181. M I Bruce, A G Swincer, R C Wallis *J. Organomet. Chem,* 1979, **171** C5
182. M Castiglioni, R Giordano, E Sappa *J. Organomet. Chem.*, 1984, **275** 119
183. L J Farrugia, A D Miles, F G A Stone *J. Chem. Soc., Dalton Trans.*, 1985, 2437
184. V G Andrianov, Yu T Struchkov, N E Kolobova, et al. *J. Organomet. Chem.*, 1976, **122** C33
185. N E Kolobova, L L Ivanov, O S Zhvanko *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 956
186. N E Kolobova, L L Ivanov, O S Zhvanko, P V Petrovskii *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 432
187. N E Kolobova, L L Ivanov, O S Zhvanko *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1435
188. A B Antonova, S V Kovalenko, E D Korniyets, et al. *Inorg. Chim. Acta*, 1985, **96** 1
189. H Otto, F J Garcia Alonso, H Werner *J. Organomet. Chem.*, 1986, **306** C13
190. A B Antonova, S V Kovalenko, E D Korniyets, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 1146
191. A B Antonova, S V Kovalenko, E D Korniyets, et al. *J. Organomet. Chem.*, 1984, **267** 299
192. A B Antonova, S V Kovalenko, N A Deikhina, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2827
193. S V Kovalenko, A B Antonova, N A Deikhina, A A Ioganson *IV Vsesoyuznaya Konferentsiya po Khimii Karbenov. Tezisy Dokladov* (IV All-Union Conference on the Chemistry of Carbenes: Abstracts of Reports), Izd. Nauka, Moscow, 1987, p. 93
194. S Attali, R Mathieu *J. Organomet. Chem.*, 1985, **291** 205
195. H Werner, J Wolf, G Müller, G Krüger *Angew. Chem.*, 1984, **96** 421
196. H Werner, A Höhn, R Weinand *J. Organomet. Chem.*, 1986, **299** C15
197. E L Hoel, G B Ansell, S Leta *Organometallics*, 1984, **3** 1633
198. C P Casey, E A Austin *Organometallics*, 1986, **5** 584
199. E L Hoel, G B Ansell, S Leta *Organometallics*, 1986, **5** 585
200. E L Hoel *Organometallics*, 1986, **5** 587
201. N E Kolobova, T V Rozantseva, Yu T Struchkov, et al. *J. Organomet. Chem.*, 1985, **292** 247
202. K Weiß, E O Fischer, J Müller *Chem. Ber.*, 1974, **107** 3548
203. A G M Barrett, C P Brock, M A Sturgess *Organometallics*, 1985, **4** 1903
204. M Etienne, J E Guerchais *J. Organomet. Chem.*, 1986, **314** C81
205. N E Kolobova, L L Ivanov, O S Zhvanko, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 2632
206. C P Casey, S R Marder, A L Rheingold *Organometallics*, 1985, **4** 762
207. D L Davies, J A K Howard, S A R Knox, et al. *J. Organomet. Chem.*, 1985, **279** C37
208. C P Casey, M S Konings, R E Palermo, R E Colborn *J. Am. Chem. Soc.*, 1985, **107** 5296
209. N M Doherty, M J Fildes, N J Forrow, et al. *J. Chem. Soc., Chem. Commun.*, 1986, 1355
210. A J Deeming, S Hasso, M Underhill, et al. *J. Chem. Soc., Chem. Commun.*, 1974, 807
211. T K Dutta, J C Vites, T P Fehlner *Organometallics*, 1986, **5** 385
212. A J Deeming, M Underhill *J. Chem. Soc., Dalton Trans.*, 1974, 1415
213. M I Bruce, D N Duffy, M G Humphrey, A G Swincer *J. Organomet. Chem.*, 1985, **282** 383
214. A Parlier, H Rudler *J. Chem. Soc., Chem. Commun.*, 1986, 514
215. N E Kolobova, L L Ivanov, O M Khitrova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 1436
216. N E Kolobova, L L Ivanov, O S Zhvanko, et al. *J. Orgnomet. Chem.*, 1984, **265** 271
217. N E Kolobova, O M Khitrova, L L Ivanov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 188
218. N E Kolobova, O M Khitrova, A S Batsanov, Yu T Struchkov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 2057
219. A B Antonova, S V Kovalenko, E D Korniyets, A A Ioganson *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1667
220. A B Antonova, S V Kovalenko, E D Korniyets, et al. *J. Organomet. Chem.*, 1983, **244** 35
221. A B Antonova, S V Kovalenko, R A Cherkasov, et al. *Zh. Obshch. Khim.*, 1987, **57** 1030
222. J S Bradley, G W Ansell, E W Hill *J. Am. Chem. Soc.*, 1979, **101** 7417
223. L E McCandlish *J. Catal.*, 1983, **83** 362
224. A A Ioganson, A B Antonova *IV Mezhdunarodnyi Simpozium po Gomogennomu Katalizu: Tezisy Dokladov* (IV International Symposium on Homogeneous Catalysis: Abstracts of Reports), Izd. Nauka, Leningrad, 1984, Vol. 4, p. 69
225. H Yamazaki *J. Chem. Soc., Chem. Commun.*, 1976, 841
226. V A Legasov, A L Buchachenko *Usp. Khim.*, 1986, **55**(12) 1949 [English translation in *Russ. Chem. Rev.*, 1986(12)]
227. G W Parshall *Organometallics*, 1987, **6** 687
228. A G M Barrett, M A Sturgess *Tetrahedron Lett.*, 1986, **27** 3811
229. A G M Barrett, M A Sturgess *J. Org. Chem.*, 1987, **52** 3940
230. P M Meitlis *Zh. Vses. Khim. Ova im. Mendeleeva*, 1972, **17** 403
231. R B King, M S Saran *J. Chem. Soc., Chem. Commun.*, 1974, 851
232. USSR P. 1 077 896; *Byull. Izobret.*, 1984(9), 61
233. T Albiez, W Bernhardt, C von Schnering, et al. *Chem. Ber.*, 1987, **120** 141
234. T Albiez, H Vahrenkamp *Angew. Chem., Int. Ed. Engl.*, 1987, **26** 572
235. J S Adams, C Bitcon, J R Brown, et al. *J. Chem. Soc., Dalton Trans.*, 1987, 3049
236. A A Aradi, F-W Grevels, C Krüger, E Raabe *Organometallics*, 1988, **7** 812
237. M F D'Agostino, M Mlekuz, M J McGlinchey *J. Organomet. Chem.*, 1988, **345** 371
238. H G Alt, H E Engelhardt, E Steinlein, R D Rogers *J. Organomet.*, 1988, **344** 321
239. A G M Barrett, N E Carpenter *Organometallics*, 1987, **6** 2249
240. H Berke *Org. Synth.*, 1986, **3** 239
241. C Bitcon, M W Whiteley *J. Organomet. Chem.*, 1987, **336** 385
242. M I Bruce *Pure Appl. Chem.*, 1986, **58** 553
243. M I Bruce, M G Humphrey, G A Koutsantonis, M J Liddell *J. Organomet. Chem.*, 1987, **326** 247

244. D H Berry, R Eisenberg *Organometallics*, 1987, **6** 1796
245. R G Beevor, M Green, A G Orpen, D Williams *J. Chem. Soc., Dalton Trans.*, 1987, 1319
246. R Birk, H Berke, G Huttner, L Zsolnai *Chem. Ber.*, 1988, **121** 471
247. P L Bogdan, M Sabat, S A Sunshine, et al. *Inorg. Chem.*, 1988, **27** 1904
248. H Bantel, W Bernhardt, A K Powell, H Vahrenkamp *Chem. Ber.*, 1988, **121** 1247
249. G Consiglio, F Morandini *Inorg. Chim. Acta*, 1987, **127** 79
250. G Consiglio, F Morandini *Chem. Rev.*, 1987, **87** 761
251. G Consiglio, R Schwab, F Morandini *J. Chem. Soc., Chem. Commun.*, 1988, 25
252. C P Casey, L K Woo *J. Organomet. Chem.*, 1987, **328** 161
253. C P Casey, E A Austin, A L Rheingold *Organometallics*, 1987, **6** 2157
254. C P Casey, M S Konings, S R Marder *J. Organomet. Chem.*, 1988, **345** 125
255. C P Casey, M S Konings, S R Marder *Polyhedron*, 1988, **7** 881
256. A M Crespi, M J Went, S S Sunshine, D F Shriver *Organometallics*, 1988, **7** 214
257. T K Dutta, X Meng, J C Vites, T P Fehlner *Organometallics*, 1987, **6** 2191
258. M Dziallas, H Werner *J. Organomet. Chem.*, 1987, **333** C29
259. J A Davies, A A Pinkerton, R Syed, M Vilmer *J. Chem. Soc., Chem. Commun.*, 1988, 47
260. S F T Froom, M Green, K R Nagle, D J Williams *J. Chem. Soc., Chem. Commun.*, 1987, 1305
261. X L R Fontaine, S J Higgins, B L Shaw, et al. *J. Chem. Soc., Dalton Trans.*, 1987, 1501
262. X L R Fontaine, S J Higgins, B L Shaw *J. Chem. Soc., Dalton Trans.*, 1988, 1179
263. N J Grist, G Hogarth, S A R Knox, et al. *J. Chem. Soc., Chem. Commun.*, 1988, 673
264. A S Gamble, K R Birdwhistell, J L Templeton *Organometallics*, 1988, **7** 1046
265. A Höhn, H Otto, M Dziallas, H Werner *J. Chem. Soc., Chem. Commun.*, 1987, 852
266. A Höhn, H Werner *Chem. Ber.*, 1988, **121** 881
267. J A Hriljac, E M Holt, D F Shriver *Inorg. Chem.*, 1987, **26** 2943
268. R S Iger, J P Selegue *J. Am. Chem. Soc.*, 1987, **109** 910
269. J C Jeffery, M J Parrott, U Pyell, F G A Stone *J. Chem. Soc., Dalton Trans.*, 1988, 1121
270. J Krause, D-Y Jan, S G Shore *J. Am. Chem. Soc.*, 1987, **109** 4416
271. N E Kolobova, V V Derunov, O M Khitrova, et al. *Metalloorg. Khim.*, 1988, **1** 400 [English translation in *Organomet. Chem. USSR* 1988(1)]
272. N E Kolobova, V V Derunov, O S Shilova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 852
273. D R Senn, A Wong, A T Patton, et al. *J. Am. Chem. Soc.*, 1988, **110** 6096
274. U Schubert, J Grönen *Organometallics*, 1987, **6** 2458
275. D Seyferth, J B Hoke, M Cowie, A D Hunter *J. Organomet. Chem.*, 1988, **346** 91
276. M J Went, M Sailor, P L Bogdan, et al. *J. Am. Chem. Soc.*, 1987, **109** 6023
277. H Werner, J Wolf, F J Garcia Alonso, et al. *J. Organomet. Chem.*, 1987, **336** 397
278. J Wolf, H Werner *J. Organomet. Chem.*, 1987, **336** 413
279. J Wolf, R Zolk, U Schubert, H Werner *J. Organomet. Chem.*, 1988, **340** 161
280. H Werner, J Wolf, G Müller, C Krüger *J. Organomet. Chem.*, 1988, **342** 381

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Carbene methods for the introduction of acyl and acylmethyl groups into organic molecules

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ABSTRACT. A systematic account is given of data on the reactions involving the insertion of dihalogeno-, keto-, and alkoxycarbonyl-carbenes in carbon–hydrogen and carbon–heteroatom bonds as well as reactions involving the conversion of alkenes into cyclopropane derivatives followed by ring opening, leading to the introduction of acyl, acylmethyl, and alkoxycarbonylmethyl groups into organic substrates.†

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I. Introduction

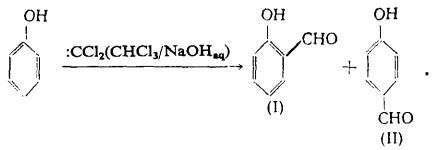
Many important methods for the synthesis of organic compounds with functional group substituents are based on the creation of a carbon–carbon bond as a result of the introduction of acyl or acylmethyl groups into an organic substrate.[1] Together with the traditional methods for the introduction of these fragments into organic molecules by means of reactions with participation of anions, radicals, and cations, methods based on the use for such purposes of carbene reactions have been acquiring recently increasing synthetic importance. The wide availability of dihalogeno-, keto-, and alkoxycarbonyl-carbenes and their specific reactivity in relation to carbon–hydrogen and carbon–heteroatom bonds as well as carbon–carbon multiple bonds constitute a basis for the effective employment of these highly reactive species as agents transferring acyl and acylmethyl groups. In the present review, an attempt is made to give a systematic account of the literature data on this question, individual aspects of which have also been examined in monographs[2,3] and other reviews.[4–12]

† This article was intended for publication in issue No. 7 (1989) of this journal, which was devoted to the chemistry of carbenes.

II. Insertion in carbon–hydrogen and carbon–heteroatom bonds

1. The Reimer–Tiemann reaction

Despite the potentially great possibilities of the method for the introduction of acyl groups into organic substrates by the insertion of heterosubstituted carbenes in carbon–hydrogen or carbon–heteroatom bonds, they remain little investigated at the present time. However, the Reimer–Tiemann reaction is an exception.[13,14] In its classical version, the yield of salicylaldehyde (I) is 20–25% and that of 4-hydroxybenzaldehyde (II) is 8–10%. Quaternary ammonium salts do not exhibit activity as phase-transfer catalysts in this reaction, whilst in the presence of catalytic amounts of tertiary amines the yield of salicylaldehyde increases to 49–65% while that of compound (II) changes only slightly:[15]



In the presence of β-cyclodextrin, dichlorocarbene attacks exclusively the *para*-position.[16] Then an essential condition for the attainment of high process selectivity is the maintenance of a chloroform : cyclodextrin molar ratio less than unity throughout the reaction. The catalytic action of cyclodextrin can be explained by the formation of its ternary complex with chloroform and phenol in which spatial proximity between the *para*-position of the aromatic ring and dichlorocarbene, formed in a cyclodextrin cage as a result of the reaction of chloroform with the hydroxide ion, is ensured.[17]

The selectivity of the Reimer–Tiemann reaction also increases after the addition of poly(ethylene glycol) to the reaction mixture as a result of the formation, according to Neumann and Sasson,[18] of its complex with the phenoxide anion in which the *ortho*-positions in the benzene ring are sterically blocked.

2. Insertion of keto- and alkoxycarbonyl-carbenes in carbon–hydrogen bonds

The introduction of acylmethyl and alkoxycarbonylmethyl groups into organic substrates via the insertion of keto- and alkoxycarbonyl-carbenes, generated from the corresponding diazocarbonyl compounds, in carbon–hydrogen bonds is an important synthetic method, to the development of which numerous studies have been devoted (see the relevant reviews[7,9,19,20]). The highest yields of the products

are then produced when rhodium carboxylates are used as catalysts:[21–24]

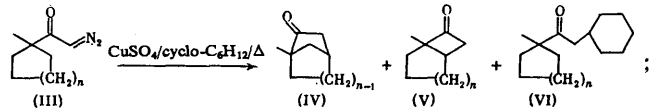
$$R-H+N_2CHCOOC_2H_5 \xrightarrow{Rh(OCOCF_3)_2/22\,^\circ C} \underset{29-92\%}{R-CH_2COOC_2H_5} + N_2,$$

$R = C_5-C_8$ alkyl, cycloalkyl.

The synthetic value of the method is limited owing to the low regioselectivity of the reaction and also the necessity to use a large excess of the alkane to prevent the oligomerisation of the carbene and the poisoning of the catalyst.[22]

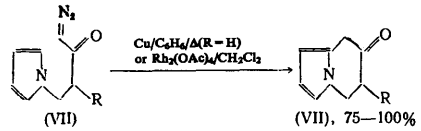
The insertion of keto- and alkoxycarbonyl-carbenes in C–H bonds of alkenes, alkynes, arenes, and heteroarenes usually competes with processes involving cyclo-addition to multiple bonds.[7,9,20,25] Diethyl diazomalonate and α-diazoacetophenone are also capable of affording the products of the insertion of the corresponding carbenes into the allyl C–H bonds of vinyl ethers.[26]

In contrast to intermolecular reactions in which ketocarbenes are inserted in non-activated C–H bonds, intramolecular processes of this kind are frequently characterised by a higher regioselectivity.[25,27–33] Thus the thermal decomposition of diazomethyl ketones (III) in cyclohexane over anhydrous copper sulphate affords mixtures of cyclopentanones (IV), cyclobutanones (V), and the products (VI) of the insertion of the ketocarbene in the solvent:[27]



$n = 3$ (a), 2 (b), 1 (c), 0 (d).

With the exception of the reaction of 1-diazoacetyl-1-methylcyclobutane (IIId), derivatives of cyclopentanone (IV) are the main products [the yields are 50–75% of (IVa), 58% of (IVb), 19% of (IVc), and 1% of (IVd)] for a cyclopentanone : cyclobutaneone = 8–16 : 1 ratio; the products of insertion in the C–H bonds of cyclohexane (VI) are formed in an insignificant amount. The diazoketone (IIId) is converted under these conditions predominantly into compound (VId) (yield 29%). The authors demonstrated the possibility of using this method for the construction of the cyclopentane ring in steroids.[27] On the other hand, the reactions involving the intramolecular insertion of ketocarbenes in non-activated C–H bonds in conformationally less mobile systems proceed with a low regioselectivity and as a rule lead to products in low yields.[27] This method has been used effectively for the synthesis of bicycloanones containing the indole fragment.[34,35,41] Thus the decomposition of 1-diazo-4-(1-pyrrolyl)-2-butanone (VII) in the presence of copper powder leads to a quantitative yield of dihydroindolizinone (VIII):[34]



R = H (a), C_6H_5 (b), 4-$CH_3OC_6H_4$ (c); 4-$NO_2C_6H_4$ (d).

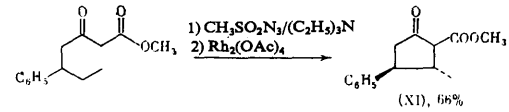
In the case of compounds (VIIb–d), the corresponding indanones are formed in 14–22% yield as a result of the competing insertion of the ketocarbene in the benzene ring.

In view of the important role which β-dicarbonyl compounds play in organic synthesis and the possibility of their ready conversion into α-diazo-derivatives,[35] the results of studies[25,28,30,32,33,36,37] on the intramolecular insertion of α-acetyl-substituted alkoxycarbonylcarbenes in C–H bonds have atttracted attention. In contrast to the corresponding α-diazoketones (see above), in this case the conformationally mobile compounds (IX) exhibit a much more marked tendency towards intramolecular cyclisation with formation of 2-methoxycarbonylcyclopentanones (X):[28]

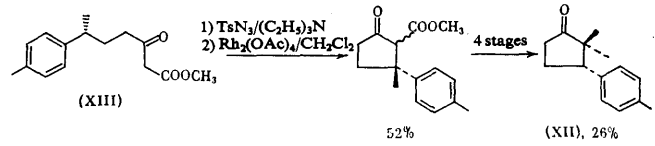


$R^1 = CH_3$, iso-C_3H_7, C_8H_{17}, $CH=CH_2$, $CH_2CH=C(CH_3)_2$;
R^2, $R^3 = H$, CH_3.

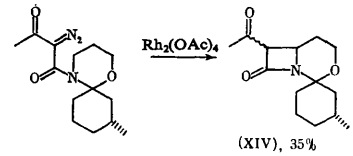
Detailed study of the dependence of the regioselectivity of this reaction on the electronic and steric effects of the substituents[28,29] led to the conclusion that the reactivity decreases in the following sequence in relation to the carbene centre: tertiary > secondary > primary C–H bonds. The allyl and benzyl C–H bonds are less reactive. The reactions are also characterised by a high degree of diastereoselectivity.[30,33] For example, the cyclopentanone derivative (XI) with the *trans*-disposition of the phenyl and methyl substituents is formed on cyclisation of the δ-phenyl-substituted α-diazo-β-ketoester:[30]



An important advantage of this method is also the retention of the absolute configuration of the carbon atom subjected to carbene attack.[7,9,32] The effective synthesis of (+)-α-cuparenone (XII) from the chiral β-ketoester (XIII) serves as a good illustration of this:[32]



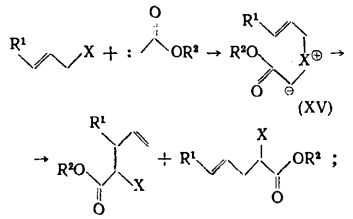
It has been found recently that the cyclisation of α-diazo-β-dicarbonyl compounds containing carbocyclic[36] and heterocyclic substituents[37] can also be used effectively for the synthesis of four-membered rings, which has been demonstrated, in particular, in relation to the synthesis of compound (XIV)—a key intermediate in the synthesis of thienamycin analogues:[37]



3. Insertion of keto- and alkoxycarbonyl-carbenes in carbon–heteroatom bonds

A specific method for the introduction of acyl and acylmethyl groups into organic substrates is also based on reactions involving the insertion of the corresponding carbenes in carbon–heteroatom bonds (see the relevant reviews[7,9,11]). Compounds containing

heterosubstituents in the allyl position relative to the multiple bond exhibit an increased tendency to undergo reactions of this kind. The generally accepted mechanism of these reactions includes the initial attack by the carbene on the heteroatom with formation of the corresponding ylide (XV), which then undergoes a [2,3]- or [1,2]-sigmatropic rearrangement:[7,8,11,38,45]

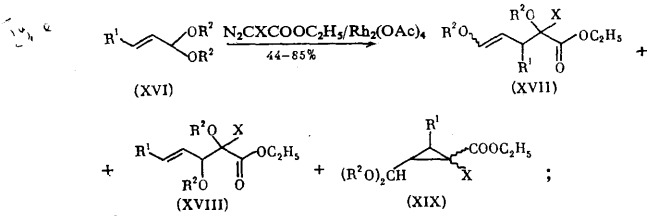


(XV)

X=Cl, Br, I, OR^3, SR^3, NR^3_2.

As in the reactions involving insertion in C–H bonds (see above), the yields of the products of the intermolecular reactions in which carbonyl-containing carbenes are inserted in carbon–heteroatom bonds are as a rule low and the conversion of the substrate into a cyclopropane derivative is frequently a competing process. It was of interest that the ratio of the insertion of cycloaddition products depends to a large extent on the conditions in the generation of the alkoxycarbonylcarbene. The decomposition of diazo-compounds by direct photolysis or under the influence of metallic catalysts leads to the preferential formation of insertion products, while photosensitised decomposition of diazo-compounds, affording a triplet carbene, gives rise to cycloaddition products. The difference in the behaviour of the carbene species is apparently caused by the inability of triplet carbene to form the corresponding ylides (XV).[7,9,11] It has also been established that the use of rhodium(II) acetate or the hexarhodium carbonyl cluster $Rh_6(CO)_{16}$ as catalysts of the decomposition of diazoacetic ester leads to the exclusive formation of the products of the [2,3]sigmatropic rearrangement in reactions with allyl iodides, aryl sulphides, and dialkylallylamines (yield 49–96%). In order to obtain similar products in the reactions with allyl bromides and chlorides, it is preferable to use copper catalysts.[38,39]

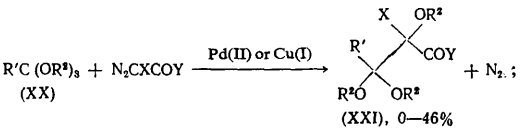
In contrast to alkyl allyl ethers, which afford products of conversion into cyclopropane derivatives in reactions with ethyl diazoacetate and dimethyl diazomalonate, the acetals (XVI) are converted into the corresponding 2,5-dialkoxy-4-alkenoates (XVII); the products of the "direct" insertion in the C–O bond [compounds (XVIII)][40,43] and of conversion into cyclopropane derivatives [compounds (XIX)] are formed only as minor components:



(XVI) (XVII) (XVIII) (XIX)

R^1 = H, C_6H_5; R^2 = CH_3, C_2H_5, $(CH_2)_2$; X = H, $COOC_2H_5$.

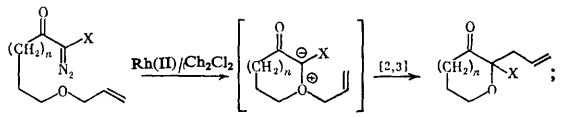
The decomposition of diazocarbonyl compounds in the presence of the orthoesters (XX) and copper (II) triflate or rhodium(II) acetate also leads to the insertion of the corresponding carbenes in the C–O bond, but the yields of the products (XXI) are in most cases low:[46]



(XX) (XXI), 0—46%

R′=H, CH_3, C_2H_5; R^2=CH_3, C_2H_5, X=H, $COOCH_3$; Y=OCH_3, OC_2H_5, C_6H_5.

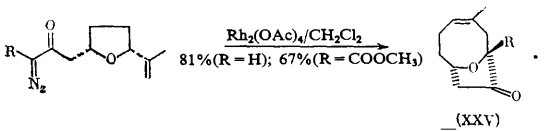
The intramolecular generation of the allyloxonium ylides (XXII) from α-diazocarbonyl compounds (XXIII) and their subsequent [2,3]sigmatropic rearrangement constitute a convenient method of synthesis of five-membered oxygen-containing heterocycles:[44,45]



(XXIII) (XXII) (XXIV)

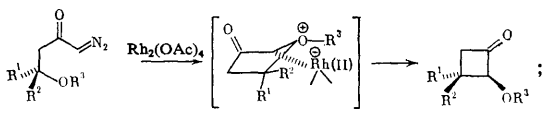
X = H, $COOCH_3$, $COOC_2H_5$; n = 0,1.

The yields of 2-substituted 3-furanones (XXIV, n = 0) are 67–95%, while an increase in the chain length by one carbon atom (n = 1) greatly increases the fraction of the products of insertion in the C–H bond.[44,45] A similar reaction has been used effectively in the synthesis of the bicyclanones (XXV) with an eight-membered oxygen-containing ring:[45]



(XXV)

The insertion of ketocarbenes in C–O bonds has also been used to synthesise the cyclobutanones (XXVI):[44]



(XXVIII) (XXVII), 45–68% (XXVI)

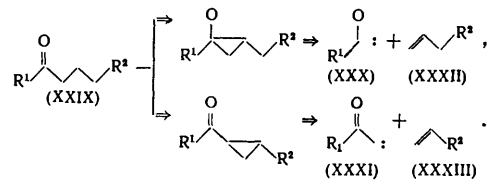
R^1 = H, CH_3; R^2 = CH=CH_2, C_6H_5; R^3 = CH_3; R^2R^3 = $(CH_2)_2$.

It is suggested[44] that the reaction proceeds via the formation of the oxonium ions (XXVII) and their subsequent decomposition with regeneration of the rhodium catalyst. It is remarkable that the cyclisation of the ketone (XXVIII, R^1=R^3=CH_3, R^2=C_6H_5) proceeds under these conditions with retention of the absolute configuration of the quaternary carbon atom.[44]

III. Conversion into cyclopropane derivatives and subsequent ring opening

Apart from the methods for the insertion of carbonyl groups via carbene reactions, examined in the previous Section, the use of the two-stage sequence of reactions involving the cycloaddition of the carbene to the alkene and the opening of the ring in the product formed also frequently proved effective. As in the insertion reactions, methods based on the conversion of alkenes into cyclopropane derivatives by dihalogeno-, keto-, and alkoxycarbonylcarbenes have the greatest synthetic importance. The retrosynthetic analysis of the formation of the carbonyl compounds (XXIX) with

the aid of this reaction leads to the carbenes (XXX) and (XXXI) and the corresponding alkenes (XXXII) and (XXXIII):

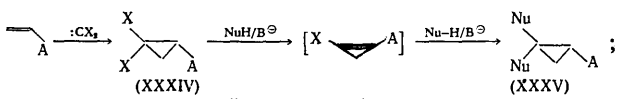


(XXIX) (XXX) (XXXII) (XXXI) (XXXIII)

Evidently, the efficiency of the formation of compound (XXIX) with the aid of the synthetic equivalents of the carbene synthons (XXX) and (XXXI) is determined not only by the efficiency of the cyclopropane formation stage but also by the possibility of the regiospecific ring opening in the cyclopropane intermediate. By virtue of the high internal strain in the three-carbon ring and the pronounced influence of substituents on the strength of its carbon–carbon bonds,[47,50] ring opening in many cyclopropane derivatives with functional group substituents can be achieved under mild conditions with high degrees of conversion and a high regioselectivity. The so called "donor–acceptor cyclopropanes", containing *p*-electron-donating and π-electron-accepting substituents in the vicinal positions, are especially promising in this respect. Their concerted activating effect weakens the C–C ring bond nearest to the two substituents and the bond undergoes ready heterolytic cleavage.[2,4,6,11,12,50]

1. Reactions of dihalogenocarbenes

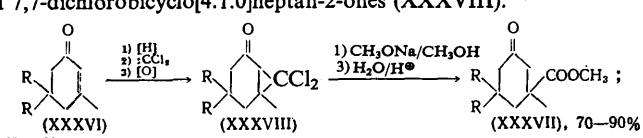
The dihalogenocarbene precursors are at the present time the most convenient synthetic equivalents of the carbene synthons (XXX) for preparative purposes. The cycloaddition of dihalogenocarbenes to alkenes has been investigated in a large number of instances and can be readily achieved experimentally in many cases.[3,51] However, reactions of the type of cyclopropyl–allyl isomerisation with the opening of the C–C ring bond located opposite to the halogen atom are characteristic of the *gem*-dihalogenocyclopropanes formed.[3,12,52] Favourable conditions for the dissociation of one of the nearest C–C ring bonds can be created by substituting the halogen atoms by *p*-electron-donating groups. Such reactions can be achieved fairly easily only between nucleophiles and *gem*-dihalogenocyclopropanes (XXXIV) containing a mobile hydrogen atom in the α-position relative to the π-electron-accepting substituent:[2,3,8,12,53–63]



(XXXIV) (XXXV)

A=CHO, COAlk, COAr, COOAlk, CON(Alk)$_2$, CN, Ar; X=F, Cl, Br; Nu=AlkO, ArO, ArS, Alk$_2$N.

The substitution of halogen atoms in compounds (XXXIV) takes place via the elimination–addition mechanism and leads to the corresponding "donor–acceptor" cyclopropanes (XXXV) or the products of their subsequent reactions with ring opening. Thus 3-substituted 2-cyclohexenones (XXXVI) can be readily converted into the corresponding 3-methoxycarbonylcyclohexanones (XXXVII) via 7,7-dichlorobicyclo[4.1.0]heptan-2-ones (XXXVIII):[56,62]

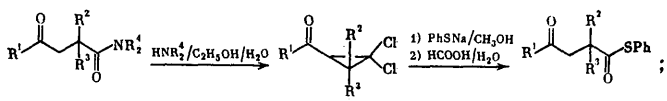


(XXXVI) (XXXVIII) (XXXVII), 70–90%

R=H, CH$_3$.

The electrophilic dichloroacarbene plays in this sequence of reactions the role of a synthetic equivalent of the nucleophilic alkoxycarbonylanion and ensures the formation of compounds (XXXVII), in which the alkoxycarbonyl group is linked to a quaternary carbon atom. Similar reactions have been observed between sodium alkoxides and monocyclic 1-acyl-2,3-dichlorocyclopropanes (XXXIX) and derivatives of 2,2-dichlorocyclopropanecarboxylic acids.[2,3,8,12,53–55,59,61]

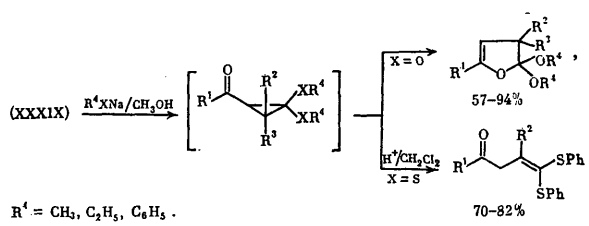
When secondary amines or sodium thiophenoxide are used as nucleophiles in reactions with acylcyclopropanes (XXXIX), it is possible to obtain high yields of the corresponding dialkylcarbamoyl derivatives (XL)[57] and phenylthiocarbonyl derivatives (XLI):[64]



(XL) (XXXIX), 60–90% (LI)

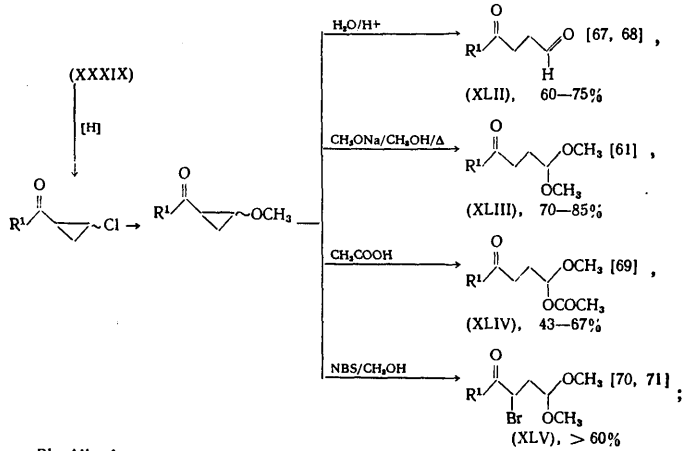
R^1, R^2, R^3 = H, Alk, Ar; R^4 = C$_2$H$_5$; R$^4_2$ = (CH$_2$)$_5$, (CH$_2$)$_2$O.

One of the advantages of this method for the introduction of acyl substituents into organic substrates is the possibility of their generation in a protected form at the stage involving the opening of the cyclopropane ring:[64,65]



R^4 = CH$_3$, C$_2$H$_5$, C$_6$H$_5$. 57–94% 70–82%

This gives rise to the possibility of modifying one of the carbonyl groups of the latent 1,4-dicarbonyl compounds and also of achieving the regiospecific introduction of additional substituents.[64,66] The latent ester group can also be modified at the stage involving the dihalogenocyclopropane intermediate, because the corresponding monohalogenocyclopropanes exhibit similar properties in relation to nucleophiles:[61,68–71]‡



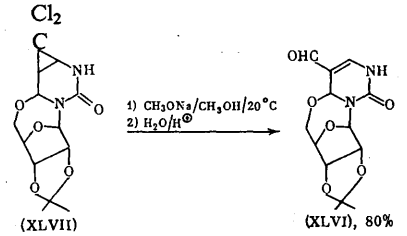
(XXXIX) (XLII), 60–75% (XLIII), 70–85% (XLIV), 43–67% (XLV), > 60%

R^1=Alk, Ar.

‡ In the formulae below and henceforth, the numerals in square brackets denote references (Ed. of Translation).

Thus the addition to a double bond of the formyl group, in the free or protected form, with formation of compounds (XLII) and (XLIII)–(XLV) respectively can be achieved with the aid of dichlorocarbene.

An interesting example of the introduction of the formyl group via the formation of *gem*-dichlorocyclopropane is also provided by the formation of the aldehyde (XLVI) on treatment of the cyclopropa[4,5]pyrimidine system (XLVII) with sodium methoxide:[72]

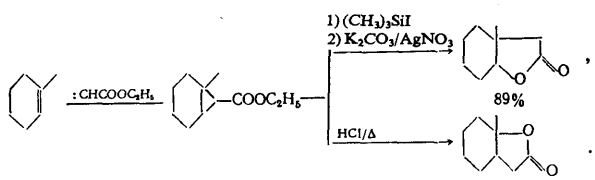


(XLVII) (XLVI), 80%

The key stages in this reaction are probably the elimination of a proton from the nitrogen atom of the pyrimidine ring under the influence of the base, the opening of the cyclopropane ring induced by the anion formed under these conditions, and the subsequent nucleophilic substitution of the chlorine atoms.[72]

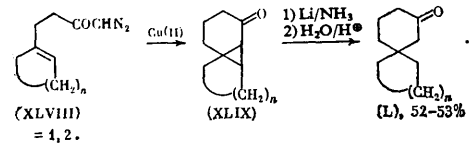
2. Reactions of keto- and alkoxycarbonyl-carbenes

The main difficulties in the introduction of functional groups into alkenes not containing *p*-electron-donating substituents at the double bond via conversion into cyclopropane derivatives by means of keto- and alkoxycarbonyl-carbenes are associated with the carrying out of the stage involving the opening of the cyclopropane ring. Although the opening of the ring in cyclopropanes having two π-electron-accepting substituents usually proceeds comparatively readily (see the relevant reviews[2,5,6]), the analogous reactions of the corresponding monosubstituted compounds require much more severe conditions and the use of acid reagents or catalysts.[2,6] It has recently been possible to overcome these difficulties in many respects by using trialkylhalogenosilanes as the electrophiles.[73,76] When the latter are allowed to react with acylcyclopropanes having different structures, the ring is as a rule opened under mild conditions and with a high regioselectivity. Examples of the successful use of these reagents are provided by the general methods for the conversion of alkenes into γ-butyrolactones[75] and α-methylene-γ-butyrolactones.[73] The formation of the lactone can then exhibit the opposite regiospecificity compared with the proton-catalysed reactions:[75]



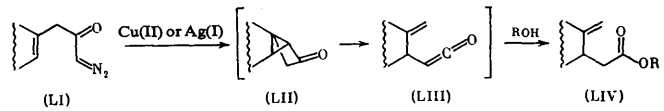
Pyridine hydrochloride[77] and acylmethanesulphonates[78,79] are also effective reagents for the opening of the ring in acylcyclopropanes.

The reactions involving the reductive cleavage of the ring in cyclopropyl ketones are likewise of considerable preparative value.[80] For example, the intramolecular conversion of monocyclic unsaturated diazoketones (XLVIII) into cyclopropane derivatives and the subsequent regioselective reduction of the tricyclic ketones (XLIX) with lithium in liquid ammonia constitutes a general method of synthesis of spiran bicyclic systems (L), which has been used successfully in the synthesis of certain natural sesquiterpenes:[80]



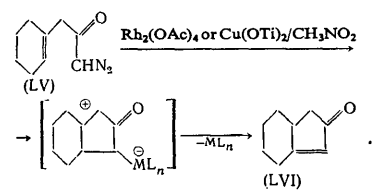
(XLVIII) (XLIX) (L), 52–53%
= 1, 2.

Acyclic and monocyclic βγ-unsaturated α′-diazoketones (LI) undergo the vinylogue Wolff rearrangement in the presence of copper(II) or silver(I) in alcohols, affording satisfactory yields of the esters of the corresponding γδ-unsaturated acids.[82,83] Evidence has been obtained showing that the skeletal rearrangement involves the initial conversion of the double bond into a cyclopropane derivative with formation of substituted bicyclo[2.1.0]pentan-2-ones (LII). The subsequent cleavage of the three-carbon ring leads to the substituted ketens (LIII) and, after the addition of an alcohol, to the final products (LIV):[83]



(LI) (LII) (LIII) (LIV)

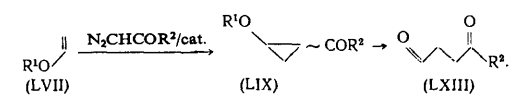
On the other hand, in the absence of protic solvents, the decomposition of the diazoketone (LV) by copper(II) and rhodium(II) leads to the corresponding bicyclic ketone (LVI), which the authors believe to proceed via the stage involving the intramolecular addition of the electrophilic metallocarbene complex to the double bond:[46]



(LVI)

$Cu(OTf)_2$ = copper(II) trifluoromethanesulphonate.

The introduction of functional group substituents into the enol ethers (LVII) by diazocarbonyl compounds, leading to 1,4-dicarbonyl compounds (LVIII) and their derivatives (important intermediates in the synthesis of five-membered carbocycles and heterocycles), is of great preparative value:

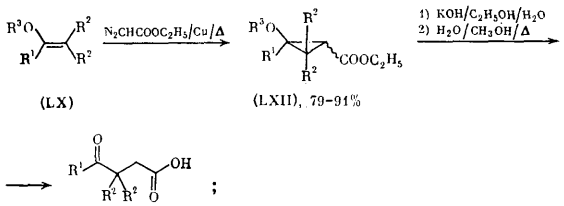


(LVII) (LIX) (LXIII)

The key stage of the process is the formation of the corresponding hydroxycyclopropane intermediates (LIX), usually achieved by the copper-catalysed decomposition of diazo-compounds in the presence of an excess of the enol ether (see the relevant reviews[4,7,9,10]). The use of copper catalysts sometimes induces the formation of considerable amounts of products of rearrangements or of insertion in C–H bonds. The employment of rhodium catalysts has advantages as regards the selectivity of the process for a nearly equimolar reactant ratio characteristics of each reactant also have the course of the reaction. Among diazoc esters of diazoacetic,[7,9–11] diazopyruvic,[85] a

diazoacetoacetic acids[86–88] as well as diazoketones[4,89–93] and derivatives of diazodiacetyl[95,96] have been investigated in reactions with alkyl vinyl ethers. Under these conditions, the corresponding acylcyclopropanes are formed as a rule in satisfactory yields when diazocarbonyl reagents containing only one π-electron-accepting group conjugated with the diazo-group are used. Otherwise the formation of derivatives of the dihydrofuran series, formally corresponding to the 1,3-dipolar cycloaddition of the ketocarbene to the double bond of the enol ether, is normally observed.[9,85,86] The reactions of the dialkyl acetals of ketens with diazoketones leads to similar compounds,[92] while the reactions with ethyl diazoacetate make it possible to obtain, together with products of rearrangements, also cyclopropane adducts.[92,94–96] The latter are likewise formed readily in the reactions of alkyl diazoacetates with silyl ethers of enols.[9,97–104]

Depending on the nature of the substituent at the ether oxygen atom in compounds (LIX), reactions involving the cleavage of the C(1)–C(2) bond in three-membered ring take place under the conditions of acid or base catalysis. Thus the conversion of the double bond into a cyclopropane derivative by ethyl diazoacetate, the hydrolysis of the resulting stereoisomeric esters of 2-alkoxycyclopropanecarboxylic acids (LXII), and the hydrolytic cleavage of the three-membered ring in the latter by brief refluxing in aqueous methanol constitutes a convenient method for the conversion of the enol ethers (LX) into 4-ketocarboxylic acids (LXI):[100]

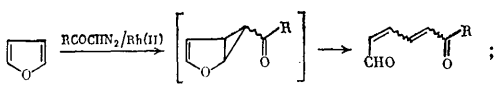


(LX) (LXII), 79–91%

(LXI), 84–95%

R^1 = C_6H_5, 3,4-$(CH_3O)_2C_6H_4$, $(CH_3)_2CH$, $(CH_3)_3C$; R^2 = H, CH_3; R^3 = CH_3, C_2H_5.

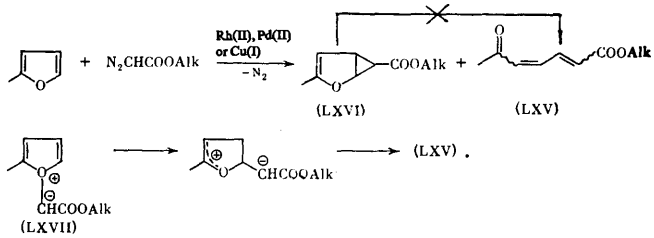
The acid-catalysed solvolysis of 2-alkoxycyclopropanecarboxylic acid esters and 2-alkoxycyclopropyl ketones, leading to the formation of the corresponding 1,4-dicarbonyl compounds or their derivatives, also takes place under mild conditions.[61,67–70, 93–97] On the other hand, the adducts (LXIII) of ketocarbenes with furan, which are bicyclic analogues of 2-alkoxycyclopropyl ketones, are spontaneously converted into *cis,trans*-6-oxoalka-2,4-dienals (LXIV) with a high stereoselectivity:[105]



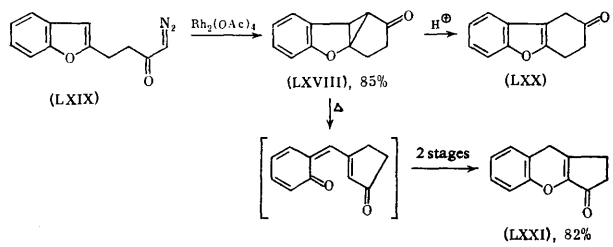
(LXIII), 50–72% (LXIV)

R = CH_2—C≡C—$(CH_2)_3$ $COOCH_3$, CH_2—C≡C—CH_2—C≡C—C_5H_{11}.

In this case, the process proceeds via the dissociation of the C(1)–C(3) bond in the 2-alkoxycyclopropyl ketone fragment of compound (LXIII), which may be induced by factors similar to those which are responsible for the preferential attack by the electrophile on the α-carbon atom of the furan ring. The reaction is probably general,[20,106] but it has been found that, in the interaction of alkoxycarbonylcarbenes with sylvan, the stereoisomeric esters of 6-oxoheptadionoic acids (LXV) are not formed from the cyclopropane precursors (LXVI) but are probably generated by the rearrangement of the ylides (LXVII):[106]



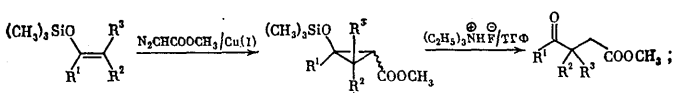
The ring opening reactions in the products of the intramolecular conversion of furyl-substituted ketocarbenes into cyclopropane derivatives proceed similarly and lead to the corresponding cycloalkenones.[107] On the other hand, in the reaction with the benzofuran derivative (LXVIII), obtained by the intramolecular cyclisation of the diazoketone (LXIX), the regiospecificity of the ring opening changes rapidly as a function of the conditions selected. Treatment of the ketone (LXVIII) with trace amounts of protic acids leads to high yield of the benzofuran (LXX), while heating of the ketone (LXVIII) at 180 °C affords the benzopyran (LXXI):[107]



(LXIX) (LXVIII), 85% (LXX)

(LXXI), 82%

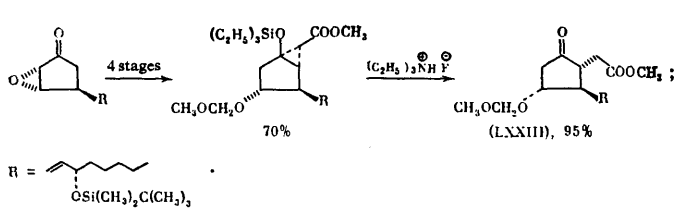
The opening of the three-membered ring in 2-trimethylsiloxycyclopropanecarboxylic acid esters (LXXII) takes place both in the presence of strong acids[102,108] and under virtually neutral conditions on treatment with triethylammonium fluoride:[98,101,109]



(LXII), 55–97% 67–93%

R^1, R^2, R^3 = H, alkyl, alkenyl, $OSi(CH_3)_3$.

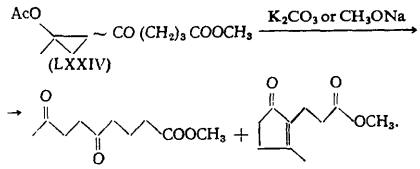
Trialkylsilyl ethers of enols can be usually obtained under much milder conditions and with a higher regioselectivity than the corresponding alkyl ethers, which made it possible, in particular, to use successfully suitable cyclopropane intermediates in the key stage of a new synthesis of the familiar prostaglandin precursor (LXXIII):[101]



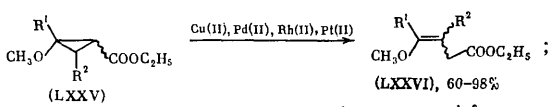
70%

When functional groups are substituted into enol acetates by diazocarbonyl compounds, the opening of the three-membered ring

in the cyclopropane intermediates (LXXIV) takes place readily in an alkaline medium:[90]



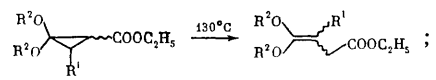
2-Alkoxycyclopropanecarboxylic acid esters (LXXV) are capable of isomerising to the corresponding vinyl esters (LXXVI) in the presence of catalytic amounts of transition metal salts:[110–112]



(LXXV) (LXXVI), 60–98%

$R^1 = CH_3$, $CH_2{=}CH$, C_6H_5, $CH_2{=}C(OCH_3)$; $R^2 = H$, C_6H_5; $R^1R^2 = (CH_2)_4$.

Ethyl 2,2-dialkoxycyclopropanecarboxylates (LXXVII) rearrange to keten dialkyl acetals (LXXVIII) in the absence of catalysts[92] at 130 °C:

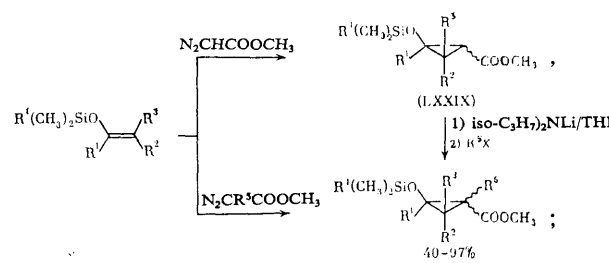


(LXXVII) (LXXVIII), ~100%

$R^1 = H$, CH_3; $R^2 = CH_3$, C_2H_5.

The similar isomerisation of 2-trimethylsiloxycyclopropanecarboxylic acid esters in the presence of iodotrimethylsilane or nonafluorotrimethylsilylbutanesulphonate has also been reported.[113]

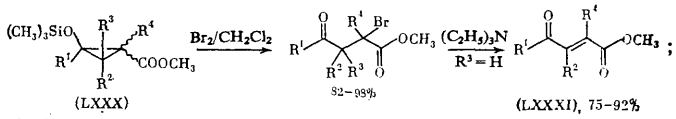
An important advantage of the methods for the introduction of functional groups into alkenes via the intermediate formation of activated cyclopropanes is the possibility of modifying the cyclopropane intermediate by carrying out reactions with retention of the three-membered ring and also the possibility of using ring opening reactions for the introduction of additional functional groups into the molecule or the formation of new carbon–carbon bonds. Since diazocarbonyl compounds containing substituents in the geminal position relative to the diazo-group are as a rule much less readily available than the corresponding unsubstituted reagents, a more convenient pathway to the target molecule may proceed via the intermediate stage involving the alkylation of alkoxycarbonylcyclopropanes (LXXIX):[109,114,115]



(LXXIX) 40–97%

R^1, R^2, R^3, R^4, R^5 = H, alkyl, alkenyl, aryl; X = Br, I, OSO_3CH_3.

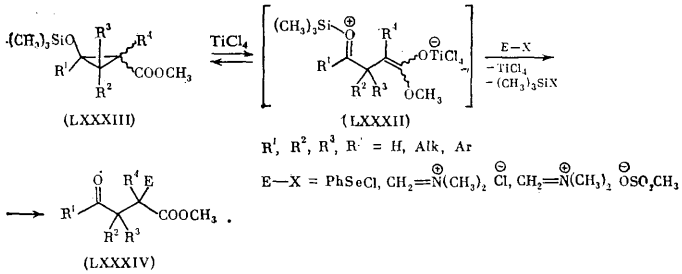
The oxidative cleavage of the three-membered ring in the donor–acceptor cyclopropanes (LXXX) by successive bromination–dehydrobromination reactions proceeds under mild conditions and constitutes a convenient method of synthesis of 4-oxo-2-alkenoates (LXXXI):[116]



(LXXX) 82–99% (LXXXI), 75–92%

R^1, R^2, R^3, R^4 = H, D, CH_3, $C(CH_3)_3$, SCH_3.

The enolate (LXXXII), formed as an intermediate from substituted 2-trimethylsiloxycyclopropanecarboxylates (LXXXIII) in the presence of Lewis acids, reacts readily with electrophiles, affording the corresponding esters of 2-substituted 4-oxoalkanoic acids (LXXXIV):[117–120]



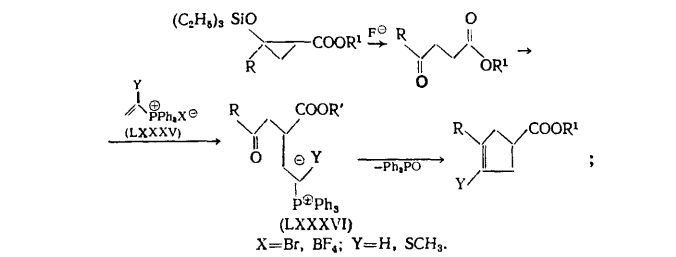
(LXXXIII) (LXXXII)

R^1, R^2, R^3, R^4 = H, Alk, Ar

E—X = PhSeCl, $CH_2{=}\overset{\oplus}{N}(CH_3)_2\ \overset{\ominus}{Cl}$, $CH_2{=}\overset{\oplus}{N}(CH_3)_2\ \overset{\ominus}{OSO_2CH_3}$

(LXXXIV)

The use of triphenyl(vinyl)phosphonium salts (LXXXV) as the electrophiles in a similar reaction leads to the intermediate phosphonium ylides (LXXXVI), which subsequently undergo the Wittig reaction:[121]



(LXXXV) (LXXXVI)

X=Br, BF_4; Y=H, SCH_3.

The entire sequence of reactions constitutes a new type of [3 + 2]annelation, which has been used effectively in the synthesis of tricyclo[6.3.0.$0^{2,6}$]undecanes with functional group substituents.[121]

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It follows from the data presented in this review that the introduction of acyl and acylmethyl fragments into organic substrates by means of carbene reactions makes it possible in many instances to achieve unique reactions ensuring the formation of new carbon–carbon bonds under mild conditions with a high regioselectivity and stereoselectivity. The carbene species then frequently behave as reagents with "inverted" polarity of the reaction centre, and the significant dependence of the chemical properties of the carbene intermediates on their spin state and on the presence of a complex forming agent imparts additional flexibility to the synthetic methods. The possibility of achieving alternative pathways leading to the opening of the ring in cyclopropane intermediates and their great synthetic possibilities also give rise to excellent prospects for the introduction of functional groups into alkenes by means of carbene reactions.

References

1. D Barton, W D Ollis *Comprehensive Organic Chemistry* (Translated into Russian), Izd. Khimiya, Moscow, 1982, p. 488
2. L A Yanovskaya, V A Dombrovskii, A Kh Khusid *Tsiklopropany s Funktsional'nymi Gruppani* (Cyclopropanes with Functional Groups), Izd. Nauka, Moscow, 1980
3. N S Zefirov, N V Kazimirchik, K A Lukin *Tsikloprisoedinenie Dikhlorkarbena k Olefinam* (The Cycloaddition of Dichlorocarbene to Alkenes), Izd. Nauka, Moscow, 1985
4. E Wenkert *Acc. Chem. Res.*, 1980, **13** 27
5. S Danishefsky *Acc. Chem. Res.*, 1979, **12** 66
6. A Meijere *Angew. Chem., Int. Ed. Engl.*, 1979, **18** 809
7. A P Marchand, N M Brockway *Chem. Rev.*, 1974, **74** 431
8. V S Aksenov, V A Terent'eva, Yu V Savinykh *Usp. Khim.*, 1980, **49**(6) 1039 [English translation in *Russ. Chem. Rev.*, 1980(6)]
9. M P Doyle *Chem. Rev.*, 1986, **86** 919
10. T V Mandel'shtam, M M Komendantov *Alifaticheskie Diazosoedineniya v Organicheskom Sinteze* (Aliphatic Diazo-Compounds in Organic Synthesis), Izd. Leningr. Gos. Univ., Leningrad, 1985, p. 22
11. T V Mandel'shtam *Sovremennye Problemy Organicheskoi Khimii* (Modern Problems in Organic Chemistry), Izd. Leningr. Gos. Univ., Leningrad, 1987, p. 87
12. O G Kulinkovich *Sovremennye Problemy Organicheskoi Khimii* (Modern Problems in Organic Chemistry), Izd. Leningr. Gos. Univ., Leningrad, 1987, p. 161
13. H Wynberg *Chem. Rev.*, 1960, **60** 189
14. H Wynberg, E W Meijere *Org. React.*, 1982, **8** 1
15. Y Sasson, M Yonovich *Tetrahedron Lett.*, 1979, 3753
16. M Komiyama, H Hirai *J. Am. Chem. Soc.*, 1983, **105** 2018
17. M Komiyama, H Hirai *Bull. Chem. Soc. Jpn.*, 1981, **54** 2053
18. R Neumann, Y Sasson *Synthesis*, 1986, 569
19. S D Burke, P A Grieco *Org. React.*, 1979, **26** 361
20. A E Vasil'vitskii, V M Shostakovskii, O M Nefedov *Khim. Geterotsikl. Soedin., 1982, 723*
21. A J Auclaux, A J Hubert, A F Noels, et al. *J. Org. Chem.*, 1980, **45** 695
22. A Demonceau, A F Noels, A J Hubert, P J Teyssie *Chem. Commun.*, 1981, 688
23. H J Callot, F Metz *Tetrahedron Lett.*, 1982, **23** 4321
24. A Demonceau, A Noels, A J Hubert, P J Teyssie *Bull. Soc. Chim. Belg.*, 1984, **93** 945
25. D F Taber, J C Amedio, R G Sherrill *J. Org. Chem.*, 1986, **51** 3382
26. M P Doyle, J H Griffin, V Bagheri, R L Dorow *Organometallics*, 1984, **3** 53
27. E Wenkert, L L Davis, B L Mylary, et al. *J. Org. Chem.*, 1982, **47** 3242
28. D F Taber, E H Petty *J. Org. Chem.*, 1982, **47** 4808
29. D F Taber, R E Ruckle *J. Am. Chem. Soc.*, 1986, **108** 7686
30. D F Taber, R E Ruckle *Tetrahedron Lett.*, 1985, **26** 3059
31. C W Jefford, A Zaslona *Tetrahedron Lett., 1985,* **26** 6035
32. D F Taber, E H Petty, K J Raman *J. Am. Chem. Soc.*, 1985, **107** 196
33. D F Taber, K J Raman *J. Am. Chem. Soc.*, 1983, **105** 5935
34. C W Jefford, W Johncock *Helv. Chim. Acta*, 1983, **66** 2666
35. D F Taber, R E Ruckle, M J Hennessy *J. Org. Chem.*, 1986, **51** 4077
36. D E Cane, P J Thomas *J. Am. Chem. Soc.*, 1984, **106** 5295
37. T C Smale *Tetrahedron Lett.*, 1984, **25** 2913
38. W H Tamblin, S R Hoffmann, M P Doyle *J. Organomet. Chem.*, 1981, **216** 64C
39. M P Doyle, W H Tamblyn, V Baghery *J. Org. Chem.*, 1981, **46** 5094
40. M P Doyle, M L Trudell, J W Terpatra *J. Org. Chem.*, 1983, **48** 5146
41. T V Mandel'shtam, A V Balycheva *Zh. Org. Khim.*, 1983, **19** 232
42. B T Golding, S Kibende *Chem. Commun.*, 1983, 1103
43. M P Doyle, G H Griffin, M S Chinn, D Van Leusen *J. Org. Chem.*, 1984, **49** 1917
44. E J Roskamp, C R Johnson *J. Am. Chem. Soc.*, 1986, **108** 6062
45. M C Pirrung, J A Werner *J. Am. Chem. Soc.*, 1986, **108** 6060
46. M P Doyle, M L Trudell *J. Org. Chem.*, 1984, **49** 1196
47. A Meijere *Angew. Chem., Int. Ed. Engl.*, 1979, **18** 809
48. C J M Stirling *Tetrahedron*, 1985, **41** 1613
49. K B Wiberg *Angew. Chem., Int. Ed. Engl.*, 1986, **25** 312
50. A I Ioffe, O M Nefedov *Stroenie Proizvodnykh Tsiklopropana* (The Structure of Cyclopropane Derivatives), Izd. Nauka, Moscow, 1986
51. W P Weber, G W Gokel *Phase Transfer Catalysis in Organic Synthesis* (Translated into Russian), Izd. Mir, Moscow, 1980, p. 65
52. A I Ioffe, O M Nefedov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 1536
53. I G Tishchenko, O G Kulinkovich, N V Masalov *Zh. Org. Khim.*, 1980, **16** 1203
54. I G Tishchenko, O G Kulinkovich *Zh. Org. Khim.*, 1980, **16** 303
55. Y Kobayashi, T Taguchi, T Morikawa, et al. *J. Org. Chem.*, 1982, **47** 3232
56. M G Banwell *Chem. Commun.*, 1983, 1453
57. M G Tishchenko, O G Kulinkovich, N V Masalov *Synthesis*, 1982, 268
58. O G Kulinkovich, I G Tishchenko, I V Reznikov, N A Roslik *Zh. Org. Khim.*, 1982, **18** 1654
59. O G Kulinkovich, I G Tishchenko, Yu N Romashin *Zh. Org. Khim.*, 1984, **20** 242
60. O G Kulinkovich, I G Tishchenko, N A Roslik *Zh. Org. Khim.*, 1984, **20** 532
61. O G Kulinkovich, I G Tishchenko, V L Sorokin *Zh. Org. Khim.*, 1984, **20** 2548
62. O G Kulinkovich, I G Tishchenko, Yu N Romashin *Zh. Org. Khim.*, 1985, **21** 90
63. V D Novokreshchennykh, S S Mochalov, Yu S Shabarov *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1985, **26** 82
64. O G Kulinkovich, I G Tischenko, N V Masalov *Synthesis*, 1984, 886
65. O G Kulinkovich, I G Tischenko, N A Roslik *Synthesis*, 1982, 931
66. O G Kulinkovich, I G Tishchenko, J N Romashin, L N Savitskaya *Synthesis*, 1986, 378
67. O G Kulinkovich, I G Tishchenko, V L Sorokin *Zh. Org. Khim.*, 1985, **21** 1658
68. O G Kulinkovich, I G Tischenko, V L Sorokin *Synthesis*, 1985, 1058
69. O G Kulinkovich, I G Tishchenko, Yu N Romashin, Yu A Zaitsev *Zh. Org. Khim.*, 1987, **23** 1178
70. O G Kulinkovich, I G Tishchenko, Yu N Romashin *Zh. Org. Khim.*, 1986, **22** 2474

71. O G Kulinkovich, I G Tishchenko, S V Sviridov *Zh. Org. Khim.*, 1987, **23** 2535
72. V E Marques, K V B Rao, J V Silverton, J A Kelley *J. Org. Chem.*, 1984, **49** 912
73. T Hiyama, H Saimoto, K Nishio, et al. *Tetrahedron Lett.*, 1979, 2043
74. No reference in the Russian (Ed. of Translation)
75. H Miller *J. Org. Chem.*, 1981, **46** 2412
76. M Demuth, G Mikhail *Tetrahedron*, 1983, **39** 991
77. E Giaciomini, M A Loreto, L Pellacani, P A Tardella *J. Org. Chem.*, 1980, **45** 519
78. M Demuth, P R Raghavan *Helv. Chim. Acta*, 1979, **62** 2338
79. P K Dieter, S Pounds *J. Org. Chem.*, 1982, **47** 3174
80. J D White, J F Ruppert, M A Avery, S Torii *J. Am. Chem. Soc.*, 1981, **103** 1813
81. W S Murphy, S Wattanasin *Tetrahedron Lett.*, 1981, **22** 695
82. A B Smith, B H Toder, S J Branca *J. Am. Chem. Soc.*, 1984, **106** 3995
83. A E Smith, B H Toder, R C Richmond, S J Brance *J. Am. Chem. Soc.*, 1984, **106** 4001
84. M P Doyle, D VanLeusen, W H Tamblyn *Synthesis*, 1981, 787
85. M E Alonso, P Jano, M I Hernandes, et al. *J. Org. Chem.*, 1983, **48** 3047
86. M E Alonso, A Morales, W A Chitty *J. Org. Chem.*, 1982, **47** 3747
87. M Alonso, M Gomez, S P Sierraalta, P Jano *J. Heterocycl. Chem.*, 1982, **19** 369
88. M Alonso, M I Hernandes, M Gomez, et al. *Tetrahedron*, 1985, **41** 2343
89. E Wenkert, T D Halls, L D Kwart, et al. *Tetrahedron*, 1981, **37** 4017
90. E Wenkert, M L F Bakuzis, B L Buckwalter, P D Woodgate *Synth. Commun.*, 1981, **11** 533
91. E Wenkert, R S Greenberg, M S Raju *J. Org. Chem.*, 1985, **50** 4681
92. M L Graciano, R Scarpati *J. Chem. Soc., Perkin Trans. 1*, 1985, 289
93. J Adams, M Belly *Tetrahedron Lett.*, 1986, **27** 2075
94. E Wenkert *Heterocycles*, 1980, **14** 1703
95. E Wenkert, M E Alonso, B L Buckwalter, E L Sanchez *J. Am. Chem. Soc.*, 1983, **105** 2021
96. O Pelletier, K Jankowski *Can. J. Chem.*, 1982, **60** 2383
97. M L Graziano, M R Iesce *Synthesis*, 1985, 762
98. H U Reissig, E Hirsch *Angew. Chem., Int. Ed. Engl.*, 1980, **19** 813
99. K Saigo, S Okagawa, H Nohira *Bull. Chem. Soc. Jpn.*, 1981, **54** 3603
100. H Kunz, M Lindig *Chem. Ber.*, 1983, **116** 220
101. J P Marino, R Fernandes, P E Laborde *J. Org. Chem.*, 1984, **49** 5279
102. K Saigo, H Kurihara, H Miura, et al. *Synth. Commun.*, 1984, **14** 787
103. E Kunkel, I Reichelt, H U Reissig *Liebigs Ann. Chem.*, 1984, 512
104. E L Crimm, R Zschiesche, H U Reissig *J. Org. Chem.*, 1985, **50** 5543
105. J Adams, Y Leblanc, J Rokach *Tetrahedron Lett.*, 1984, **25** 1227
106. O M Nefedov, O E Saltykova, A E Vasil'vitskii, V M Shostakovskii *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2625
107. A Padwa, T Wisnieff, E J Walsh *J. Org. Chem.*, 1986, **51** 5036
108. E Kunkel, I Reichelt, H U Reissig *Liebigs Ann. Chem.*, 1984, 802
109. J Bohm, E Hirsch, H U Reissing *Angew. Chem., Int. Ed. Engl.*, 1981, **20** 574
110. M P Doyle, D Van Leusen *J. Am. Chem. Soc.*, 1981, **103** 5917
111. M P Doyle, D Van Leusen *J. Org. Chem.*, 1982, **47** 5326
112. M E Alonso, M C Garcia *J. Org. Chem.*, 1985, **50** 988
113. H U Reissig *Tetrahedron Lett.*, 1985, **26** 3943
114. I Reichelt, H U Reissig *Liebigs Ann. Chem.*, 1984, 531
115. C Bruckner, H U Reissig *Chem. Commun.*, 1985, 1512
116. I Reichelt, H U Reissig *Liebigs Ann. Chem.*, 1984, 828
117. H U Reissig *Tetrahedron Lett.*, 1981, **22** 2981
118. H U Reissig, I Reichelt, H Lorey *Liebigs Ann. Chem.*, 1986, 1924
119. H U Reissig, I Reichelt *Tetrahedron Lett.*, 1984, 5879
120. H U Reissig, H Lorey *Liebigs Ann. Chem.*, 1986, 1914
121. J P Marino, E Laborde *J. Am. Chem. Soc.*, 1985, **107** 734

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Carbonylcarbenes in the specific synthesis of natural products

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ABSTRACT. Studies on the specific synthesis of natural products and their analogues, using alkoxycarbonyl- and keto-carbenes as well as their synthetic equivalents, are surveyed. Properties of carbonylcarbenes such as cycloaddition to alkenes and reactions involving intermolecular and (especially) intramolecular insertion in C–H, N–H, and C–X (X = heteroatom) bonds have found wide scale application. These reactions permit the stereoselective and regioselective synthesis of a wide variety of carbon atom and heteroatom molecular skeletons which are difficult to obtain by other procedures.†

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I. Introduction

The varied chemical properties of keto- and alkoxycarbonylcarbenes have been described in a series of reviews and monographs[1–6] and many of their reactions have been recommended as convenient preparative methods for the construction of various structural fragments. This review deals with the way in which these recommendations are used in practice in the specific synthesis of biologically active natural products and their analogues. The author did not attempt to provide an exhaustive bibliography on this question; the studies quoted serve merely as an illustration of the possibility of the synthetic use of carbenes.

† This review was intended for publication in issue No. 7 (1989) of this journal, which was devoted to the chemistry of carbenes.

II. Synthetic equivalents of carbonylcarbenes

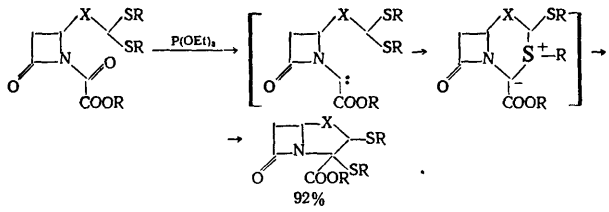
In the selection of a reagent for the creation of a structural element of the target compound, the detailed mechanism of its interaction with the substrate is of secondary importance; the question of the limits of the applicability of the method and the procedures for increasing the regio- and stereo-selectivity of the reagent comes to the fore. For this reason, the differences between free carbenes and carbenes bound in complexes and even between their precursors are unimportant for synthetic chemists provided that these species behave in the same way. All these compounds with the aid of which it is possible to introduce the $R-\overset{|}{\underset{|}{C}}-COOR$ or $R-\overset{|}{\underset{|}{C}}-COR$ synthons into the molecule, are combined in the concept of "synthetic equivalents of carbonylcarbene".

Diazocarbonyl compounds are a traditional source of carbonylcarbenes. Virtually only the catalytic decomposition of the latter is used in specific synthesis, because the carbenes generated by the thermolysis or photolysis of diazo-compounds are too active and their reactions are insufficiently selective. The experiments where it is necessary to carry out the Wolff rearrangement, which is known to occur best under photolytic conditions, are an exception.

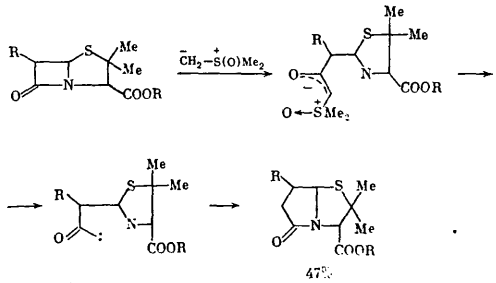
Various compounds are used as catalysts of the decomposition of diazoketones and diazoesters:[7,8] copper, rhodium, ruthenium, platinum, and tungsten complexes. In selecting a particular catalyst, the aim is to reduce the decomposition temperature of the diazocompound, to alter its regioselectivity, and to increase the stereoselectivity of the reaction.

Bivalent rhodium salts (the acetate, trifluoroacetate, etc.) have been used particularly frequently in the specific synthesis in recent years. Indeed, in the presence of these compounds it is frequently possible (but not always) to carry out the decomposition of diazocompounds at room or an even lower temperature and the regioselectivity of the reaction proves to be higher than that of the reaction using copper salts. Rhodium acetate is superior to copper compounds as the catalyst of the reactions involving the insertion of the carbene in a C–H bond[9] and its addition to arenes.[10] On the other hand, copper compounds have not lost their importance in the catalysis of reactions involving cycloaddition to alkenes. Copper acetylacetonate [$Cu(acac)_2$] or its hexafluoro-derivative [$Cu(F_6\text{-}acac)_2$] are frequently used for this purpose. The employment of copper complexes with chiral ligands (L*) as catalysts of the decomposition of diazoacetic acid ester enabled a number of investigators[11–15] to achieve a high degree of stereocontrol in the synthesis of chrysanthemic and related acids.

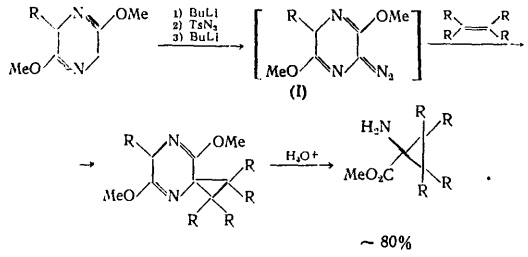
Communications have been recently published about new sources of carbonylcarbenes. Thus, according to Kametani et al.,[16] carbonylcarbene arises when a substituted oxalic acid amidoester is acted upon by triethyl phosphite:



A carbonylcarbene, which underwent the Wolff rearrangement, has been obtained by the reaction of a β-lactam with dimethylsulphoxonium methylide:[17]



A derivative of diazodihydropyrazine (I), which reacts with alkenes with evolution of nitrogen at the instant of its formation, may be called a synthetic equivalent of aminomethoxycarbonylcarbene:



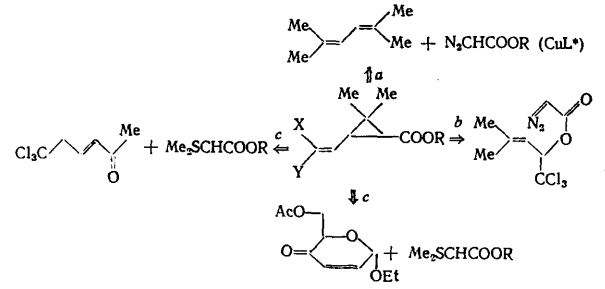
Acid hydrolysis of the spiroadduct led to the formation of aminocyclopropanecarboxylic acid.[18]

The carbene generated in the presence of copper is known[1-6] to possess electrophilic properties. Nevertheless, in certain cases it has been possible to add this species to the "activated" double bond of acrylic esters. This result has been achieved[19] by adding to the reaction mixture copper sulphate and a carbene acceptor—dimethyl sulphide. The addition of the diazoester yielded a sulphonium ylide,[20] which served as a reagent transferring the nucleophilic alkoxycarbonylcarbene.[21] A similar result was obtained in the reaction of "activated" double bonds with dimethylsulphonium methylides, synthesised beforehand by other methods,[22-24] which makes it possible to regard these compounds as the synthetic equivalents of alkoxycarbonylcarbene.

III. The use of the [1 + 2]cycloaddition reaction for the synthesis of the cyclopropane fragment of the molecular skeleton

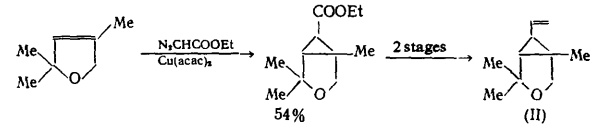
Fairly numerous natural products whose skeleton contains a three-carbon ring are known. The [1 + 2]cycloaddition reactions of carbonylcarbenes are widely used to construct this structural fragment.

The carbene synthesis is most important for the preparation of a wide variety of pyrethroids, which are based on chrysanthemic acid and its derivatives.[25] Various ways of synthesising acids of this group with the aid of equivalents of alkoxycarbonylcarbene are known:

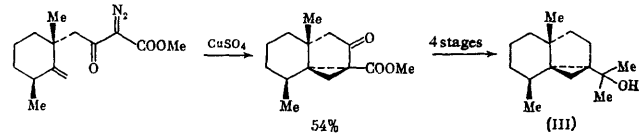


(*a*) Stereoselective[26,27] and asymmetric[11-14] synthesis involving the use of a bulky group in the diazoacetic ester and (or) the application of copper complexes with chiral ligands as catalysts; (*b*) the stereocontrolled intramolecular cycloaddition of the carbene C atom to a weakly nucleophilic double bond;[15,18] (*c*) the use of sulphonium ylides to convert an "activated" double bond into a cyclopropane derivative.[22-24]

The intermolecular conversion of an alkene into a cyclopropane derivative by diazoacetic ester has been used in the unambiguous synthesis of artemiseole (II), a natural monoterpene having a skeleton which conflicts with the isoprene biosynthesis rule:[29]

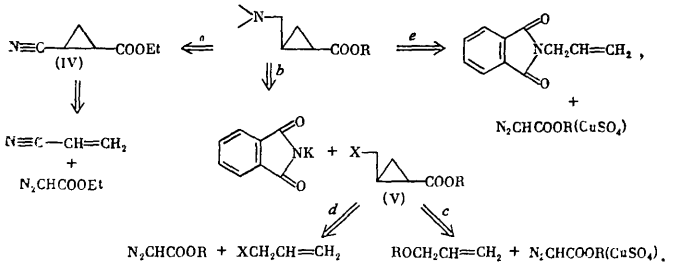


The intramolecular cyclopropane formation reaction has been the key stage in the synthesis of a sesquiterpene antibiotic—cycloeudesmol (III). With the aid of this method, it has been possible to introduce the quaternary C atom common to the three condensed rings and having the necessary configuration:[30]



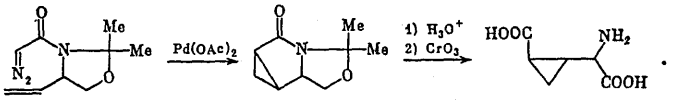
The rigidity of the system in this instance led to the formation of only one stereoisomer of the compound. The intermolecular conversion of the double bond into a cyclopropane derivative with the aid of diazoacetic ester [CuI.P(OMe)$_3$ catalyst, yield 74%] has been used in the synthesis of 23,24-dihydrocalysterol.[31]

Aminoacids of the cyclopropane series occupy an outstanding place among biologically active natural products.[32] Various approaches to the synthesis of the cyclic analogue of γ-aminobutyric acid (GABG) have been demonstrated on the basis of the scheme presented below:



(*a*) The addition of diazoacetic ester to acrylonitrile, the pyrolysis of the resulting pyrazoline, and the hydrogenation of the nitrile (IV);[33] (*b*) the alkylation of potassium phthalimide by the halogenomethylcyclopropanecarboxylic acid ester (V).[34] The ester (V) can be obtained (*c*) by treating allyl acetate[35] or allyl alcohol[36] with diazoacetic ester and subsequent substitution of the hydroxy-group in compound (V) (X = OH) by a halogen.[37] The same ester can be obtained by another procedure (*d*) involving the interaction of diazoacetic ester with allyl chloride in the presence of copper sulphate.[38] The ester of 2-chlorobut-3-enoic acid is then formed as the side product as a result of the rearrangement of the intermediate chloronium ylide.[39] The formation of the ylide and hence of the unsaturated ester can be avoided if the reaction of the diazoester with allyl chloride is performed under the conditions of photosensitised deazotisation, i. e. with participation of triplet ethoxycarbonylcarbene,[40] or if rhodium acetate is used as the catalyst of the decomposition of the diazoester.[41] Finally, the cyclic analogue of GABA can be obtained by converting *N*-allylphthalimide into a cyclopropane derivative. By virtue of the influence of the phthalimide group, the nucleophilicity of the nitrogen atom in *N*-allylphthalimide is reduced and the formation of the ylide in the insertion reaction does not therefore take place[42] (pathway *e*).

An analogue of glutamic acid, containing a three-carbon ring, has been obtained[43] by the intramolecular cycloaddition of a diazoamide to the double bond and the subsequent hydrolysis and oxidation of the alcohol group:



IV. The use of the [1 + 2]cycloaddition reaction for the synthesis of active intermediates

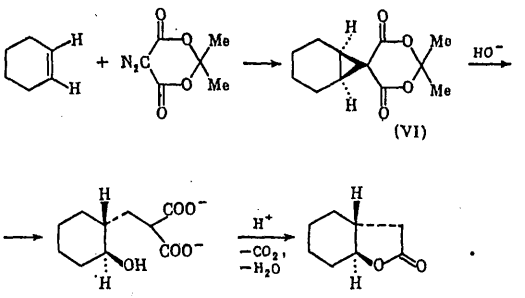
Compounds with a three-carbon ring, obtained as a result of the [1 + 2]cycloaddition of carbonylcarbenes to carbon–carbon double bonds, are frequently convenient synthons for the construction of a wide variety of structural elements. This is associated, on the one hand, with the ease of the formation of carbonyl cyclopropanes by carbene synthesis and, on the other hand, by the large store of energy in these compounds and hence the frequently high tendency towards ring opening, which takes place regio- and stereo-selectively.

A monograph (Ref. 44, Chapter 4) and a review[45] have been devoted to the use of cyclopropanecarboxylic acids, their derivatives, and cyclopropyl ketones in organic synthesis. Here we shall quote only individual examples.

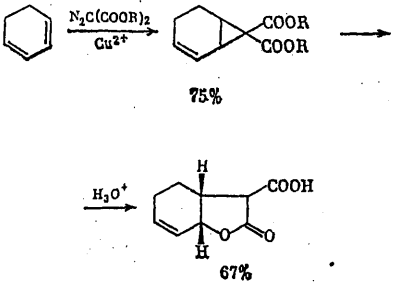
1. The ring opening in cyclopropanes and the problem of the reversal of the polarity of the synthons

The electron density in cyclopropanes containing the electron-accepting carbonyl group is known[46] to be distributed non-uniformly in such a way that the C–C bond of the ring lying opposite the substituent is stronger than the bond adjoining the substituent. The C(1)–C(2) bond is in fact dissociated when carbonylcyclopropanes are acted upon by electrophiles and nucleophiles or, catalytically, by excited hydrogen. The nucleophilic species always add to the second carbon atom of the three-membered ring with inversion of the configuration of the atom; the electrophilic species is found at the first carbon atom. This atom usually undergoes racemisation.[47]

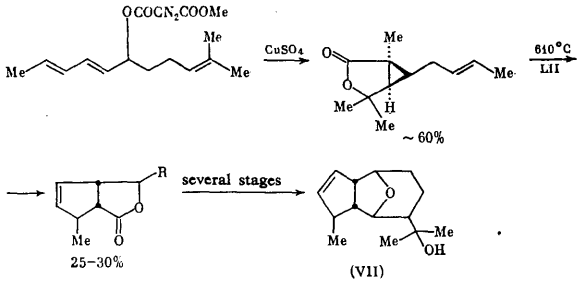
The nucleophilic opening of the ring or the homocoupled addition to carbonylcyclopropanes proceeds under mildest conditions if the compound contains two electron-accepting groups at one carbon atom, the bisecting [staggered] conformation of the two groups being optimal. This is achieved in spiran derivatives of type (VI):[47]



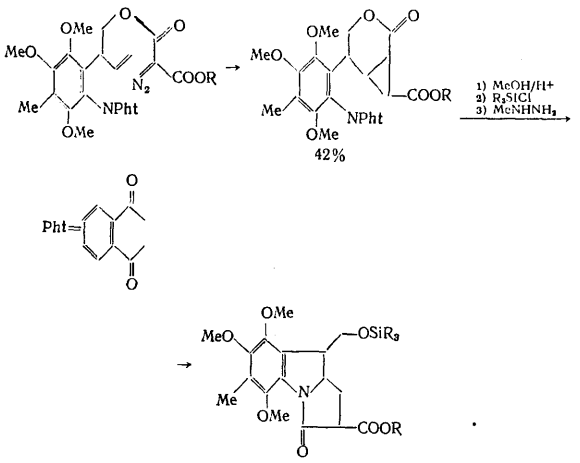
The γ-butyrolactone fragment, condensed with a larger ring, enters into the composition of many natural products.[48] Compounds with both *cis*- and *trans*-fused rings are known. Danishefsky's strategy,[47] consisting in the formation of a spiro-activated cyclopropane and the opening of the three-membered ring of the latter with the aid of a base, makes it possible to obtain *trans*-fused lactones (see above). Conversely, the opening of the ring in cyclopropanecarboxylic acids in an acid medium leads to the formation of *cis*-fused lactones:[49,50]



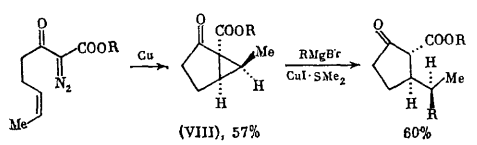
cis-Fused lactones can also be obtained by the intramolecular conversion of the esters of unsaturated alcohols into cyclopropane derivatives. The combination of this method and the vinylcyclopropane–cyclopentene rearrangement (see below) made it possible[51] to devise an approach to the creation of the guaiane system (VII):



If the nucleophilic centre is in the side chain of the cyclopropane carboxylic acid or cyclopropyl ketone, then its homocoupled addition to the activated three-carbon ring proceeds under mild conditions under rigorous stereocontrol and, depending on the character of the nucleophilic centre, leads to the formation of carbocycles or heterocycles.[47] The use of this reaction for the synthesis of a precursor of the alkaloid mitomycin is illustrated below:

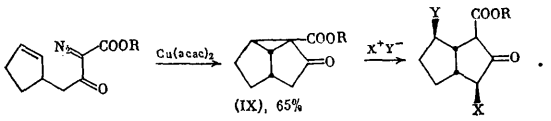


The intramolecular conversion of the double bond into a cyclopropane derivative and subsequent homocoupled addition of alkyl cuprate to the bicyclo[3.1.0]hexan-2-one (VIII) constitutes a convenient method of synthesis of cyclopentanones with control of the stereochemistry of the side chain:[53]



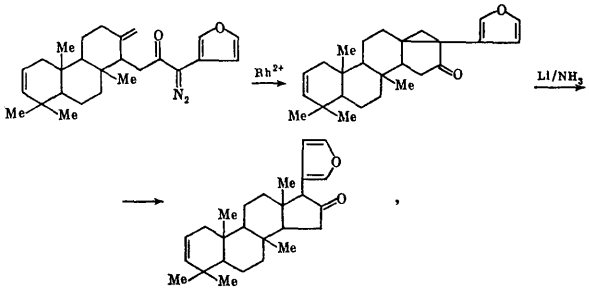
This strategy has found applications in the synthesis of prostaglandins, terpenoids, and other natural products (see, for example, Adams and Belley[54]).

The intramolecular cycloaddition of carbonylcarbene to the double bond of the cyclopentene fragment and subsequent electrophilic or nucleophilic opening of the three-membered ring of the tricyclic compound (IX) afford a condensed system made up of two five-membered rings having a defined stereochemistry:[55]



This reaction is of interest in connection with the synthesis of polyquinanes and iridoid monoterpenes.[56]

Finally the opening of the ring in cyclopropyl ketones, also obtained by the intramolecular cyclopropane formation reaction, with the aid of lithium in liquid ammonia has been used in the synthesis of the cyclic system of limonoids:[57]

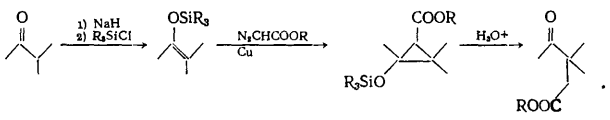


and also in the synthesis of pentalenene.[58]

The acid-catalysed ring opening in cyclopropane derivatives obtained by the carbene synthesis[59–64] is used widely in the synthesis of sesquiterpenes, diterpenes, gibberellins, and steroids. The reaction proceeds especially readily, frequently spontaneously, at room temperature or on slight heating in those cases where there is an electron-donating group at the second carbon atom of the carbonylcyclopropane.

Bifunctional fragments in which the functional groups are separated by an odd number of carbon atoms are known[65] to constitute a definite problem in organic synthesis, because the usual isohypsic reactions lead to the formation of compounds with an odd number of carbon atoms between the functional groups. Carbonylcyclopropanes are synthetic equivalents of the $^{+}C-C-C-C=O$ synthon with inverted polarity at the γ-carbonyl atom. Derivatives of 2-hydroxycyclopropanecarboxylic acids are very useful in synthesis from this point of view.[66]

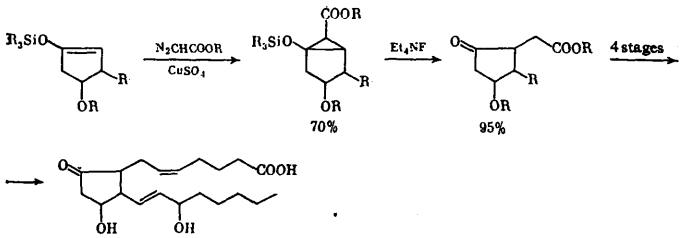
The acid-catalysed ring opening in siloxycyclopropane produces a result equivalent to the α-alkylation of a carbonyl compound:



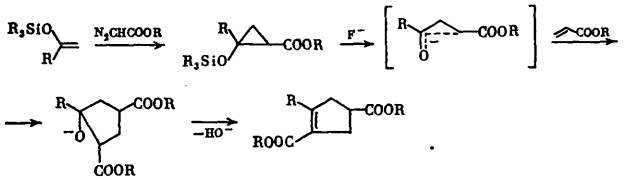
Quaternary centres in the α-position in the ketone can be obtained in this way.

The copper sulphate-catalysed addition of alkoxycarbonylcarbene to the silyl ethers of enols and subsequent ring opening with the aid of the fluoride ion constitutes a new strategy for the synthesis of

1,4-dicarbonyl compounds. In particular, it has been used to synthesise dihydrocompactin,[67] prostaglandins,[68] and related compounds,[69] for example:

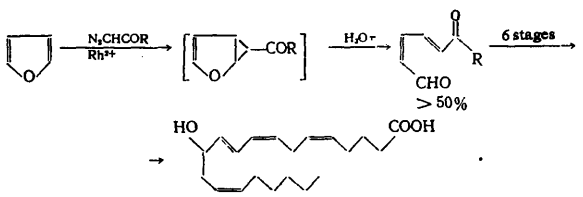


A new strategy for [2 + 3]annelation is based on the interaction of the fluoride ion with siloxycyclopropanecarboxylic acids.[70] The essential feature of this strategy consists in carrying out three consecutive reactions: the conversion of the silyl ether of an enol into a cyclopropane derivative, the opening of the ring in the latter with the aid of the fluoride ion, and the trapping of the carbanion formed in this process by electrophilic alkene.



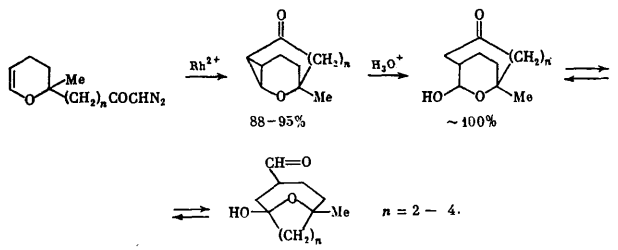
The reaction results in the formation of a cyclopentene derivative.

The reaction of ketocarbenes with furan and its homologues provides a unique possibility for the stereoselective synthesis of (*Z*, *E*)-isomers of dienealdehydes. This method has been used successfully to synthesise isomeric hydroxyeicosanetetraenoic acids:[71-73]



The analogous reaction with sylvan made it possible to obtain (7*E*, 9*Z*)-dodeca-7,9-dien-1-yl acetate[74]—the pheromone of one of the pests on grapevine.

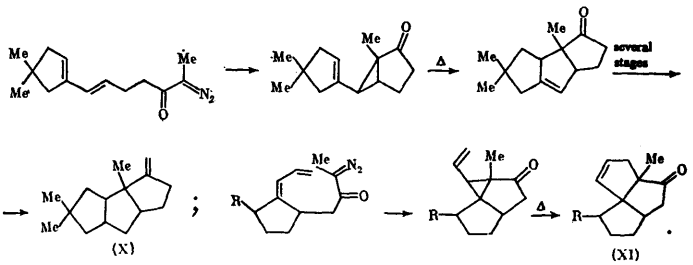
The opening of the ring in 2-alkoxycyclopropyl ketones constitutes a pathway leading to rings of moderate size (7-membered—10-membered),[75] in particular to widdrol:



The thermal isomerisation of the adducts of ethoxycarbonylcarbene with pyrimidines and isoquinolines led to the synthesis of modified and alkaloids.[76]

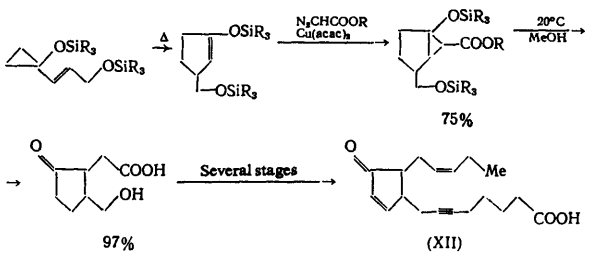
2. The vinylcyclopropane—cyclopentene rearrangement

The conversion of conjugated dienes into cyclopropane derivatives affords vinylcyclopropanes, which are capable of isomerising to cyclopentene on heating.[77] This rearrangement constitutes yet another way of obtaining polycyclic systems. Examples of the synthesis with its aid of the sesquiterpenes hirsutene (X) and isocomene (XI) are presented below:



The two-stage process involving the cycloaddition of the carbene fragment and rearrangement, which can be achieved without isolating the intermediate vinylcyclopropane, is equivalent to [4 + 1]cycloaddition, permitting at the same time the closure of several rings. The vinylcyclopropane—cyclopentene rearrangement ensures an effective stereocontrol of the reaction: *cis*-fused rings are formed. The reaction can be catalysed by lithium iodide.[78]

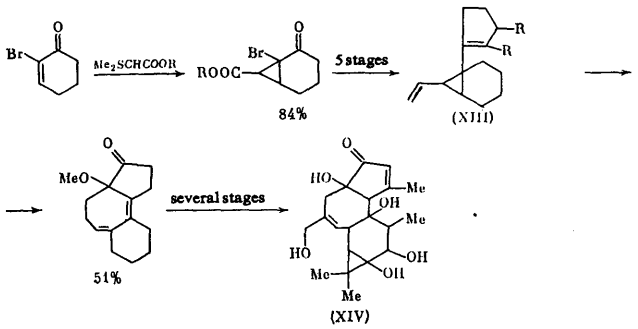
In the synthesis of dicranenone A—an aliphatic acid related to prostaglandins (XII)—the fragment containing the cyclopentane ring and two carbonyl groups in the 1,4-positions and involving the *trans*-dispositions of the ring substituents was constructed using the methodologies described above: the vinylcyclopropane—cyclopentene rearrangement, the formation of the cyclopropane derivative, and the opening of the ring in siloxycyclopropanecarboxylic acid:[69]



3. The Cope rearrangement of divinylcyclopropanes

The Cope rearrangement of *cis*-divinylcyclopropane takes place spontaneously and leads to the formation of cycloheptadiene. The similar reaction of compound (XIII), obtained by the conversion of the corresponding bromovinyl ketone into a cyclopropane derivative by means of dimethylsulphonium methylide, has been used in the

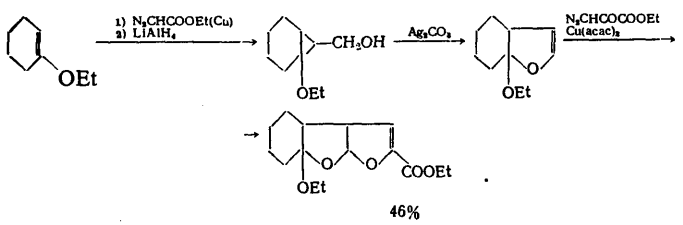
synthesis of tricyclic and tetracyclic diterpenes, in particular phorbol (XIV), which has interesting pharmacological properties:[79]



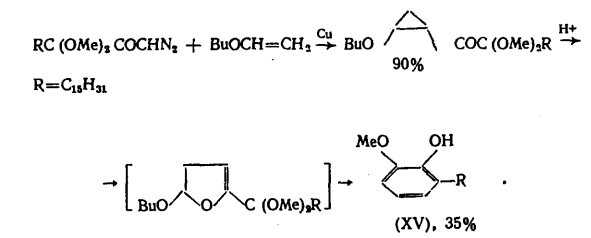
The above rearrangement allows the conversion of bicyclo[4.1.0]-heptadienes into cycloheptatrienes and hence makes it possible to obtain seven-membered rings via the reactions of carbenes with mononuclear aromatic compounds. The carbene method of synthesis of azulenes has been known for a long time. This method has undergone a new development in studies of recent years. It was found that the reaction can be carried out intramolecularly, providing a new and simple method of synthesis of compounds of this class.[80,81] Ring-substituted aryldiazoketones cyclise regio-selectively in the presence of rhodium trifluoroacetate; the bicyclic ketones obtained can be converted into substituted azulenes or into tetralones. McKervey et al.[82] suggest that the method which they describe be used for the synthesis of sesquiterpenes of the perhydroazulene series.

V. The use of other cycloaddition reactions of carbonylcarbenes

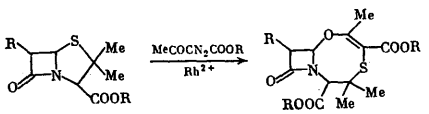
Carbonylcyclopropanes are capable of rearranging to dihydrofuran derivatives. In certain cases, dihydrofurans are formed directly in the reaction of a carbonylcarbene with an alkene.[8,45] This formal [2 + 3]cycloaddition of the 1,3-dipolar form of carbonylcarbene has found an application in organic synthesis. Dihydrofurancarboxylic acid esters, having a structure similar to that of aflatoxin, have been obtained in this way:[83]



A series of natural products containing the furan ring,[84] intermediates in the synthesis of eburnamonine and certain other alkaloids,[85] as well as the monomethyl ether of hydrourushiol (XV), a natural derivative of catechol,[86] have been obtained by the same method:

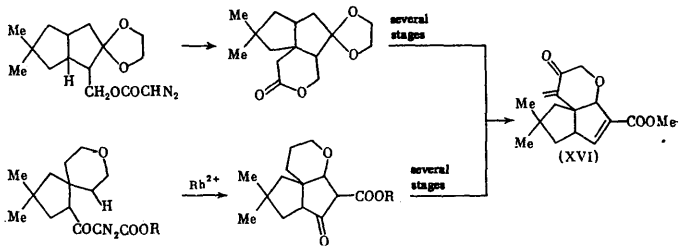


The insertion of the 1,3-dipolar form of a carbonylcarbene in the carbon–sulphur bond of a penicillannic acid, which results in the formation of a new antibiotic of the β-lactam group, has been described:[87]



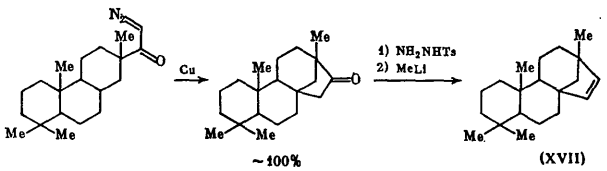
VI. The use of reactions involving the insertion of carbonylcarbenes in a C–H bond

The reactions involving the intramolecular insertion of carbonylcarbenes and their equivalents in C–H bonds have come to be widely used synthetically in recent times. The reaction leads to the formation of cyclopentane derivatives. The rigidity of the transition state in the insertion reaction ensures high regio- and stereo-control. The insertion of the carbene C atom in a tertiary C–H bond has been used[88] in the synthesis of the pentalenolactone (XVI); subsequently, the same compound was obtained[9] by the reaction involving insertion in a secondary C–H bond:

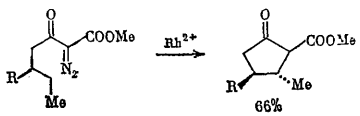


The advantage of this method of synthesis of cyclopentanes is evident: in contrast to other methods of ring closure, which require the presence of two functional groups in the compound, here one is sufficient and it is possible to achieve in one stage an appreciable increase in the complexity of the molecule.

Bridged structures, for example hibaene (XVII), are obtained with the aid of the reaction involving insertion in a C–H bond:[89,90]

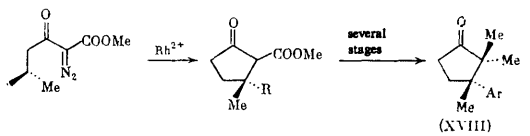


The intramolecular insertion of a carbonylcarbene proceeds with a high degree of regioselectivity via a pathway leading to the formation of five-membered rings.[92,92] The insertion in diastereotopic C—H bonds is characterised in addition by stereoselectivity:[93]



A *trans*-3,4-disubstituted cyclopentanone is formed preferentially.

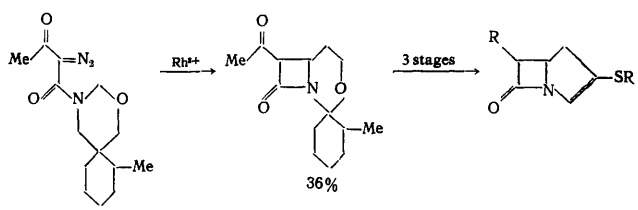
In the deazotisation of a 2-diazo-3-ketoester in the presence of the rhodium catalyst, the insertion in a C—H bond can proceed with retention of configuration, as happened in the synthesis of α-cuparenone (XVIII):[96]



Thus the reaction represents a general strategy for the enantioselective synthesis of carbocycles having a chiral centre.

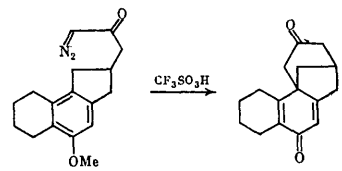
The use of a divalent palladium complex of benzonitrile as the catalyst of the decomposition of a diazoester makes it possible to obtain products of insertion in C—H bonds even when the reacting molecule contains a C=C double bond.[95] The insertion proceeds regioselectively at a decreasing rate in the sequence CH > CH_2 > CH_3. Allyl and benzyl C—H bonds proved to be less reactive than the C—H bonds of saturated compounds. The insertion in aromatic C—H bonds has been achieved successfully.[96,97] In the presence of the rhodium catalyst, the insertion in tertiary C—H bonds predominates over cycloaddition, but secondary and primary C—H bonds are less reactive than the C=C bonds. The replacement of the catalyst by a copper catalyst leads to the predominance of cycloaddition in all cases.[98]

The reaction involving insertion in a C—H bond has not been used solely for the synthesis of carbocycles; heterocycles[99] and intermediates in the synthesis of analogues of thienamycin,[100] penicillin,[101] and cephalosporin[102,103] have been obtained by this method:



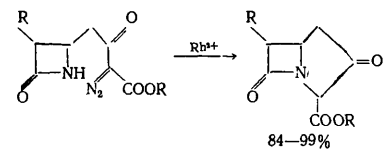
When an attempt was made to carry out the same reaction photolytically,[103] it was found that it is insufficiently selective.

An unusual reaction has been observed for ketocarbenes containing in the δ- or ε-position an aromatic ring with an alkoxy-group in the *para*-position, capable of being converted into a quinone. Treatment of these ketones with a strong acid yielded bridged systems, which were subsequently used in the syntheses of gibberellins and diterpenoids:[104]

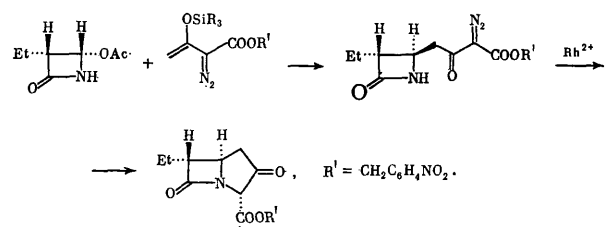


VII. The use of reactions involving insertion of carbonylcarbenes in a N—H bond

The insertion of carbonylcarbenes in N—H bonds is used in the synthesis of β-lactam antibiotics:[105,106]

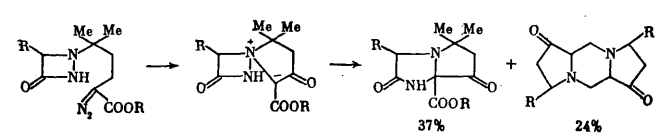


Phosphorus analogues of thienamycin[107] and nuclear analogues of β-lactam antibiotics[108] have been obtained by the same procedure. It is possible to synthesise pure enantiomers of β-lactams and carbapenems by starting with a pure enantiomer of a β-lactam and a diazoester having a bulky alcoholic group:[109]

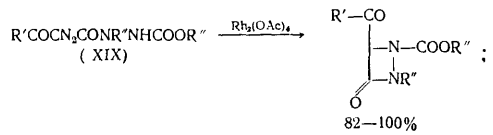


The reaction involving insertion in a N—H bond has been used also in other asymmetric syntheses, in particular for the preparation of a pure alanine enantiomer.[110]

The programme undertaken to synthesise aza-analogues of β-lactam antibiotics by the insertion of a carbene in a N—H bond led to an unexpected result:[111] tricyclic compounds were obtained as a result of the carbene attack not on the lactam but on the amine nitrogen atom in diazetidines and the subsequent rearrangement of the ylide. This afforded a new group of pharmacologically interesting compounds:



At the same time, the decomposition of the diazodihydrazide (XIX) in the presence of the rhodium catalyst was accompanied by the almost quantitative insertion of the carbene in the amide N–H bond:[112]

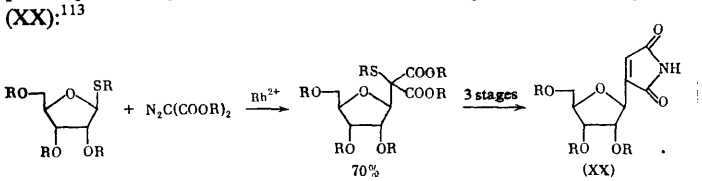


82—100%

R‴ = Bu^t, CH_2Ph; R″ = CH_2Ph, COOEt; R′ = Me, OEt.

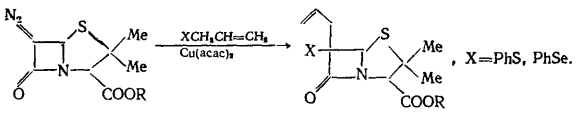
VIII. The use of reactions involving the insertion of carbonylcarbenes in C–X bonds

The interaction of carbenes with compounds containing heteroatoms is known to entail the formation of ylides. Sulphur ylides are formed particularly readily.[21] The rearrangement of the ylides can produce a synthetically interesting result.[39] The insertion in a C–S bond at the anomeric carbon atom in pentoses opens a pathway to the synthesis of the antitumour compound showdomycin (XX):[113]



70% (XX)

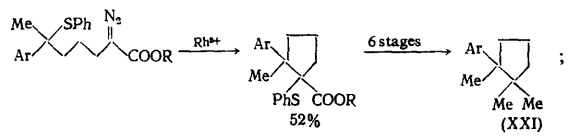
The rearrangement of the ylides formed as a result of the intramolecular attack by a copper carbenoid on the sulphur atom in penicillins constitutes a general method for the formation of a new C–C bond in compounds of this class.[114] The rearrangement of the ylides constitutes the basis of the synthesis of penems and carbopenems from diazopenicillin:[115,116]



33—66%

Another source of a carbonylcarbene for the synthesis of penems and carbopenems with the aid of the reaction involving insertion in a C–S bond was described above.

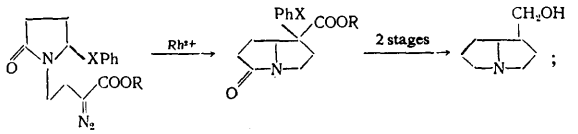
The reaction of diazoacetic ester with benzyl sulphides is used to generate a quaternary centre in the benzyl position in the synthesis of the aromatic sesquiterpene cuparene (XXI):[117,118]



52% (XXI)

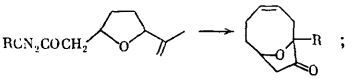
Art = *p*-$C_6H_4CH_3$.

The same procedure has been used in the synthesis of pyrrolizidine alkaloids trachelanthamidine, isoretronecanol, etc.:[119–121]



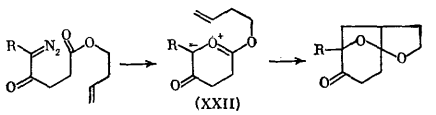
X=S (55%), X=Se (36%).

The formation of oxonium ylides proceeds with greater difficulty than that of the sulphur ylides. Nevertheless, the rearrangement of a tetrahydrofuran ketocarbene, which led to the bicyclic heterocycle oxocane, apparently occurred with their participation:[122]



R = H(81%), R = COOEt (67%).

Oxonium ylides of type (XXII) are intermediates in the recently proposed[123] method of synthesis of complex heterocyclic systems encountered in various groups of natural products:

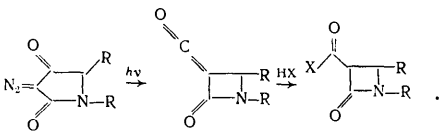


(XXII)

IX. The use of other reactions of carbonylcarbenes

One of the most interesting properties of ketocarbenes—the Wolff rearrangement—has also found an application in the specific synthesis of natural products. This rearrangement is very widely used in the synthesis of homologous acids by the Arndt–Eistert method and in the ring contraction reactions for cycloalkanes and their heterocyclic analogues. A detailed description of this problem is outside the scope of the review and we shall confine ourselves to several examples.

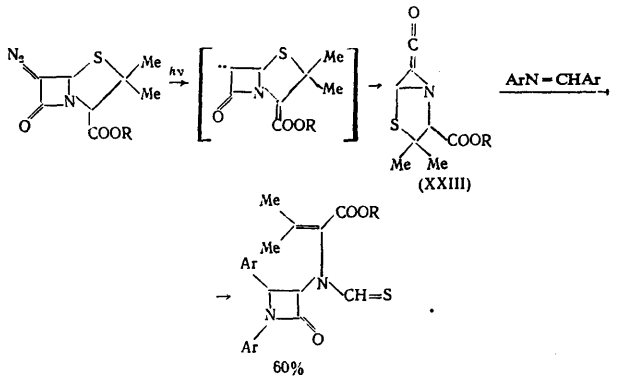
Certain β-lactam antibiotics[124] and their aza-analogues[125] have been synthesised with the aid of the Wolff rearrangement: this method has proved very suitable for the synthesis of a strained β-lactam ring:



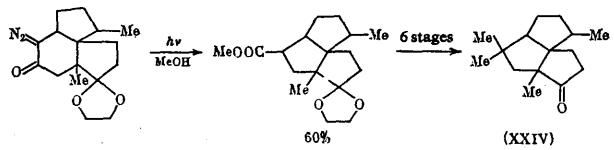
~ 90%

The Wolff rearrangement of a ketocarbene obtained by a non-traditional method[17] has been used, as shown above, for the synthesis of penicillin homologues. The addition of a ketone—the product of the Wolf rearrangement of the amidocarbene (XXIII)—to a Schiff base affords (after the opening of the aziridine ring) new

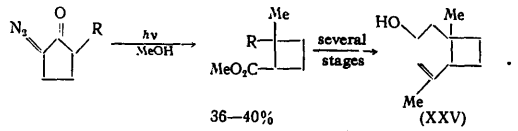
compounds with a β-lactam fragment which are potential antibiotics:[126]



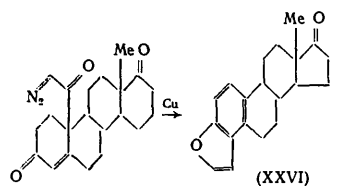
The rearrangement has also been used in the synthesis of 3-oxosilphinine (XXIV):[127]



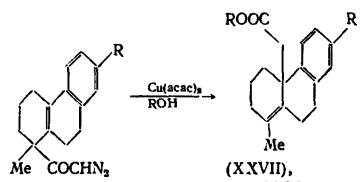
The method of ring contraction with the aid of this rearrangement has proved convenient for the synthesis of precursors of grandisol and fragranol (XXV):[128]



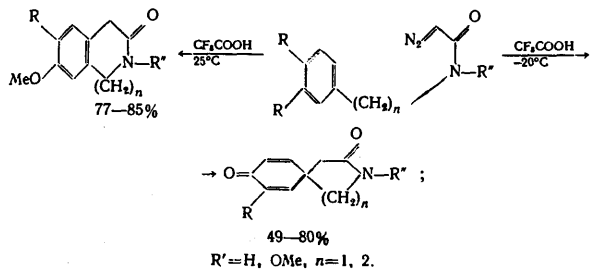
Finally, the vinylogue Wolff rearrangement[129] helped to obtain the modified oestrone (XXVI):



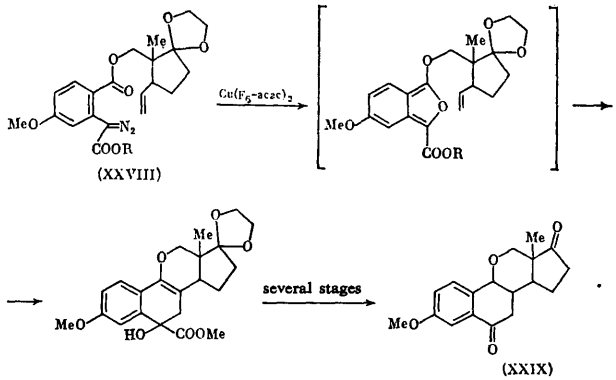
The same reaction can serve as a method of synthesis of angularly substituted polycyclic compounds of type (XXVII):[130]



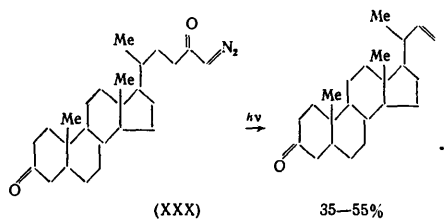
One may note certain other reactions of α-diazocarbonyl compounds, which have been used in the specific synthesis of the structural fragments of natural products and in which either carbonylcarbenes or their synthetic equivalents were involved. Thus the acid-catalysed cyclisation of aromatic diazoacetamides has been used[131] for the synthesis of isoquinolinones and benzazepinones having the structural elements of natural alkaloids:



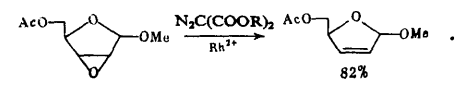
The copper-catalysed decomposition of the diazoester (XXVIII) led[132] to the 6-oxo-11-oxasteroid (XXIX) via the intermediate formation of an isobenzofuran derivative:



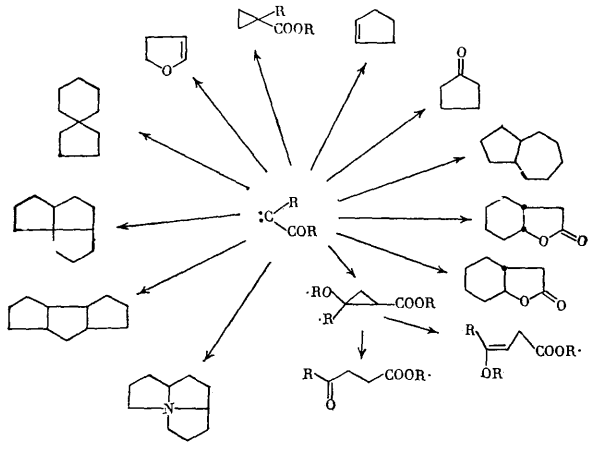
Carbene reactions sometimes play an auxiliary role in the synthesis of natural products. Thus the photolysis of the α-diazoketone (XXX) in the presence of imidazole, leads to the formation of nor-olefins. This method has been used in the degradation of the side chains of bile acids:[133]



Diazomalonic ester has been used to remove the oxiran group protecting a double bond, which has been used in the synthesis of biologically important $\Delta^{2,3}$-nucleosides:[134]



Various structural fragments of natural products, which can be synthesised with the aid of carbonylcarbenes and their synthetic equivalents, are presented in the scheme below:



The wide variety of these structures shows that the chemistry of carbonylcarbenes makes an important contribution to the range of available methods in synthetic organic chemistry.

References

1. W Kirmse *Carbene Chemistry* (Translated into Russian), Izd. Mir, Moscow, 1966
2. M Jones, R A Moss (Editors) *Carbenes*, Wiley, New York, 1973, Vol. 1
3. A P Marchand, N Mac Brockway *Chem. Rev.*, 1974, **74** 431
4. A L Fridman, G S Ismagilova, V A Zalesov, S S Novikov *Usp. Khim.*, 1972, **41**(4) 722 [English translation in *Russ. Chem. Rev.*, 1972(4)]
5. V Dave, E W Warnhof *Organic Reactions* (Edited by W G Dauben), Wiley, New York, 1970, Vol. 18, p. 217
6. S D Burke, P A Grieco *Organic Reactions* (Edited by W G Dauben), Wiley, New York, 1979, Vol. 26, p. 361
7. M P Doyle *Acc. Chem. Res.*, 1986, **19** 348
8. M P Doyle *Chem. Rev.*, 1986, **86** 919
9. D F Taber, J L Schuchardt *J. Am. Chem. Soc.*, 1985, **107** 5289
10. A J Anciaux, A Demonceau, A F Noels, et al. *J. Org. Chem.*, 1981, **46** 873
11. I S Lishanskii, V I Pomerantsev, N G Illarionova, et al. *Zh. Org. Khim.*, 1971, **7** 1803
12. T Aratani, Y Yomyoshi, T Nagase *Tetrahedron Lett.*, 1977, 2599
13. A Demonceau, A F Noels, A J Anciaux, et al. *Bull. Soc. Chim. Belg.*, 1984, **93** 949
14. D A Laidler, D J Milner *J. Organomet. Chem.*, 1984, **270** 121
15. K Kondo, T Takashima, A Negishi *Pestic. Sci.*, 1980, **11** 180; *Chem. Abs.*, 1981, **94** N 102877z
16. T Kametani, S D Chu, A Itoh, et al. *Chem. Commun.*, 1988, 544
17. Y Maki, M Sako, N Kurahashi, et al. *Chem. Commun.*, 1988, 110
18. U Schöllkopf, M Hauptreif, J Dippel, et al. *Angew. Chem.*, 1986, **98** 187
19. R P Short, J-M Reval, B C Ranu, T Hudlicky *J. Org. Chem.*, 1983, **48** 4453
20. V A Nikolaev, I K Korobitsyna *Zh. Vses. Khim. Obshch. im. Mendeleeva*, 1979, **24**(5) 496
21. B M Trost, L S Melvin *Sulfur Ylides. Emerging Synthetic Intermediates. Org. Chem. A Series of Monographs* Acad. Press, New York, 1975, Vol. 31
22. G A Tolstikov, F Z Galin, R G Davletov, V N Iskadarova *Zh. Org. Khim.*, 1983, **19** 1759
23. B J Fitzsimmons, B Fraser-Reid *Tetrahedron*, 1984, **40** 1279
24. H Mack, M Hanack *Angew. Chem.*, 1986, **98** 181
25. A Kh Khusid, O M Nefedov *Zh. Vses. Khim. Obshch. im. Mendeleeva*, 1988, **3**(6) 653
26. T Matsumoto, A Nagai, Y Takahashi *Bull. Chem. Soc. Jpn.*, 1963, **36** 481
27. A Demonceau, A F Noels, A J Anciaux *Bull. Soc. Chim. Belg.*, 1984, **93** 945
28. M Fujita, T Hiyama, K Kondo *Tetrahedron Lett.*, 1986, **27** 2139
29. D V Banthorpe, P N Christou *J. Chem. Soc., Perkin Trans. I*, 1981, 105
30. E I Chen *J. Org. Chem.*, 1984, **49** 3245
31. J R Proudfoot, C Djerassi *J. Chem. Soc, Perkin Trans. I*, 1987, 1283
32. I Wagner, H Musso *Angew. Chem.*, 1983, **95** 827
33. I V Ivanskii, V N Maksimov *Zh. Org. Khim.*, 1972, **8** 52
34. P D Kennewell, S S Matharu, J B Taylor, et al. *J. Chem. Soc., Perkin Trans. I*, 1982, 2563
35. I A D'yakonov, O V Guseva *Zh. Obshch. Khim.*, 1952, **22** 1355
36. I A D'yakonov, N D Pirogova *Zh. Obshch. Khim.*, 1951, **21** 1979
37. I A D'yakonov, O V Guseva *Sbornik Statei po Obshchei Khimii* (Collected Papers on General Chemistry), 1953, Vol. 1, p. 425
38. I A D'yakonov, N B Vinogradova *Zh. Obshch. Khim.*, 1952, **22** 1349
39. T V Mandel'shtam, M I Komendantov *Alifaticheskie Diazosoedineniya v Organicheskom Sinteze* (Aliphatic Diazo-compounds in Organic Synthesis) (Edited by I K Korobitsyna), Izd. Leningr. Gos. Univ., Leningrad, 1985, p. 22
40. W Ando, S Kondo, T Migata *J. Am. Chem. Soc.*, 1969, **91** 6516
41. B T Golding, S Mwesigye-Kibende *Chem. Commun.*, 1983, 1103
42. T V Mandel'shtam, A V Balycheva *Zh. Org. Khim.*, 1983, **19** 232
43. K Yamanoi, Y Ohfune *Tetrahedron Lett.*, 1988, **29** 1181
44. L A Yanovskaya, V A Dombrovskii, A Kh Khusid *Tsiklopropany s Funktsional'nymi Gruppami* (Cyclopropanes with Functional Groups), Izd. Nauka, Moscow, 1980
45. T V Mandel'shtam *Sovremennye Problemy Organicheskoi Khimii* (Modern Problems in Organic Chemistry) (Edited by K A Ogloblin), Izd. Leningr. Gos. Univ., Leningrad, 1987, p. 87
46. A I Ioffe, V A Svyatkin, O M Nefedov *Stroenie Proizvodnykh Tsiklopropana* (The Structure of Cyclopropane Derivatives), Izd. Nauka, Moscow, 1986
47. S Danishefsky *Acc. Chem. Res.*, 1979, **12** 66
48. **H M R Hoffmann, J Rabe** *Angew. Chem.*, 1985, **97** 96

49. T V Mandel'shtam, L D Kristol, L A Bogdanova, T N Ratnikova *Zh. Org. Khim.*, 1968, **4** 992
50. P F Hudrlik, D T W Chou, M A Stephenson *J. Org. Chem.*, 1982, **47** 2987
51. T Hudlicky, S V Govindan, J O Frazier *J. Org. Chem.*, 1985, **50** 4166
52. S Danishefsky, J Regan, R Doehner *J. Org. Chem.*, 1981, **46** 5255
53. D F Taber, K R Krewson, K Raman, A L Rheingold *Tetrahedron Lett.*, 1984, **25** 5283
54. J Adams, M Belley *Tetrahedron Lett.*, 1986, **27** 2075
55. P Callant, H De Wilde, M Vandewalle *Tetrahedron*, 1981, **37** 2079
56. P Callant, R Ongena, M Vandewalle *Tetrahedron*, 1981, **37** 2085
57. E J Corey, J G Reid, A G Myers, R W Hahl *J. Am. Chem. Soc.*, 1987, **109** 918
58. T Ymanishi, F Ninbari, M Yamashita, C Iwata *Chem. Pharm. Bull.*, 1986, **34** 2268
59. A K Singh, R K Bakshi, E J Corey *J. Am. Chem. Soc.*, 1987, **109** 6187
60. J M Hood, L N Mander, R Urech *J. Org. Chem.*, 1984, **49** 3250
61. G A Schiehser, J D White *J. Org. Chem.*, 1980, **45** 1864
62. A R Daniewski, Kowalczyk-Przewlova *J. Org. Chem.*, 1985, **50** 2976
63. J Lafontaine, M Mongrain, L Ruest, et al *Can. J. Chem.*, 1980, **58** 2460
64. E J Corey, C Wiss, Bin Xiang Yi, A K Singh *J. Am. Chem. Soc.*, 1987, **109** 4717
65. D Seebach *Angew. Chem., Int. Ed. Engl.*, 1979, **18** 239
66. E Wenkert *Acc. Chem. Res.*, 1980, **13** 27
67. J P Marino, J K Long *J. Am. Chem. Soc.*, 1988, **110** 7916
68. J P Marino, R F de la Prodilla, E Laborde *J. Org. Chem.*, 1984, **49** 5279
69. J Ollivier, J Salaun *Chem. Commun.*, 1985, 1269
70. J P Marino, E Laborde *J. Am. Chem. Soc.*, 1985, **107** 734
71. J Rokach, J Adams, R Perry *Tetrahedron Lett.*, 1983, **24** 5185
72. J Adams, J Rokach *Tetrahedron Lett.*, 1984, **25** 35
73. Y Leblanc, B J Fitzsimmons, J Adams, et al. *J. Org. Chem.*, 1986, **51** 789
74. V M Shostakovskii, L E Saltykova, A E Vasil'vitskii, O M Nefedov *Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Khimii Karbenov* (Abstracts of Reports at the IV All-Union Conference on the Chemistry of Carbenes), Moscow, 1987, p. 150
75. J Adams, R Frenette, M Belley, et al *J. Am. Chem. Soc.*, 1987, **109** 5432
76. U K Pandit *Heterocycles*, 1977, **6** 1520
77. T Hudlicky *Organic Reactions* (Edited by A S Kende), Wiley, New York, 1985, Vol. 33, p. 247
78. S Hashimoto, T Shinodo, S Kegami *Tetrahedron Lett.*, 1986, **27** 2885
79. P A Wender, C L Hillamann, M J Szymonika *Tetrahedron Lett.*, 1980, **21** 2205
80. L T Scott, M A Minton, M A Kirms *J. Am. Chem. Soc.*, 1980, **102** 6311
81. M Kennedy, M A McKervey *Chem. Commun.*, 1988, 1028
82. M A McKervey, S M Yulander, M F Twohig *Chem. Commun.*, **1984**, 129
83. M S Alonso, P Jano, M Hernandez, et al. *J. Org. Chem.*, **1983**, **48** 3047
84. E Wenkert, M E Alonso, B L Buckwalter, et al. *J. Am. Chem. Soc.*, 1977, **99** 4778
85. E Wenkert, T D J Halls, L D Kwart, et al. *Tetrahedron*, 1981, **37** 3047
86. E Wenkert, M E Alonso, B L Buckwalter, E L Sanchez *J. Am. Chem. Soc.*, 1983, **105** 2021
87. T Kametani, N Kanaya, T Mochizuki, T Honda *Tetrahedron Lett.*, 1983, **24** 221
88. D E Cane, P J Thomas *J. Am. Chem. Soc.*, 1984, **106** 5295
89. B L Buckwalter, I R Burfitt, H Felkin, et al. *J. Am. Chem. Soc.*, 1978, **100** 6445
90. S K Maity, D Mukherjee *Tetrahedron Lett.*, 1983, **24** 5919
91. G Stork, K Makatani *Tetrahedron Lett.*, 1988, **29** 2283
92. H J Monteiro *Tetrahedron Lett.*, 1987, **28** 3459
93. D F Taber, R E Ruckle *Tetrahedron Lett.*, 1985, **26** 3059
94. D F Taber, E H Petty, K Raman *J. Am. Chem. Soc.*, 1985, **107** 196
95. D F Taber, J C Amedio, R G Sherrill *J. Org. Chem.*, 1986, **51** 3382
96. M Hrytsak, T Durst *Chem. Commun.*, 1987, 1150
97. M P Doyle, et al. *J. Org. Chem.*, 1988, **53** 1017
98. D F Taber, R E Ruckle *J. Am. Chem. Soc.*, 1986, **108** 7686
99. M P Doyle et al. *J. Org. Chem.*, 1988, **53** 3384
100. T C Smale *Tetrahedron Lett.*, 1984, **25** 2913
101. E J Corey, A M Felix *J. Am. Chem. Soc.*, 1965, **87** 2518
102. D H R Barton (Editor) *Comprehensive Organic Chemistry* (Russian translation from English edited by N K Kochetkov, M A Chlenov), Izd. Khimiya, Moscow, 1986, Vol. 10, p. 361
103. G Lowe, J Parker *Chem. Commun.*, 1971, 577
104. S K Marry, D Mukherjee *Tetrahedron*, 1984, **40** 757
105. R W Ratcliffe, T N Salzmann, B G Christensen *Tetrahedron Lett.*, 1980, **21** 31
106. J Fetter, K Lempert, T Gizur, et al. *J. Chem. Soc., Perkin Trans. I*, 1986, 221
107. C-P Mak, C Mayerl, H Fliri *Tetrahedron Lett.*, 1983, **24** 347
108. J V Heck, M J Szymonifka, B G Christinsen *Tetrahedron Lett.*, 1982, **23** 1519
109. D J Hart, C. S. Lee, W H Pirkle *J. Am. Chem. Soc.*, 1986, **108** 6054
110. J F Nicoud, H G Kagan *Tetrahedron Lett.*, 1971, 2065
111. E C Taylor, H M L Davies *J. Org. Chem.*, 1984, **49** 113
112. C J Moody, C J Pearson, G Lawton *Tetrahedron Lett.*, 1985, **26** 3171
113. T Kametani, K Kawamura, T Honda *J. Am. Chem. Soc.*, 1987, **109** 3010
114. I Ernest *Tetrahedron*, 1977, **33** 547
115. I Fujimoto, Y Iwano, K Hirai *Bull. Soc. Chem. Jpn.*, 1986, **59** 1887
116. P J Giddings, D I John, E J Thomas *Tetrahedron Lett.*, 1980, **21** 395
117. T Kametani, K Kawamura, M Tsubuki, T Honda *Chem. Commun.*, 1985, 1324
118. T Kametani, K Kawamura, M Tsubuki, T Honda *J. Chem. Soc., Perkin Trans. I*, 1988, 193
119. T Kametani, H Yukawa, T Honda *Chem. Commun.*, 1986, 651
120. T Kametani, et al. *Chem. Commun.*, 1988, 685
121. T Kametani, H Yukawa, T Honda *J. Chem. Soc., Perkin Trans. I*, 1988, 833
122. **M C Pirrung, J A Werner *J. Am. Chem. Soc.*, 1986, 108, 6060**

123. A Padwa, S P Carter, H Nimmesgern, P D Stull *J. Am. Chem. Soc.*, 1988, **110** 2894
124. G Lowe, D D Ridley *Chem. Commun.*, 1973, 328
125. C J Moody, C J Pearson, G Lawton *Tetrahedron Lett.*, 1985, **26** 3167
126. J E Elliot, M M Khalaf, V J Jepheote, et al. *Chem. Commun.*, 1986, 584
127. M Ihara, A Kawaguchi, M Chchiro, et al. *Chem. Commun.*, 1986, 671
128. U K Banerjee, R V Venkateswaran *Tetrahedron Lett.*, 1983, **24** 423
129. J L Mateus, V M Ceronado *Rev. Latinoamer. Quim.*, 1975, **6** 72, quoted after *J. Am. Chem. Soc.*, 1984, **106** 3995
130. B Saha, G Bhattacharjee, U R Ghatan *J. Chem. Soc., Perkin Trans. I*, 1988, 939
131. G M Rishton, M A Schwartz *Tetrahedron Lett.*, 1988, **29** 2643
132. K Hildebrandt, T Debaerdemaeker, W Friedrichsen *Tetrahedron Lett.*, 1988, **29** 2045
133. R Pellicciari, B Natalini, C Cecchetti, S Santucci *Tetrahedron Lett.*, 1984, **25** 3103
134. M G Martin, B Ganem *Tetrahedron Lett.*, 1984, **25** 251

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The present state of the chemistry of aminonitrenes and oxynitrenes

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ABSTRACT. The principal aspects of the chemistry of amino- and oxy-nitrenes—the nitrogen analogues of carbenes in which the sextet of the nitrogen atom is linked to another nitrogen atom or two oxygen—are examined. The available information about the methods of detection, structure, methods of generation, and properties of these usually unstable intermediate species are analysed critically. Attention is concentrated on the comparison of amino- and oxy-nitrenes, their rearrangements, and their interactions with unsaturated compounds.†

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I. Introduction

Vigorous studies on the nitrogen analogues of carbenes—the nitrenes X—N̈: (I)—have led to the creation of a large and rapidly developing field of chemistry.[1,2] The so called heteronitrenes, where the sextet of the nitrogen atom adjoins a heteroatom (see Scriven,[2] Chapter 5) and in the first place aminonitrenes (*N*-nitrenes or 1,1-diazenes) (I, X = R_2N), occupy a special place in this field. It is determined by the important role which aminonitrenes play in numerous reactions of organic hydrazine derivatives[3] and the wide variety of their synthetic applications, in particular for the preparation of *N*-aminoaziridine and other nitrogen heterocycles, which are otherwise difficult to obtain, and new classes of acyclic polynitrogen compounds. This is perhaps the most thoroughly investigated type of nitrenes and therefore special attention will be devoted to it in the present review. Information about the oxygen analogues of aminonitrenes—oxynitrenes (or *O*-nitrenes) (I, X = RO), which are of interest as possible intermediates in reactions of hydroxylamine derivatives, is much more scanty, but data obtained in recent years permit a comparative characterisation of these two types of nitrenes, which was lacking in the previous reviews.

The hypothesis of the existence of aminonitrenes, which arose in the middle of the 1950's (see Ioffe et al.,[3] Chapter 3) received rapid recognition and the last two decades have becomes a period of vigorous development of the chemistry of aminonitrenes. A number of methods for their generation and the variety of their reactions have rapidly increased and the first synthetic applications of the reactions of these unstable species became outlined. At the end of the 1960s, search was begun for evidence indicating the existence of the analogous oxynitrenes, which rapidly led to the successful synthesis of alkoxyaziridines, which stimulated the systematic investigation also of heteronitrenes of this kind. The principal results of this kind have been summarised in monographs[1–3] and a number of reviews.[4–7]

At the end of the 1970s there was a return to a more critical analysis of the accumulated data. A rigorous revision of the results began and more attention began to be paid to the demonstration of the involvement of *N*- or *O*-nitrenes in particular reactions and to the relation between their structure and behaviour. Studies on the reactivity of these nitrenes were concentrated on aspects promising from the synthetic point of view such as reactions with unsaturated groups, including heteroatomic groups, and a wider variety of intermolecular cyclisations. At the same time the search for milder methods for the generation of these species and their new reactions did not cease.

A series of fundamentally important results, which have significantly altered the features of this branch of the chemistry of nitrenes, have been obtained during the past decade. Most of them have not been included in the latest reviews[2,7] and we have therefore endeavoured to survey these data, covering the literature up to the middle of 1987.

II. Structure and properties

1. The results of quantum-chemical calculations

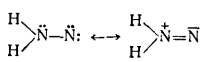
Quantum-chemical calculations have until recently been the only source of information about the structure of amino- and oxy-nitrenes. As a result of the adjoining positions of the heteroatoms with the unshared (lone) electron pairs (LEP), here preference was usually given to non-empirical methods. Furthermore, the incomplete electron cloud to the "nitrene" nitrogen atom requires allowance for configuration interaction in order to obtain reliable results. All these features have sharply complicated the calculations and have virtually restricted them to the simplest molecules, such as aminonitrene itself H_2NN (II) or hydroxynitrene HON. Admittedly, these compounds are incorporated in a kind of "set of tests" for the testing of new bases and new computational schemes and even new results appear annually for these species (see, for example, Decleva and Lisini[8] and the annual bibliography of non-empirical calculations in the "Journal of Molecular Structure"). However, there have been nevertheless few studies of real value to experimental chemists and among them one would wish to mention in the first place calculations of the structure of the simplest aminonitrene (II)

† This article was planned for publication in issue No. 7, 1989, which was devoted to the chemistry of carbenes.

by the general valence bond method taking into account the configuration interaction.[9]

These calculations made it possible for the first time to demonstrate reliably that nitrene (II) has a singlet ground state (S_0). The first triplet state (T_1) has an energy higher by 63 kJ mol^{-1} and the energy of the first excited singlet state (S_1) is higher by 212 kJ mol^{-1},[9] which corresponds to absorption in the visible region of the electronic spectrum at above 560 nm (the $S_0 \rightarrow S_1$ transition). The calculated first ionisation potential is 9.4 eV.[9] The calculated enthalpy of formation of aminonitrene is $\Delta H^{298} = 361$ kJ mol^{-1}, i.e. is higher by 123 kJ mol^{-1} than ΔH^{298} for the isomeric *trans*-HN=NH and is higher by 103 kJ mol^{-1} than ΔH^{298} for *cis*-N_2H_2.[9,10]

In the ground state (S_0), the $H_2N\ddot{N}$: molecule is planar and the nitrogen–nitrogen bond length is 125 pm—a value typical for the N=N bond in azo-compounds. This indicates a decisive contribution of the polar structure (IIb) to the resonance stabilisation of aminonitrene via the transfer of the electron density of the LEP of the amino-nitrogen atom to the unoccupied *p* orbital of the nitrene atom:



(IIa) (IIb)

The large calculated dipole moment of aminonitrene (4D) is entirely consistent with this find, the nitrogen atom constituting the negative end of the dipole.[9]

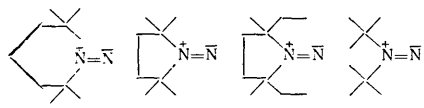
On exciting of the molecular of compound (II), the electron of one of the LEP of the nitrone nitrogen atom is transferred to the unoccupied *p* orbital. As a result, the molecule resembles a hydrazyl radical and the role of resonance stabilisation diminishes sharply. In agreement with this finding, the H_2NN molecule in the T_1 state is no longer planar (although the barrier to the inversion of the amino-nitrogen atom is only 0.8 kJ mol^{-1}), while the equilibrium N–N bond length increases to 137 pm.[9] At the same time it is nevertheless shorter than the N–N single bond in hydrazines (145 pm [3]); together with the appreciable dipole moment (2.35 D), this shows that in the triplet state of the nitrene (II), the LEP of the amino-nitrogen atom is appreciably delocalised. Similar changes in geometry occur also in $S_0 \rightarrow S_1$ transition.[9]

The calculated N–H bond energy is 180 kJ mol^{-1},[10] which makes it possible to estimate the C–N bond strength in substituted aminonitrenes as ~100 kJ mol^{-1}. Aminonitrenes should therefore be comparatively resistant to decomposition with rupture of the N–H or C–N bond which gives rise to the hope that they may be detected and identified.

2. The synthesis and properties of stable aminonitrenes

One of the ways of stabilising unstable intermediate species such as carbenes or nitrenes is their binding in complexes. At the beginning of the 1970s, the first complexes of *N*-nitrenes, including also the simplest aminonitrene (II),[11] with tungsten and molybdenum ions, were already discovered. Later complexes of aminonitrenes were obtained with rhenium, niobium, and tantalum,[12,16] as well as a series of iron-porphyrin complexes.[17,18] As a rule, these are very stable compounds and the properties of the aminonitrenes bound in them should naturally differ appreciably from those of the free species.

However, it was found that aminonitrenes can be detected in a state other than the complexes. As early as 1978, immediately after the calculations of Davis and Goddard,[9] a series of studies began to be published[19–26] on this synthesis (specifically the synthesis) and properties of stable aminonitrenes. It was shown that, when there are tertiary substituents at the amino-nitrogen atom, the dialkyl-aminonitrenes (III)–(VI), relatively stable at low temperatures, can be obtained by the classical method—the oxidation of the corresponding 1,1-disubstituted hydrazines by t-butyl hypochlorite in the presence of triethylamine[19–21,23–26] or active nickel peroxide:[226]



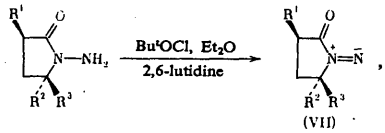
(III) (IV) (V) (VI)

cis (a), *trans* (b)

Bright crimson or purple solutions of the nitrenes (III)–(V) in ether are stable at –78 °C for several days and at –85 °C they can be actually purified by chromatography on Al_2O_3. However, they decompose rapidly on raising the temperature to 0 °C. The nitrene (VI) can be stored only at –127 °C, decomposing rapidly even at –90 °C.[25] The comparative stability of these compounds can be accounted for by the presence of the bulky tertiary substituents which prevent both intermolecular reactions (dimerisation to tetrazenes) and intramolecular reactions (for example rearrangement to hydrazones).

The structure of the *N*-nitrenes (III)–(VI) has been unambiguously demonstrated by a set of spectroscopic characteristics (Table 1), which demonstrate agreement with calculated data,[9] as well as by their reactions on raising the temperature (decomposition, dimerisation to tetrazenes), which are entirely similar to the familiar reactions of unstable dialkylaminonitrenes (see also Section IV). Indeed, in agreement with predictions,[9] the nitrenes (III)–(VI) have a broad absorption band with a fine structure in the visible region. The low intensity of this band and its hypsochromic shift following an increase in the polarity of the solvent agree with its assignment to the $n-\pi^*$ transition in the $\rangle\overset{+}{N}=\overline{N}$ chromophore, isoelectronic with the carbonyl group, while the position of the transition between the zero-point vibrational levels (λ_{0-0}) agrees well with the calculated estimate (~560 nm [9]). The marked difference between the electronic absorption and fluorescence spectra indicates a marked change in the equilibrium geometry, also predicted by calculations,[9] on transition from the ground (S_0) to the first excited singlet state (S_1). The high frequency of the ν(N–N) vibrations in the IR spectra (the assignment of the band has been confirmed by isotope substitution), which actually exceeds somewhat the usual frequency of the N=N double bond vibrations (1574 cm^{-1} in azomethane) agrees with the conclusion[9] that the nitrogen–nitrogen bond in the simplest aminonitrene has a significant double bond character. The frequency ν(N–N) in the IR spectra then virtually agrees with the fine structure interval in the fluorescence spectra of compounds (IV) and (V), which constitutes additional confirmation of the assignment. It is remarkable that, on passing from the six-membered amino-nitrene (III) to the five-membered aminonitrenes (IV) and (V), the characteristics of the IR and the electronic spectra change in the same way as for the isoelectronic cyclohexanone and cyclopentanone derivatives.[24] The structure of the hydrocarbon substituents in compounds (III)–(VI) follows from their ^{1}H NMR spectra, while the unusual character of the nitrene nitrogen atoms is reflected in the enormous value of its chemical shift (δ = 917 p.p.m.) in the ^{15}N NMR spectrum of the nitrene (III).

The even more stable cyclic acylaminonitrenes (VII) were synthesised by the same method in 1984:[27,28]



R^1=H, R^2=R^3=Ph (a);
R^1=H, R^2=Me, R^3=Ph (b);
R^1=Me, R^2=Ph, R^3=Me (c);
R^1=Me, R^2=Me, R^3=Ph (d);
R^1=R^2=H, R^3=Ph (e).

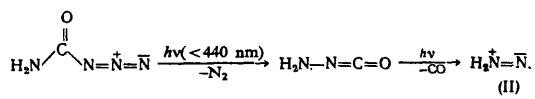
Compounds (VIIa–d) are stable in solutions at room temperature for several days and even weeks, but the nitrene (VIIe), having a hydrogen atom in the α-position, isomerises rapidly under these conditions to the corresponding tetrahydropyridazinone (see Section IV).

Table 1. The properties of the nitrenes (II)–(VII).

Compound	Electronic absorption spectrum: λ_{max} ($\lambda_{0\text{-}0}$), nm	Fluorescence spectrum (−196 °C): $\lambda_{0\text{-}0}$, nm	ν(N–N), cm^{-1}	$E^{\ddagger}_{decomp}$, kJ mol^{-1}
(II)	636	—	1574	—
(III)	543* (620)	684	1595	80—84
(IV)	497* (572)	607	1638	80—84
(V)	507* (568)	620	1630	80—84
(VI)	506	715	—	54
(VIIb)	520**	—	—	122

* $\varepsilon_{max} \simeq 18-20$.
** $\varepsilon_{max} \simeq 90$.

Finally, in 1984 it was possible to detect in a matrix and to characterise by IR and UV spectroscopy (see Table 1) also the simplest aminonitrene (II),[29] generated by the photolysis of the azide of carbamic acid (the Curtius rearrangement):



The isotopomers of the nitrenes (II) with two deuterium atoms and a nitrene ^{15}N were obtained in the same study, which made it possible to confirm the assignment of the IR bands, in particular the ν(N=N) band, whose frequency (1574 cm^{-1}) is much higher than for the isomeric *trans*-diazene HN=NH [ν(N=N) = 1529 cm^{-1} in the Raman spectrum[29]]. The spectroscopic properties of compound (II) fit one series with the properties of the substituted aminonitrenes (III)–(VI) (see Table 1) and agree well with the calculated estimates.[9] However, they differ sharply from Wiberg's "isodiazene",[30,31] to which the structure (II) was also attributed. According to the set of available data, Wiberg's report of the detection of the nitrene (II) on decomposition of the caesium salt of toluene-*p*-sulphonic acid hydrazide should probably be regarded as erroneous.

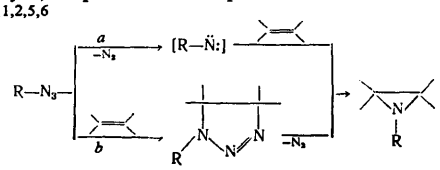
III. Methods of generation

The reactions in which the formation of amino- and oxy-nitrenes has been postulated are very numerous,[3–7] but the oxidation of 1,1-disubstituted hydrazines and alkoxyamines is most often employed for the generation of these species. The alkaline cleavage or thermolysis of the corresponding sulphonamides, the decomposition of sulphimines and sulphoximines, a series of cheletropic reactions, in particular the decomposition of *N*-aminoaziridines, and incomplete reduction of nitrosamines are of considerable interest. The neutralisation of the corresponding diazenium salts is a convenient method for the generation of dialkylaminonitrenes.[3]

The hypothesis of the existence of aminonitrenes was put forward initially to account for the so-called "anomalous" (with evolution of nitrogen and the formation of hydrocarbons) oxidation of 1,1-disubstituted hydrazines. The "anomalous" reduction of nitrosamines and the decomposition of sulphonic acid hydrazides was almost immediately included in this group of reactions. The similarity of the products of these reactions suggested a common intermediate—aminonitrene. Admittedly, the involvement of aminonitrenes in the normal course of these processes remained debatable. The next landmark was the stereospecific synthesis of *N*-aminoaziridine derivatives by the oxidation of a whole series of hydrazines in the presence of alkenes (see Section IV)—by analogy with the chemistry of carbenes, this was explained by the intermediate generation of aminonitrenes and their addition to the C=C bond. Naturally, the synthesis of *N*-alkoxyaziridines via the oxidation of *N*-alkoxyamines in the presence of alkenes, which soon followed, was immediately regarded as proof of the oxidative generation of alkoxynitrenes. Finally, the formation of a whole series of aminonitrenes in oxidation reactions was recently convincingly demonstrated by spectroscopic methods.

Hitherto, the main piece of evidence for the involvement of amino- or oxy-nitrenes in the reaction has usually been the similarity of the products of the given reaction to those of others for which the nitrene mechanism has already been established. Even more remote analogies are sometimes employed, for example, the analogy with the rules governing the occurrence of carbene reactions (Skell's postulate is usually invoked). Having demonstrated the nitrene mechanism of the reaction in relation to 1–2 examples, it is then usually subsequently extended to other similar reactions.

Such reasoning is entirely natural and acceptable in practice. However, it is at the same time extremely vulnerable. Indeed, it is actually clear that for the same process mechanism the composition of the products depends markedly on the specific reaction conditions: the method of generation of the nitrene, temperature, solvent, the presence of oxidants and reductants, the pH of the medium, etc. In order to compare the results, it is therefore necessary to resort in this instance to fairly bold extrapolations. On the other hand, typical "nitrene" products can sometimes be obtained without any involvement of nitrenes. A classical example is provided by the interaction of azides with alkenes, where, depending on the reaction conditions, aziridines can be formed both via nitrenes (pathway *a*) and wholly via the "azide" mechanism, as a result of the decomposition of the primary 1,3-dipolar addition products—2-triazolines (pathway *b*):[1,2,5,6]



Thus unambiguous demonstration of the nitrene mechanism of the reaction requires the consideration of very many of its aspects, in the first place a set of kinetic data. There have so far been few such studies in the chemistry of amino- and oxy-nitrenes and we usually deal merely with the hypothesis of the involvement of nitrenes in the reaction, which is not always sufficiently well founded. The data described below should be considered from precisely this point of view.

1. Oxidation of amino-compounds

Historically the first[3-6] and hitherto the most convenient and most widely used method for the generation of amino- and oxy-nitrenes (I) is the oxidation of corresponding hydrazines or hydroxylamines:

$$X{-}NH_2 \xrightarrow[-HY]{YZ} \left[X{-}N\begin{matrix}Z\\H\end{matrix}\right] \xrightarrow{-HZ} X{-}\ddot{N}: \quad ; \qquad (1)$$

(VIII) (I)

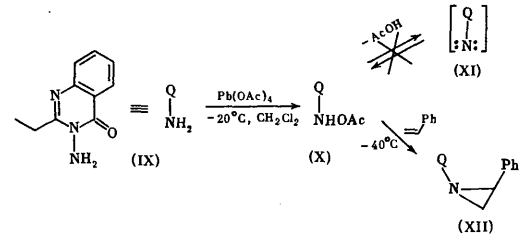
X=R_2N, RO.

The assortment of oxidants employed is extremely wide,[3-7] but the lion's share of the results have been obtained using 2–3 most popular reagents. Yellow mercury oxide was usually employed in the early studies. Nowadays lead tetraacetate (LTA), t-butylhypochlorite, and nickel peroxide are most often used.

The formation of the nitrenes (I) in a whole series of oxidation reactions has been demonstrated extremely reliably—it is sufficient to recall that stable aminonitrenes have been obtained by precisely this procedure (see above). However, we may note that, according to Eqn. (1), the oxidative generation of nitrenes should include at least two stages: the formation of the intermediate compound (VIII) and the subsequent α-elimination of HZ. The nature of the group Z is determined by the oxidant and it is evident that, depending on its leaving capacity, the tendency of the molecule of compound (VIII) to undergo α-decomposition varies significantly. In principle, the intermediate (VIII) may prove to be fairly stable and can participate in subsequent reactions without decomposing to the nitrene.[3] It is sometimes fairly difficult to distinguish reactions proceeding via the nitrenes (I) from reactions involving their precursors (VIII).

This problem has already been discussed in the literature.[3,32] In particular, it has been noted that, for certain oxidants the reactions with 1,1-disubstituted hydrazines afford only a small amount of the usual aminonitrene conversion products (hydrocarbons, hydrazones, etc.) and sometimes they are altogether absent. Such a discrepancy (the dependence of the results on the nature of the oxidant) clearly indicates a decisive role of the first oxidation stage. The oxidation of 1,1-disubstituted hydrazines by derivatives of tetravalent selenium may serve as an example.[33,34] According to the authors, intermediate compounds of type (VIII) with a N–Se bond are formed during this reaction but the process does not go as far as the formation of aminonitrenes.

The case where the reactions of the nitrene precursor (VIII) resemble those expected for the nitrene itself is much more insidious and unexpected. Thus a communication has been published recently stating that the low-temperature oxidation of *N*-aminoquinazolinone (IX) by LTA, i.e. under the "standard" conditions for the generation of amino- and alkoxy-nitrenes, affords almost quantitatively the *N*-acetoxy-derivative (X), which is stable in solution up to ~0 °C.[35] However, even at –40 °C the addition of styrene (1.5 equiv.) to this solution leads to the rapid disappearance of compound (X) and the formation of the *syn*-invertometer of the aziridine (XII) in 76% yield, which has always been regarded as typical for the corresponding aminonitrene (XI):



Furthermore, the involvement of the nitrene (XI) or the nitrenium ion, which are intermediates in equilibrium with compound (X), in the reaction is ruled out because neither the NH proton nor the acetoxy-group are exchanged in CF_3COOD, while the hypothesis of the non-equilibrium generation of the nitrene (XI) with its subsequent addition to the double bond conflicts with the observed dependence of the rate of disappearance of the acetoxy-derivative (X) on the alkene concentration.[35]

Hitherto the oxidation of amino-compounds by LTA was regarded as one of the most reliable methods for the generation of most varied nitrenes and the principal piece of evidence was in fact the stereospecific formation of the corresponding aziridine derivatives in the presence of alkenes. An alternative interpretation has now appeared: since the acetoxy-derivative of type (X) is in essence the nitrogen analogue of peracetic acid, the formation of aziridines can be treated similarly to the epoxidation of alkenes by peracids, which is incidentally also stereospecific. Evidently the non-trivial results of Atkinson and Kelly[35] require a critical analysis of the mechanism of not only the formation of aziridines but also of a whole series of seemingly typical "nitrenes" reactions.

It is remarkable that intermediates of the non-nitrene type in the oxidation of hydrazine by LTA had already been sought earlier[36] but it had been assumed that they must be compounds of the type X–NH–$Pb(OAc)_3$. For the oxidation of *N*-aminopyrrole derivatives by LTA and lead tetrabenzoate, on the one hand, or by $PhI(OAc)_2$ and $PhI(OCOCHCl_2)_2$, on the other, it was then shown that the results are almost independent of the type of oxidant and hence the involvement of a lead-containing compound in the rate-determining state of the reaction is unlikely.[36] An *N*-acetoxy-compound of type (X) also occurred more than 10 years ago in the mechanism of the oxidation of *N*-aminophthalimide by LTA [37] but it was assumed that it is obtained as a transient formation as a result of a side process—the interaction of phthalimidonitrene with acetic acid, and that it does not play a significant role in this reaction.

In conclusion of the discussion of the study of Atkinson and Kelly,[35] one must state that its results by no means rule out the possibility of the formation of nitrenes of type (XI) in the oxidation of the corresponding amino-compounds—in fact acylaminonitrenes (VII) are obtained by precisely this procedure. However, they indicate that the acetoxy-group leaves the molecule of the nitrene precursor (VIII) extremely unwillingly and, in order to direct the reaction precisely along the aminonitrene pathway, it is best to use not LTA but another oxidant, for example t-butyl hypochlorite.

Apart from studies using the traditional range of oxidants, a number of communications have appeared in recent years concerning the oxidative generation of aminonitrenes under new conditions, in particular, in the electrochemical oxidation of certain hydrazines.[38,39] The formation of aminonitrenes has been postulated in the oxidation

of 1,1-disubstituted hydrazines by oxygen,[40] nitrogen dioxide,[41] and nitrobenzene[42] and also in the pyrolysis of 2,2-dimethyltriazanium chloride,[43] the result of which can be regarded as an intramolecular oxidation-reduction reaction. However, in all these cases one is dealing merely with hypotheses while reliable evidence for the intermediate formation of *N*-nitrenes in the above investigations[40–43] is lacking.

2. Decomposition of sulphonic acid derivatives and other methods

A second general method for the generation of amino- and oxy-nitrenes is the alkaline decomposition of the corresponding sulphonamides:[3–7]

$$XNHSO_2R' \xrightarrow[\Delta]{B^-} \underset{(I)}{X{-}\ddot{N}:} + BH + R'SO_2^-;$$

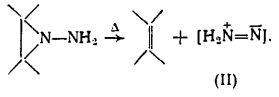
$$X = R_2N,\ RO;\quad R' = Me,\ Ph,\ p\text{-}MeC_6H_4.$$

This procedure is especially suitable for the generation of the nitrenes (I) at a high temperature.[3–7,32,44] The high-temperature decomposition of the sulphonic acid hydrazides themselves[45] as well as the thermolysis of dry salts of the type R_2NNMSO_2R', where M is an alkali metal,[46,47] are variants of this method. It has been claimed that the last reaction is one of the "cleanest" methods of generating aminonitrenes.[47]

The reactions discussed above exhaust the known methods for the preparation of *O*-nitrenes. The approaches used to obtain *N*-nitrenes are significantly more varied[3,7] but the applicability of many of them is extremely limited. Thus the formation of aminonitrenes in the reduction of nitrosamines[3] is evidently an exception rather than the rule: typical "aminonitrene" reactions are observed in this instance mainly when sodium hydrogen sulphite is used as the reductant but even then not always:[3,32]

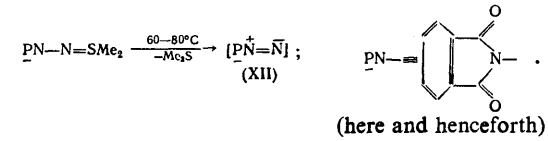
$$R_2N{-}NO \xrightarrow[OH^-]{Na_2S_2O_4} R_2N{-}\ddot{N}:$$

In the remaining cases the participation of aminonitrenes in the reaction must be postulated with much caution[48] and their presence in complex mechanisms of the reactions of a wide variety of nitrosamines[49–51] bears in our view a formal character in many respects. The possibility of the formation of the simplest amino-nitrene (II) in the thermolysis of a number of *N*-aminoaziridines is purely tentative,[52] although here one may note that the generation of acylaminonitrenes by the thermolysis and photolysis of the corresponding substituted derivatives has already been described in the literature:[3]



(II)

Few new methods for the generation of aminonitrenes have appeared during the last decade. In 1979 it was suggested that phthalimidonitrene (XII), perhaps the most thoroughly investigated aminonitrene, be generated by decomposing its adduct with Me_2S at a comparatively low temperature:[53]

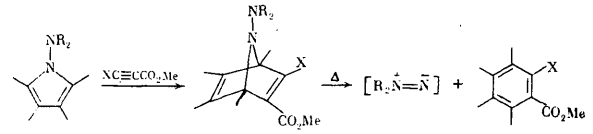


(XII)

(here and henceforth)

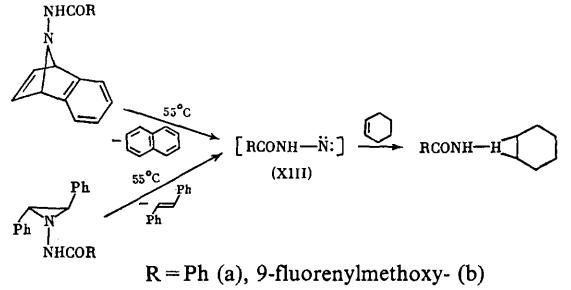
This method of generation makes it possible to obtain adducts of the nitrene (XII), which are sensitive to strong heating, oxidants, or acids. In particular, it has been possible to obtain aziridine in the reaction with *p*-methoxystyrene by this procedure.[54]

The intermediate formation of *N*-nitrenes in the reactions of various *N*-aminopyrroles with electron-deficient acetylenes has been postulated:[55–57]



R = H, Me, $PhCH_2$; R_2N = $NHCO_2Me$, $N(CH_2CH_2)_2O$; X = CO_2Me, SO_2Ph.

Subsequently a similar reaction was used to obtain acylamino-nitrenes (XIII) [58] and here it proved possible to observe for the first time an intermolecular reaction of monosubstituted nitrenes:



(XIII)

R = Ph (a), 9-fluorenylmethoxy- (b)

In addition, the nitrene (XIIIb) has been obtained also by a more traditional method—the decomposition of the corresponding 2,3-diphenylaziridine.[58]

IV. Reactions of amino- and oxy-nitrenes

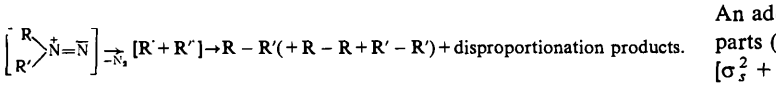
The known reactions of amino- and oxy-nitrenes can be divided into three large groups: decomposition, isomerisation, and addition to double bonds or unshared electron pairs. The occurrence of the reaction via a particular pathway is determined in the first place by the structure of the nitrene. Decomposition has been observed so far only for aminonitrenes and its driving force is evidently the formation of the stable nitrogen molecule. The presence of substituents of the benzyl or allyl type at the amino-nitrogen atom makes decomposition the principal reaction pathway. The tendency of amino- and oxy-nitrenes to undergo rearrangements with migration of groups to an atom with an incomplete electron shell is determined in many respects by the migrating capacity of the substituents. Finally, if the nitrene is relatively stable in relation to intermolecular reactions, then, in the presence of a suitable reagent in the reaction mixture, it can add to multiple bonds or can attack an unshared electron pair with formation of the corresponding adducts.

All these processes usually occur simultaneously and the contribution of each is determined additionally by the reaction conditions and the comparative reactivities of the components of the reaction mixture. An increase in temperature usually increases the contribution by fragmentation and rearrangement processes. On the other hand, the addition of a large excess of active nitrene "trapping" agents, such as dimethyl sulphoxide (DMSO), makes it

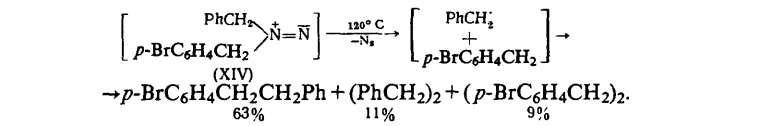
possible to obtain adducts even for nitrenes which usually tend to undergo rearrangements or decomposition.

1. Decomposition of aminonitrenes

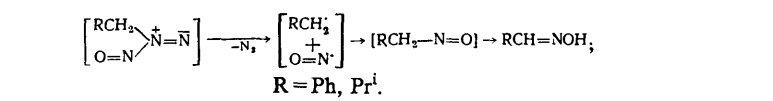
Decomposition with evolution of nitrogen is one of the most general reactions of aminonitrenes for the most varied methods of their generation. The ease of their decomposition and its mechanism depend significantly on the structure of the nitrene, but in most cases the available data fit satisfactorily within the framework of the biradical mechanism with a strong cage effect, which increases the stereospecificity of the reaction:[3,46,47]



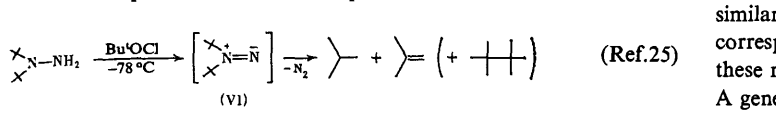
The decomposition with the recombination of the radicals formed is most typical for dibenzylaminonitrene derivatives. It is, on the one hand, a convenient method of synthesis of bibenzyl derivatives[3] and, on the other hand, it is a kind of diagnostic test for the aminonitrene reaction mechanism.[32,39,42,46,47,55] The radical decomposition of dibenzylaminonitrene has been demonstrated reliably by EPR methods using "spin trapping agents"[46] and CINP [47] and it has been established that dibenzylaminonitrene produces a singlet radical pair and therefore decomposes in the singlet state, which is apparently the ground state[47] (cf. the calculations of Davis and Goddard[9]). The decomposition of the asymmetrically substituted nitrene (XIV) confirmed the major role of the cage effect, but, in contrast to the earlier study,[3] the cross-products,[47] obtained when the radicals emerge from the cage into the solution, were isolated in an appreciable yield:



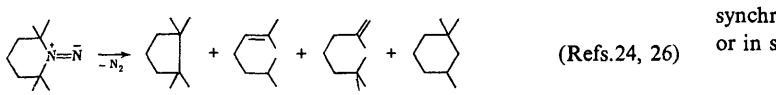
Ready decomposition with recombination of the species formed is characteristic of many other aminonitrenes having substituents at the amino-nitrogen atom which give rise to fairly stable radicals.[3] For example, the decomposition of nitrosaminonitrenes proceeds via this mechanism:[59]



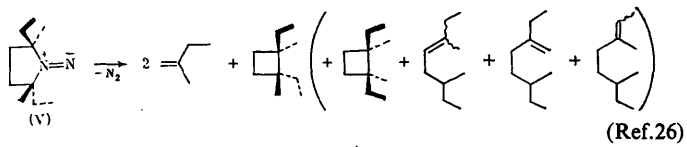
On passing to alkyl-substituted aminonitrenes, the main pathway becomes the disproportionation of their radicals,[25] while the decomposition of cyclic *N*-nitrenes[19–21,23,24,26–28,45] usually leads to a mixture of products of these two processes:



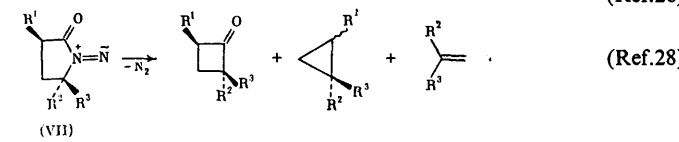
(Ref.25)



(Refs.24, 26)

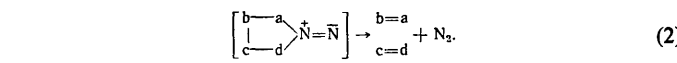


(Ref.26)



(Ref.28)

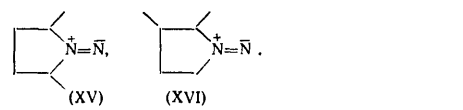
An additional possibility of concerted fragmentation into three parts (β-decomposition) via Scheme 2, symmetry-allowed as a $[\sigma_s^2 + \sigma_s^2 + \sigma_s^2]$ process, appears for five-membered aminonitrenes under these conditions:



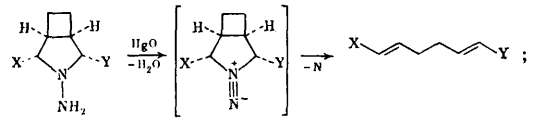
(2)

On the other hand, such decomposition can be treated also as a result of the cleavage of the central bond in the intermediate 1,4-biradical.

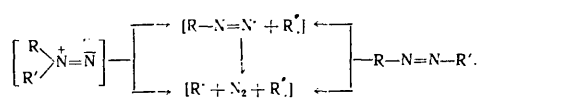
The study of the thermal and photochemical decomposition of a large series of five-membered *N*-nitrenes,[21,24,27,28] including the "stereochemically labelled" nitrenes (V) and (VIIc, d) and the *cis*- and *trans*-isomers of the nitrenes (XV) and (XVI),[45] showed that the main reaction pathways usually involve the formation of cyclobutane derivatives and β-elimination, both processes occurring highly stereospecifically with preferential retention of the relative disposition of the substituents:



The stereospecificity of the β-decomposition is especially high (> 96%),[45] which has been used in the synthesis of a series of long-chain (*E*, *E*)-1,5-dienes:[60]

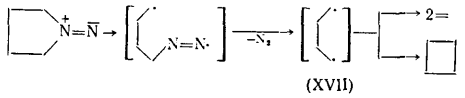


The composition and stereochemistry of the products of the thermolysis and direct photolysis of aminonitrenes are extremely similar and also resemble the outcome of the decomposition of the corresponding azo-compounds, which suggests the involvement in these reactions of common intermediate species of a radical type. A general question also arises: how are these radicals formed—synchronously, with the simultaneous cleavage of both C–N bonds, or in stages?



Computational assessment of both possibilities for the aminonitrene (II) itself,[10] diethylaminonitrene,[61] and the corresponding azo-compounds[10,61,62] has indicated in all cases that the multistage process with the intermediate formation of diazenyl radicals is preferred. This pathway agrees with experimental data for the fragmentation of azo-compounds[61,62] and in principle does not conflict with the results of studies of the decomposition of many aminonitrenes.[19-21,23-28,45] However, according to Savin,[47] the benzyldiazenyl radical is not formed as a kinetically independent species in the decomposition of dibenzylaminonitrene and both C–N bonds are therefore cleaved synchronously. This is apparently associated with the high stability of the benzyl radicals obtained, which is responsible for the sharp decrease in the strength of the C–N bonds in the aminonitrene which are weak in any case.

In any case, the decomposition of the five-membered aminonitrenes (and the corresponding azo-compounds) via the radical-mechanism should proceed via a derivative of the biradical (XVII) (tetramethylene):



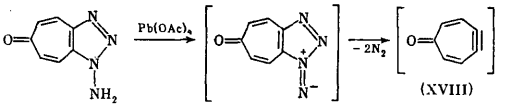
(XVII) (3)

However, a non-empirical calculation for tetramethylene yielded remarkable results: it was found that, instead of a minimum a kind of "plateau" on the energy surface corresponds to this 1,4-biradical.[63] Consequently, if one disregards entropy factors, this is not an intermediate compound but a transition state and processes with its participation can be regarded as "quasi-concerted". According to calculated data, the fate of tetramethylene depends on its geometry: the *gauche*-conformer cyclises while the *anti*-conformer undergoes non-activated decomposition into two ethylene molecules.[63]

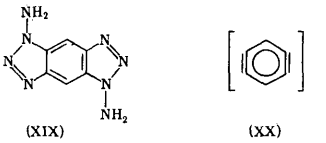
Taking into account the foregoing as well as kinetic and stereochemical data,[20,21,23,24,26-28,45] the decomposition of five-membered cyclic aminonitrenes presumably proceeds via two parallel channels:[45] as concerted β-decomposition via Scheme 2, with complete retention of the configuration of the substituents in the reaction products, and as a multistage process of type (3), which begins with the formation of the diazenyl biradical. In the absence of substituents capable of stabilising the biradical of the tetramethylene type, the subsequent cyclisation or decomposition of the latter should take place almost simultaneously with the elimination of the nitrogen molecule. The contribution of each pathway is determined by the nature of the substituents. Thus unsubstituted pyrrolidinonitrene apparently decomposes wholly via the concerted pathway into nitrogen and ethylene (although, contrary to old data, approximately 2% of cyclobutane was detected in the products[45]), while the introduction of alkyl and even more so aryl substituents in the 2- and 5-positions favours the radical process.

The usual consequence of the radical mechanism is a low stereospecificity of the reaction, but the fragmentation of aminonitrenes and of the corresponding azo-compounds represents a clear exception. The cyclisation and β-decomposition of the biradical intermediates (whatever their structure) is apparently appreciably faster in this instance than the rotation around the C–C single bonds. As was to be expected, with increase in temperature there is an increase in the fraction of the β-elimination products and the stereospecificity of the decomposition is reduced.[45] Similar changes occur on passing from the direct photolysis of stable aminonitrenes and azo-compounds to the sensitised photolysis,[26] which can be naturally accounted for by the involvement of triplet biradical species in the process.

The fragmentation of unsaturated 1-(1,2,3-triazolyl)nitrenes via Scheme 2 has found wide scale application for the generation of aromatic dehydrohydrocarbons and other unstable acetylene derivatives.[3] It has been used in recent years to obtain 4,5-dehydrotropone (XVIII) and its adducts with dienes[64,69] or enamines.[70]

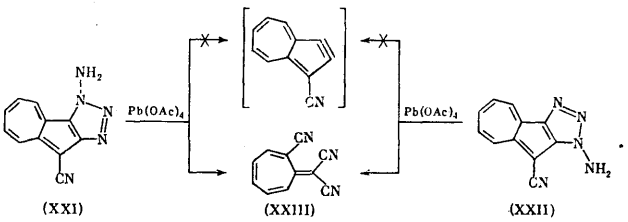


(XVIII)



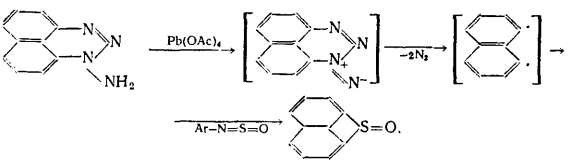
(XIX) (XX)

Similarly, 1,5-diaminobenzobistriazole (XIX) (and its 1,7-isomer) is an excellent synthetic equivalent of "1,4-dibenzyne" (XX) in 1,3- and 1,4-cycloaddition reactions (the yields of the diadducts are 40–93%);[71-73] however, when an attempt is made to obtain the corresponding dehydroazulene from the aminoazulenotriazoles (XXI) or (XXII) via the same scheme, only the rearrangement product (see below—the heptafulvene (XXIII)—is isolated:[74]

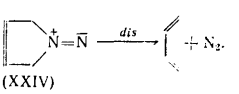


(XXI) (XXIII) (XXII)

A similar reaction has been used to generate 1,8-dehydronaphthalene:[75]



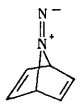
A concerted cheletropic decomposition is allowed for 3-pyrroline derivatives of type (XXIV) and it has been shown for a whole series of examples that, in conformity with the Woodward–Hoffmann rules, this process is indeed disrotatory and is fully stereospecific:[3]



(XXIV)

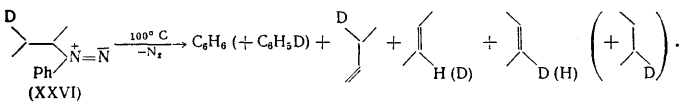
The results of recent calculations[76] have confirmed the possibility of the concerted decomposition of the nitrene (XXIV), but they predict a highly asymmetric transition state for this reaction (the process is concerted but not synchronous). The calculations permit a synchronous or almost synchronous fragmentation only for the

nitrene (XXV),[77] but, in Dewar's view, this exception merely confirmed the general conclusion that the transition state in cheletropic reactions is asymmetric:[76,77]



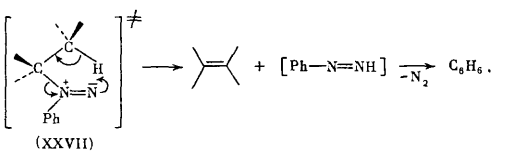
(XXV)

The study of the decomposition of the diastereoisomeric (*threo-* and *erythro-*) deuterio-substituted aminonitrenes (XXVI)[44] showed that this process proceeds highly stereospecifically as *cis*-1,2-elimination:



(XXVI)

In each case deuterium remains in only one of the two-isomeric but-2-enes, which can be explained by proton transfer to the nitrene nitrogen atom in the transition state (XXVII). This resembles the mechanism of the fragmentation of amine oxides:[44]

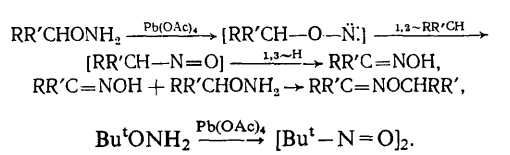


(XXVII)

Thus the concerted (but not biradical) decomposition of amino-nitrenes is possible also in the acyclic series.

2. Rearrangements

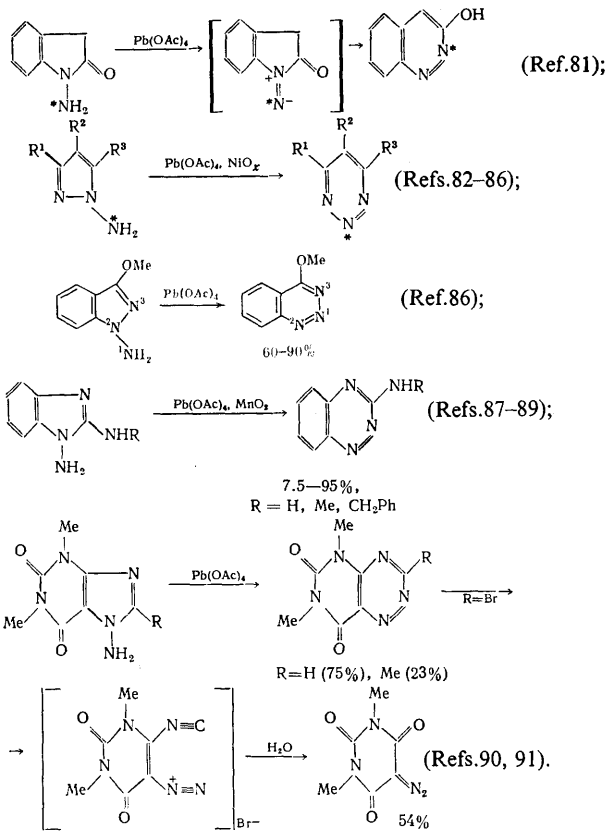
Rearrangements, including the 1,2-migration of substituents to the atom with an incomplete electron shell, are characteristic of all the sextet species, including amino- and oxy-nitrenes. For alkoxy-nitrenes, this is the cause of the permanent presence in the reaction mixtures of oximes, their ethers, and nitroso-compounds:[78,79]



The yields of the oxime ethers are 16–32% and that of the dimer of the tertiary nitroso-compound is up to 57%.

The corresponding conversion of the simplest aminonitrene (II) to the significantly more stable (by 123 kJ mol^{-1} [9]) *trans*-diazene HN=NH is symmetry-prohibited[80] but nevertheless the *trans*-diazene is one of the nitrene(II) reaction products already at 90 K.[29] On the other hand, the 1,2-migration of the alkyl group with inversion at the migrating centre is already an allowed process for dialkylaminonitrenes, but unambiguous examples of the rearrangement of dialkylaminonitrenes to aliphatic azo-compounds are not as yet available in the literature. On the other hand, a whole series of conversion of *N*-heteroarylnitrenes to the corresponding azo-compounds with ring expansion are known; many of them are of preparative value.[3] Here an additional driving force is the formation of a stable aromatic system.

Thus, cinnolinol has been obtained by oxidising *N*-amino-oxindole,[3,81] compounds of the 1,2,3-triazine series have been synthesised from *N*-aminopyrazoles[82–86] and indazoles,[86] while substituted 1,2-diaminobenzimidazoles[87–89] and theophylline derivatives[90,91] can be converted into the corresponding 1,2,4-tri-azines:

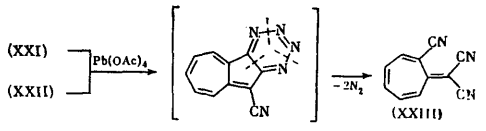


(Ref.81); (Refs.82–86); (Ref.86); (Refs.87–89); (Refs.90, 91).

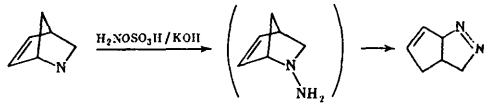
Best results are achieved as a rule by oxidising amino-compounds with LTA—the yields of 1,2,3-triazines are then usually 40–80%. However, 1-aminopyrazole itself affords only about 2% of 1,2,3-triazine when LTA is used,[85] although the yield increases to 20% on oxidation with nickel peroxide.[83–85] Such dependence of the yield on the nature of the oxidant, particularly when account is taken of the possible role of *N*-acetoxy-compounds in the oxidation of amino-compounds by LTA,[35] clearly requires a revision of the degree of involvement of aminonitrenes in the reactions described above.

Substituents have a significant and not always understood influence on the course of rearrangements. The unsubstituted 1,2,3-triazine is obtained in a low yield, while the 4,5,6-triphenyl-substituted derivative is not obtained at all.[86] Among different 2-substituted 1-aminobenzimidazoles, ring expansion is observed only for the 1,2-diamino-derivatives.[87,88] The results of studies of the mechanisms of the first three reactions with the aid of isotope substitution have also contributed little to the foregoing[81,86] (they are illustrated in the corresponding schemes).

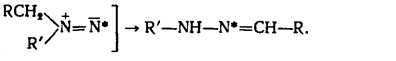
A related rearrangement but one involving the formation of the 1,2,3,4-tetrazine ring may occur on oxidation of the aminotriazoloazulenes (XXI) and (XXIII) with LTA (see above),[174] whose final product is the heptafulvene (XXIII):



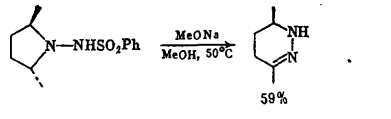
Finally, one cannot rule out the possibility that aminonitrenes participate in rearrangements of the allyl type on oxidation or reduction of certain derivatives of 2-azabicyclo[2.2.1]hept-5-ene,[48] for example:



Another variant of the isomerisation of aminonitrenes is their conversion into monosubstituted hydrazones, the so called "diazene–hydrazone" rearrangement:



Mono- and also di-substituted hydrazones (see below concerning the possible pathway leading to their formation) are the usual products of the oxidation of hydrazines,[3,39,42,43,92] the cleavage of sulphonic acid hydrazides, and other reactions in which the intermediate involvement of aminonitrene is postulated. In the heterocyclic series, the rearrangement results in ring expansion,[27,45,93] for example:[45]



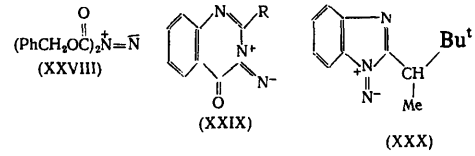
The reaction appears to be entirely similar to the rearrangement of alkoxynitrenes to oximes already considered, especially bearing in mind that aliphatic azo-compounds also isomerise comparatively readily to the more stable hydrazones.[33] However, here the similarity is mainly formal. This is demonstrated most convincingly by the results of the alkaline decomposition of 1,1-diethyl- and 1-benzyl-1-phenyl-2-arenesulphonyl[2-^{15}N]hydrazines,[3] as well as the present authors' experiments on the neutralisation of solutions of 1,1-diethyldiazenium bromide, similarly labelled with ^{15}N. In all cases hydrazones are obtained with the label present preferentially and (frequently exclusively) in the imine nitrogen atom. Furthermore, it is evident that, if the reaction occurred in accordance with the "nitrene → azo-compound → hydrazone" mechanism, both nitrogen atoms would have been labelled to equal extents. In order to explain the rearrangement, other mechanisms have also been proposed (with the intermediate formation of diaziridines, azomethine imines, etc.[3]).

3. Addition to carbon–carbon multiple bonds

The addition of amino- and alkoxy-nitrenes to the C=C bond constitutes a general method of synthesis of a wide variety of *N*-amino- and *N*-alkoxyaziridines.[1–7,94] It has been shown in numerous instances that the reaction proceeds entirely stereospecifically with retention of configuration and that the yields of products depends strongly on the nature of the substituents at the double bond and on the type of nitrene.

Calculation for the simplest model reaction of the aminonitrene $H_2N\dot{N}$: (II) with ethylene[80,95,96] has shown that it can proceed via two pathways—as the reduction of ethylene to ethane with formation of a N_2 molecule[80] (without the rearrangement of $H_2N\dot{N}$: to the *cis*-diimide HN=NH—cf. Lahti[52]) and as a linear cheletropic formation reaction of *N*-aminoaziridine[95,96] with retention of the symmetry plane as the reactants approach one another.[96] The results of *ab initio* calculations[96] and calculations by the MNDO method[95] agree that the addition is electrophilic in character. The degree of charge transfer from ethylene to the nitrene in the transition state is ~0.1–0.16 e, the excess negative charge being concentrated mainly on the central nitrogen atom. The heat of the reaction is extremely low and the activation barrier is estimated as 90–100 kJ mol^{-1}.

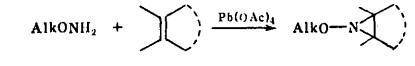
It follows from the data presented that the addition of aminonitrenes to the C=C bond is not unduly favourable from the energetic standpoint but it should be facilitated when the aminonitrene molecule contains substituents capable of stabilising the additional negative charge in the transition state. Accordingly, only aminonitrenes which have at least one or better two electron-accepting substituents enter into reactions via multiple bonds: phthalimidonitrene (PIN) (XII), the acylnitrenes (XIII) and (XXVIII), the heteroaromatic nitrenes (XXIX) and (XXX), and similar compounds:



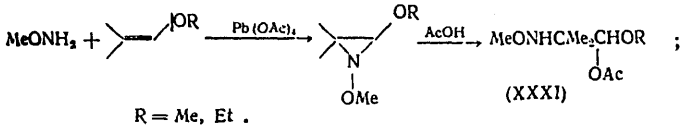
It may be that the presence of the electronegative oxygen atom in fact accounts for the ability of the alkoxynitrenes to enter into addition reactions.

N- and *O*-nitrenes are usually generated in reactions with multiple bonds by oxidising the corresponding amino-compounds with LTA. However, as already stated, at least in the oxidation of aminoquinazolinone (IX) the corresponding *N*-acetoxy-derivative (X) assumes the role of the nitrene (XI)[35] (see above). It is extremely likely (although not in fact obligatory) that in many other instances similar nitrenoids are in fact the real intermediates and instead of alkoxynitrenes we may be dealing with derivatives of *N*-acetoxyhydroxylamine. This alternative must be always borne in mind, although for the sale of brevity we shall henceforth no longer make this stipulation.

The oxidation of alkoxyamines by LTA in the presence of various alkenes affords the corresonding *N*-alkoxyaziridines:[2,5,6,94,97–99]



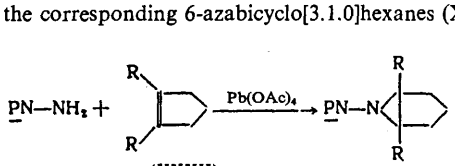
The yields of the adducts vary within wide limits (7–45%) and are apparently determined not only by the reactivity of the double bond in the alkenes but also by the ease of the corresponding rearrangements (see above). It has been shown for the stereoisomeric but-2-enes that the addition is entirely stereospecific[97] (the earlier opposite conclusion apparently arose because of errors in the determination of the structures of the products). In the reactions with vinyl ethers, the acetates (XXXI), which can be regarded as the products of the opening of the ring in the intermediate 1,2-dialkoxaziridines by acetic acid, were isolated:[101]



R = Me, Et .

The set of aminonitrenes involved in the reactions with C=C bonds in studies carried out during the last decade is fairly traditional. These are in the first place PIN (XII)[35,53,54,102–114] and nitrenes of the quinazolinone (XXIX)[35,105,115–117] and benzimidazole (XXX)[118] series. The yields of the aminoaziridines are in this instance usually 50–70% but can also approach 95% in the presence of a very slight excess of the alkene. It has recently been suggested that the diacylaminonitrene (XXVIII) be used in the synthesis of aminoaziridines,[119] but, in order to obtain even fairly moderate yields of the aziridines (30–70%), an almost hundredfold excess of the substrate is required in this case. At the same time, aziridines are formed in fair yields on addition of monosubstituted acylaminonitrenes (XIII) to cyclohexene and (*Z*)-4-methylpent-2-ene,[58] this being in general the first example of intermolecular reactions of monosubstituted nitrenes. Hitherto it has been assumed that they are too unstable and decompose instantaneously with liberation of nitrogen. At the same time the stable acylaminonitrene (VIIb) does not interact with cyclohexene, or dihydropyran, or methyl acrylate.[27]

Phthalimidonitrene (XII) and other heteroarylnitrenes react smoothly with most varied multiple bonds. The corresponding aminoaziridines have been obtained in satisfactory yields from indenes[105,108,113] and indoles[110] (cf. Meyer et al.[105]), derivatives of cyclopentadiene[108,109] and vinyl phosphonate esters,[103,117] norbornadiene and its analogues,[104,107,114] propelladiene,[102] etc. The reactions of PIN (XII) with cyclopentene derivatives (XXII) afford the corresponding 6-azabicyclo[3.1.0]hexanes (XXXIII):[105,120]

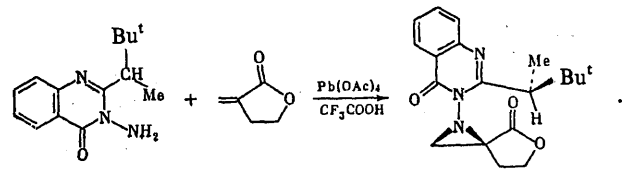


(XXXII) (XXXIII)

R = H (a), Co_2Me (b).

The nitrene (XXIX, R = Me) reacts with cyclopentene (XXXIIa) itself but not with the diester (XXXIIb).[105] Nor has it been possible to obtain its adduct with 1,2-di(methoxycarbonyl)cyclobutene,[105] whereas PIN affords the aziridine (XXXIIIb)[105] and adds even to 1,2-dichlorocyclobutene, forming the strained 1,4-dichloro-5-azabicyclo[2.1.0]pentane.[120]

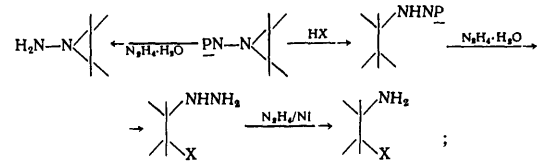
The addition of the chiral nitrenes [XXIX, R = Bu^t(Me)CH][115,116] and (XXX)[118] to prochiral alkenes leads to mixtures of diastereoisomeric aziridines in various proportions. After the addition to the reaction mixture of several equivalents of trifluoroacetic acid (TFAA), the reaction can be carried out at –60 °C, which sharply increases its stereoselectivity.[115,116] For example, in the presence of TFAA only one aziridine is formed from methylenebutyrolactone instead of approximately equal amounts of diastereoisomers:[115,116]



The addition of up to 10 equiv. of TFAA greatly facilitates the conversion of relatively unreactive substrates into aziridines by quinazolinone derivatives.[117] Thus the yield of the adduct of allyl chloride (1.5 equiv.) with the nitrene (XXIX, R = Et) increases from 10 to 90% in the presence of 6 equiv. of TFAA. Furthermore, according to data obtained by means of competing reactions, the selectivity of the reacting species increases. The protonation of the intermediate aminonitrene (XXIX) at the N(1) atom of the quinazolinone ring is believed to be a possible explanation of all these changes.[115–117]

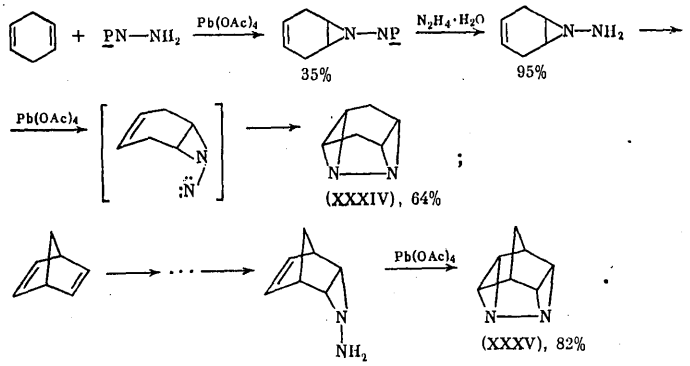
Although, as already mentioned, *N*-heteroarylnitrenes react with the most varied substrates, the view has been established that they are nucleophilic in nature (see, for example, Meyer et al.[105]). However, we have shown recently for a typical and perhaps most thoroughly investigated nitrene of this kind, namely PIN (XII), by the method of competing reactions that its addition to a series of ring-substituted styrenes is electrophilic in character.[111,113] Secondary orbital interactions of the heterocyclic ring of the *N*-nitrene with unsaturated substituents at the bond attacked (aromatic ring, double bond, carbonyl group, etc.) play a major role in the reaction.[3,112–118] For their occurrence, it is necessary that the aminonitrene and the substrate are arranged in parallel planes in the transition state, the *syn*-orientation of the unsaturated substituent and the heterocyclic residue being essential. The suitability of this structure of the transition state is clearly manifested in the preferential formation of the thermodynamically less stable *syn*-invertomers of aziridines[3,112–118] and it may be one of the causes of the asymmetric induction in the reactions of chiral nitrenes.[115,116,118]

The adducts of *N*-nitrenes with C=C bonds, which consist of a wide variety of aminoaziridines, are not only of intrinsic interest but are also of interest as possible intermediates in the synthesis of numerous derivatives of hydrazines, amines, etc. with functional group substituents.[121] *N*-Phthalimidoaziridines are especially convenient in this respect, because the phthaloyl group can be easily removed:[102,104,121]



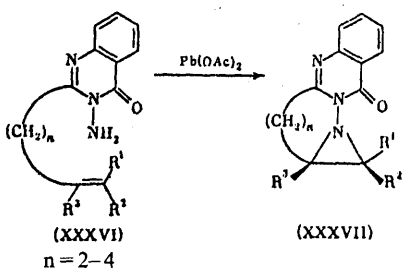
X = PhO, PhS, PhNH, TsO, OH, OAc, etc.

This possibility has been used in the synthesis of polycyclic hydrazines (XXXIV) and (XXXV):[104]



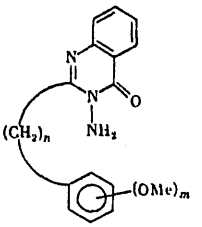
Admittedly, it is essential to note that the addition of PIN to norbornene and norbornadiene derivatives affords mainly the *exo*-adducts[104,107,114] and that the *endo*-aziridine required for the synthesis of compound (XXXV) constitutes only about 10% of the mixture of isomers.[104]

Apart from the intramolecular reactions quoted, other instances of the addition of dialkylaminonitrenes to the C=C bond are unknown. Evidently the success in this instance can be explained by the steric proximity of the interacting groups[104] (cf. Rüttimann and Ginsburg[102]). The influence of electronic and steric factors on the intramolecular addition of typical acylaminonitrenes has been investigated in detail in relation to aminoquinazolinone derivatives.[122–133] It has been shown for a large series of alkenylaminoquinazolinones (XXXVI), frequently containing two different double bonds in the branched side chain, that the reaction proceeds in all cases via a concerted mechanism and leads to the corresponding polycyclic aminoaziridines (XXXVII):[122–126]



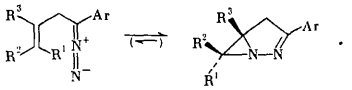
However, for a short side chain (n = 2), the symmetrical transition state must be greatly strained. The two C–N bonds are therefore formed non-synchronously and a polar seven-membered transition state is formed with the localisation of an appreciable positive charge on the β-carbon atom of the double bond.[126]

Similar conclusions follow the results of the oxidation by LTA of aminoquinazolinones (XXXVIII) containing an activated aromatic ring in the side chain.[127–133] Similarly to intermolecular reactions,[134] when n = 2–4, the products of the insertion of the nitrene in aromatic C–H bonds and also of the expansion of the aromatic ring to the azepine ring are formally produced,[127–133] but the short connecting bridge (n = 1) rules out the involvement of the aryl substituent in the reaction:[127]

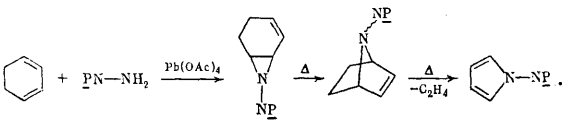


An increase in chain length by one unit (n = 2) leads to a highly polar seven-membered transition state and the process proceeds in essence via an S_E mechanism. The reaction of the long-chain compounds (n = 3, 4) includes, as usual,[1,4] stages involving the formation and cleavage of 7-azanorcaradienes.[127–133] It is important to note that in all the reactions considered[122–133] the quinazolinonylnitrene exhibits electrophilic properties.

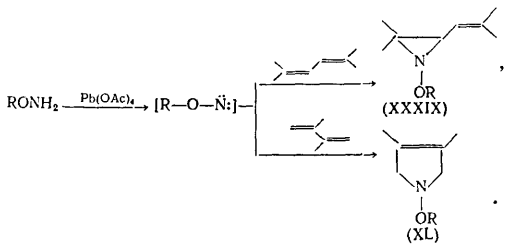
The remarkable analogy between aminonitrenes and diazocompounds can be seen from the intramolecular cyclisation of allyl-substituted aryldiazomethanes:[135]



The interaction of aminonitrenes with 1,3-dienes and cyclooctatetraene produced the corresponding aziridines in 30–70% yields. Asymmetric dienes (isoprene, penta-1,3-diene) afford a mixture of comparable amounts of two isomeric vinylaziridines. Neither diadducts nor 1,4-addition products are then formed.[3] Vinylaziridines are extremely unstable and undergo ready ring opening on treatment with nucleophiles, isomerising on heating to 3-pyrroline derivatives,[136,137] for example:[137]

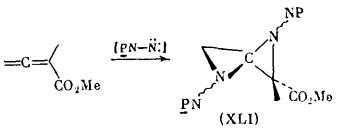


Alkoxynitrenes react with conjugated dienes in different ways:[99] their addition to 2,5-dimethylhexa-2,4-diene affords the alkoxyaziridines (XXXIX), apart from the analogous unsaturated aziridine, the isomeric 3-pyrrolines are formed from 2,4-dimethylpenta-1,3-diene, while in the reactions with 2,3-dimethylbuta-1,3-diene the main products are 1-alkoxypyrrolines (XL):[99,100]



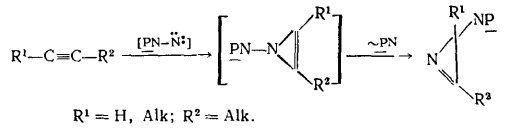
Formally 3-pyrrolines can be regarded as the products of the 1,4-addition of alkoxynitrenes but it may be that they are formed simply as a result of the ready isomerisation of the intermediate unsaturated alkoxyaziridines.[94]

The addition of PIN (XII) to the methyl ester of 2-methylbutadienoic acid leads, in contrast to 1,3-dienes, to a diadduct, to which the spiro-structure (XLI) has been attributed:[138]



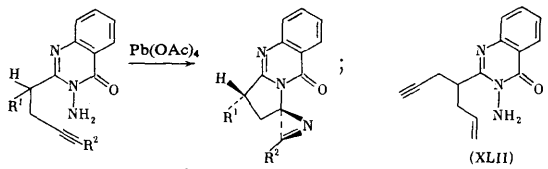
(XLI)

The interaction of the same nitrene with alkylacetylenes leads to 2*H*-azirines in low yields (2–15%).[139] The antiaromatic 1*H*-azirines are probably formed in the first stage:



$R^1 = H$, Alk; $R^2 =$ Alk.

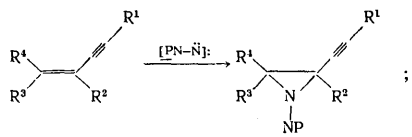
Acetylenes with electron-accepting substituents, tolane, and phenyl-t-butylacetylene do not enter into this reaction at all.[139] The intramolecular addition to the C≡C bond proceeds readily, affording azirines in 80–100% yields:[140–142]



(XLII)

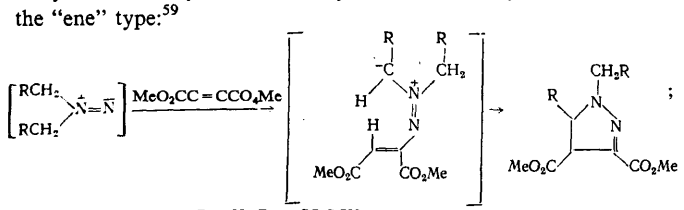
$R^1 = H$, $CH_2C{\equiv}CR^2$; $R^2 = H$, Me.

At the same time, oxidation of aminoquinazolinone (XLII) by LTA results in the formation of only the adduct involving the C=C bond in 84% yield.[142] The reaction of PIN (XII) with conjugated enynes also proceeds fully regio-selectively[139,143] § and may serve as a convenient method of synthesis of 2-alkynyl-1-aminoaziridines having different structures:



R^1–R^4=H, Alk, Ph.

Addition to multiple bonds is characteristic almost exclusively of acylaminonitrenes. However, a reaction has been described recently which is treated as the interaction of the triple bond in dimethylacetylenedicarboxylate with dialkylaminonitrenes by a mechanism of the "ene" type:[59]

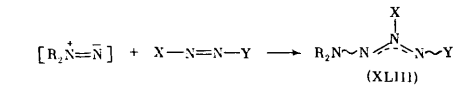


R = H; $R_2 = CO_2OCH_2$.

§ See also M A Kuznetsov, V V Semenovskii, V N Belov, V A Gindin *Khim. Geterotsikl. Soedin.*, 1989, 235.

4. The reactions with N=X (X = N, O, C) bonds

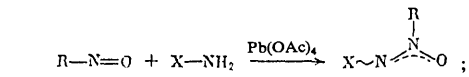
The interaction of aminonitrenes with azo-compounds leads to the formation of 1,3-dipolar compounds of a new class—aminoazimines (XLIII):



(XLIII)

Since this reaction has been described in detail in a recent review,[144] here we should like merely to note the general rule of the "mutual complementarity" of substituents in the nitrene and the azo-compounds. It has been found that PIN (XII) adds smoothly to azoalkanes, 1-pyrazolines, and azoarenes, while, conversely, diphenyl- and dialkyl-aminonitrenes react satisfactorily with derivatives of azodicarboxylic acid, but all attempts to carry out "cross reactions" have so far been unsuccessful.

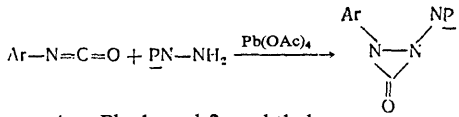
PIN (XII)[145–147] as well as a series of alkoxynitrenes[148,149] add similarly (at the LEP of the nitrogen atom) to various *C*-nitroso-compounds[145,148] and nitrosamines:[146,149]



X = PN, OAlk; R = Bu^t, t-C_5H_{11}, cyclo-C_6H_{11}, Ar, $R_2'N$. (4)

Phthalimidodiazene oxides (XLIV, X = PN) can be obtained from *C*-nitroso-compounds in 80–94% yield (with the exception of nitrosocyclohexane for which the yield is 18%[145]). The yield of the adducts of PIN with nitrosamines are 70–80%.[146] The yields of the alkoxydiazene oxides (XLIV, X = OAlk) are usually lower but they too can reach up to 60–70%.[148,149] It is important to note that, in the generation of PIN by the thermolysis of its adduct with acetylbenzofuran in the presence of nitrosocyclohexane, the corresponding diazene oxide (XLIV, X = PN, R = cyclo-C_6H_{11}) was obtained in 23% yield[145] (which is even higher than in the case where LTA is used). The attempt to extend reaction (4) to *O*-nitroso-compounds was unsuccessful: when aminophthalimide was oxidised by LTA in the presence of isopentyl nitrite, the formation of adducts was not detected.[146]

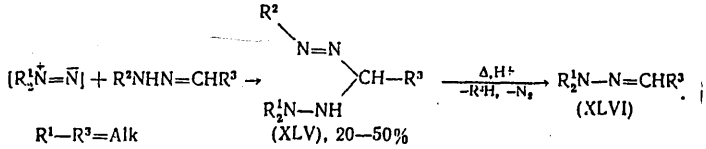
There are no reliable examples in the literature of the addition of acylaminonitrenes and alkoxynitrenes to the C=N bond. In fact it has been reported that possible adducts were not detected in the reaction mixtures after the oxidation of alkoxyamines by LTA in the presence of a large series of compounds: azomethines, azines, hydrazones, and oximes and their ethers.[98] However, it has been claimed that PIN is capable of adding to the C=N bond of aryl isocyanates, affording phthalimidodiazirinones:[150]



Ar = Ph, 1- and 2-naphthyl.

However, here one should note that aryl isocyanates react readily with primary amines, affording urea derivatives. Therefore, when they are mixed with aminophthalimide, the corresponding semicarbazide should be formed rapidly and the latter apparently is in fact oxidised further by LTA.

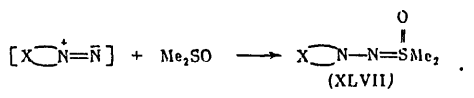
At the same time, dialkylaminonitrenes react with aldehyde monoalkylhydrazones, affording the so called geminal azohydrazines (XLV):[151]



On heating, on treatment with acids, and simply on standing, azohydrazines (XLV) decompose to the disubstituted hydrazones (XLVI).[151] Since monosubstituted hydrazones are readily obtained in the diazene–hydrazone rearrangement, it may be that the invariable presence of disubstituted hydrazones among the products of the reactions of dialkylaminonitrenes can be accounted for by this sequence of reactions.

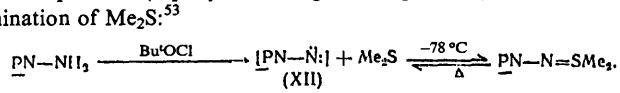
5. Reactions with dimethyl sulphide and sulphoxides. The formation of tetrazenes

The reactions listed in the heading have a common feature, namely they all reduce to the attack by the nitrene on the LEP of some kind of heteroatom. We have already seen examples of such interaction in the previous subsection—the addition of nitrenes to azo- and nitroso-compounds does actually occur at the LEP of the nitrogen atom. *N*-Heteroarylnitrenes, capable of adding to multiple bonds, react similarly with the classical "trapping agent" for sextet species—dimethyl sulphoxide, and other sulphoxides:[3,27,28,85,119]

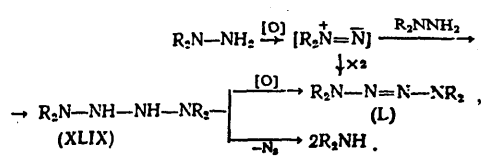


The extremely stable sulpoximines (XLVII) are then formed in a nearly quantitative yield. The attack on the LEP of the sulphur atom is so fast that vinyl-substituted sulphoxides are converted into unsaturated sulphoximines without any traces of addition to the double bond.[152] The stable nitrene (VIIb) does not react with DMSO,[27] although the sulphoximines (XLVII) corresponding to the nitrenes (VIIa, b) can be obtained by oxidising the initial acylhydrazines by LTA in DMSO.[28] Here they are clearly formed from "precursors" of the free nitrenes. Contrary to expectations, after the oxidation of alkoxyamines by LTA in DMSO, the adduct of alkoxynitrenes with the solvent could not be detected.[98]

The addition of PIN (XII) to dimethyl sulphide gives rise to a fairly labile sulphimide (XLVIII), which dissociates slowly even at room temperature (rapidly on raising the temperature) with elimination of Me_2S:[53]



The interaction of aminonitrenes with the starting materials used in their synthesis, usually hydrazine derivatives, is of a general character.[3] Here the intermediates are the extremely unstable tetrazans (XLVI), which can decompose, affording deamination products, or can be converted into 2-tetrazenes (L), which are the usual products of the oxidation of 1,1-disubstituted hydrazines:[3,85,119]



The tetrazenes (L) give rise to stable aminonitrenes simply as a result of dimerisation.[20–26]

By analogy with tetrazenes, one would expect the formation of 1,2-dialkoxydiazene RON=NOR in the oxidation of alkoxyamines but these compounds are extremely unstable and so far they have never been detected in any reactions of alkoxynitrenes.

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The last decade has provided extensive data illustrating the wide variety of the reactions of amino- and oxy-nitrenes. Although the range of reactions and methods for the generation of oxynitrenes investigated is appreciably narrower, the data obtained demonstrate their similarity to aminonitrenes. The general problem of the separation of the reactions of nitrenes proper and "nitroenoids" is associated directly with further progress in this field of the chemistry of sextet nitrogen intermediates. The properties and reactions of stable nitrenes can serve as a kind of standard. From the standpoint of theoretical organic chemistry as a whole, the study of the mechanism of the decomposition and rearrangements of amino- and oxy-nitrenes is of interest. There are good prospects that their reactions with a wide variety of unsaturated compounds will prove useful in syntheses. Evidently in the immediate future the search for new types of amino- and oxy-nitrenes, new methods for their generation, and new reactions of these species will becomes of current interest.

References

1. W Lwowski (Editor) *Nitrenes*, Wiley Intersci., New York, 1970
2. E F V Scriven (Editor) *Azides and Nitrenes: Reactivity and Utility*, Acad. Press, Orlando, 1984
3. B V Ioffe, M A Kuznetsov, A A Potekhin *Khimiya Organicheskikh Proizvodnykh Gidrazina* (The Chemistry of Organic Derivatives of Hydrazine), Izd. Khimiya, Leningrad, 1979
4. B V Ioffe, M A Kuznetsov *Usp. Khim.*, 1972, **41**(2) 241 [English translation in *Russ. Chem. Rev.*, 1972(2)]
5. B V Ioffe, V P Semenov, K A Ogloblin *Zh. Vses. Khim. Ova im D. I. Mendeleeva*, 1974, **19** 314
6. V P Semenov, A N Studenikov, K A Ogloblin *Zh. Vses. Khim. Ova im. D. I. Mendeleeva*, 1979, **24** 485
7. V N Belov *Sovremennye Problemy Organicheskoi Khimii* (Modern Problems in Organic Chemistry) (Edited by K A Ogloblin), Izd. Leningr. Gos. Univ., Leningrad, 1986, No. 8, p. 4
8. P Decleva, A Lisini *Chem. Phys.*, 1987, **112** 339
9. J H Davis, W A Goddard *J. Am. Chem. Soc.*, 1977, **99** 7111
10. C K Casewit, W A Goddard *J. Am. Chem. Soc.*, 1980, **102** 4057
11. G A Heath, R Mason, K M Thomas *J. Am. Chem. Soc.*, 1974, **96** 259
12. M W Bishop, J Chatt, J R Dilworth, et al. *J. Chem. Soc., Dalton Trans.*, 1979, 1600
13. G E Bossard, T A George *Inorg. Chim. Acta*, 1981, **54** L239
14. C F Barrientos-Penna, F W B Einstein, T Jones, D Sutton *Inorg. Chem.*, 1982, **21** 2578
15. L S Tan, G V Goeden, B L Haymore *Inorg. Chem.*, 1983, **22** 1744

16. H M Colquhoun *Acc. Chem. Res.*, 1984, **17** 23
17. D Mansuy, P Battioni, J-P Mahy *J. Am. Chem. Soc.*, 1982, **104** 4487
18. J-P Mahy, P Battioni, D Mansuy, et al. *J. Am. Chem. Soc.*, 1984, **106** 1699
19. W D Hinsberg, P B Dervan *J. Am. Chem. Soc.*, 1978, **100** 1608
20. W D Hinsberg, P B Dervan *J. Am. Chem. Soc.*, 1979, **101** 6142
21. P G Schultz, P B Dervan *J. Am. Chem. Soc.*, 1980, **102** 878
22. P B Dervan, M E Squillacote, P M Lahti, et al. *J. Am. Chem. Soc.*, 1981, **103** 1120
23. P G Schultz, P B Dervan *J. Am. Chem. Soc.*, 1981, **103** 1563
24. W D Hinsberg, P G Schultz, P B Dervan *J. Am. Chem. Soc.*, 1982, **104** 766
25. D K McIntyre, P B Dervan *J. Am. Chem. Soc.*, 1982, **104** 6466
26. P G Schultz, P B Dervan *J. Am. Chem. Soc.*, 1982, **104** 6660
27. R D Miller, P Gölitz, J Janssen, J Lemmens *J. Am. Chem. Soc.*, 1984, **106** 1508
28. R D Miller, P Gölitz, J Janssen, J Lemmens *J. Am. Chem. Soc.*, 1984, **106** 7277
29. A P Sylwester, P B Dervan *J. Am. Chem. Soc.*, 1984, **106** 4648
30. N Wiberg, G Fischer, H Bachhuber *Angew. Chem., Int. Ed. Engl.*, 1976, **15** 385
31. N Wiberg, G Fischer, H Bachhuber *Z. Naturforsch.* B, 1979, **34** 1385
32. B F Powell, C G Overberger, J-P Anselme *J. Heterocycl. Chem.*, 1983, **20** 121
33. T G Back *Chem. Commun.*, 1981, 530
34. T G Back, R G Kerr *Can. J. Chem.*, 1982, **60** 2711
35. R S Atkinson, B J Kelly *Chem. Commun.*, 1987, 1362
36. F Achröppel, J Sauer *Tetrahedron Lett.*, 1974, 2945
37. L Hoesch, A S Dreiding *Helv. Chim. Acta*, 1975, **58** 980
38. L Fuchigami, T Sato, T Nonaka *Electrochim. Acta*, 1986, **33** 365
39. T Nonaka, J K Lee *J. Chem. Soc. Jpn. (Kagaku Kaishi)*, 1984, 1769
40. M A Mathur, H H Sisler *Inorg. Chem.*, 1981, **20** 426
41. E C Tuazon, W P L Carter, R W Brown, et al. *J. Phys. Chem.*, 1983, **87** 1600
42. K Kano, M Koga, J-P Anselme *Bull. Soc. Chim. Belg.*, 1987, **96** 137
43. M A Mathur, H H Sisler, L N Morgenthaler *Inorg. Chem.*, 1979, **18** 2350
44. D C Duan, P B Dervan *J. Org. Chem.*, 1983, **48** 970
45. P B Dervan, T Uyehara *J. Am. Chem. Soc.*, 1979, **101** 2076
46. V I Savin, V I Morozov, Yu P Kitaev *Zh. Org. Khim.*, 1983, **19** 977
47. V I Savin *Zh. Org. Khim.*, 1987, **23** 19
48. A Heesing, L Keller *Chem. Ber.*, 1986, **119** 1413
49. M Nakajima, J-P Anselme *J. Org. Chem.*, 1980, **45** 3673
50. K Nishiyama, J-P Anselme *J. Org. Chem.*, 1978, **43** 2045
51. M Nakajima, J-P Anselme *Tetrahedron Lett.*, 1984, **25** 139
52. P M Lahti *Tetrahedron Lett.*, 1983, **24** 2343
53. M Edwards, T L Gilchrist, J Harris, C W Rees *J. Chem. Res. (H)*, 1979, 1687
54. V N Belov, M A Kuznetsov *Zh. Org. Khim.*, 1988, 24
55. A G Schultz, M Shen, *Tetrahedron Lett.*, 1979, 2969
56. A G Schultz, M Shen, R Ravichandran *Tetrahedron Lett.*, 1981, **22** 1767
57. M Shen, A G Schultz *Tetrahdron Lett.*, 1981, **22** 3347
58. L A Carpino, R E Padykula *Chem. Commun.*, 1986, 747
59. K Kano, C A Kelly, J-P Anselme *Tetrahedron Lett.*, 1982, **23** 1427
60. J J Tufariello, A S Milowsky, M Al-Nuri, S Goldstein *Tetrahedron Lett.*, 1987, **28** 263
61. J J Dannenberg, D Rocklin *J. Org. Chem.*, 1982, **47** 4529
62. J J Dannenberg *J. Org. Chem.*, 1985, **50** 4963
63. C Doubleday, R N Camp, H F King, et al. *J. Am. Chem. Soc.*, 1984, **106** 447
64. T Nakazawa, I Murata *Angew. Chem., Int. Ed. Engl.*, 1975, **14** 711
65. T Nakazawa, I Murata *J. Am. Chem. Soc.*, 1977, **99** 1996
66. T Nakazawa, T Niimoto, I Murata *Tetrahedron Lett.*, 1978, 569
67. T Nakazawa, K Kubo, I Murata *Angew. Chem., Int. Ed. Engl.*, 1981, **20** 189
68. H Yamochi, K Nakasuji, T Nakazawa, I Murata *Chem. Lett.*, 1982, 459
69. T Nakazawa, F Nishikawa, M Ashizawa, et al. *Chem. Lett.*, 1985, 1281
70. T Nakazawa, M Ashizawa, F Nishikawa, et al. *Tetrahedron Lett.*, 1986, **27** 3005
71. H Hart, D Ok *Tetrahedron Lett.*, 1984, **25** 2073
72. H Hart, D Ok *J. Org. Chem.*, 1986, **51** 979
73. D Ok, H Hart *J. Org. Chem.*, 1987, **52** 3835
74. T Nakazawa, M Kodama, S Kinoshita, I Murata, *Tetrahedron Lett.*, 1985, **26** 335
75. G deLuca , A Pizzabiocca, G Renzi *Chem. Ind.*, 1983, 679
76. M J S Dewar, L Chantranupong *J. Am. Chem. Soc.*, 1983, **105** 7152
77. M J S Dewar, L Chantranupong *J. Am. Chem. Soc.*, 1983, **105** 7161
78. Yu P Artsybasheva, B V Ioffe *Zh. Org. Khim.*, 1978, **14** 445
79. B V Ioffe, Yu P Artsybasheva *Zh. Org. Khim.*, 1981, **17** 911
80. D J Pasto, D M Chipman *J. Am. Chem. Soc.*, 1979, **101** 2290
81. M T Williams *J. Chem. Res. (M)*, 1986, 1185
82. A Ohsawa, H Arai, H Ohnishi, H Igeta *Chem. Commun.*, 1980, 1182
83. A Ohsawa, H Arai, H Ohnishi, H Igeta *Chem. Commun.*, 1981, 1174
84. A Ohsawa, H Arai, H Ohnishi, et al. *J. Org. Chem.*, 1985, **50** 5520
85. H Neunhoeffer, M Clausen, H-D Vötter, et al. *Liebigs. Ann. Chem.*, 1985, 1732
86. A J Boulton, R Fruttero, J D K Saka, M T Williams *J. Chem. Soc., Perkin Trans. 1*, 1986, 1249
87. A V Zeiger, M M Joullie *J. Org. Chem.*, 1977, **42** 542
88. I M Nanavyan, A F Pozharskii, V V Kuz'menko *Khim. Geterotsikl. Soedin.*, 1986, 999
89. T A Kuz'menko, V V Kuz'menko, A F Pozharskii, N A Klyuev *Khim. Geterotsikl. Soedin.*, 1988, 1226
90. A F Pozharskii, I M Nanavyan, V V Kuz'menko *Khim. Geterotsikl. Soedin.*, 1983, 1564
91. S V Shorshnev, S E Esipov, A I Chernyshev, et al. *Khim. Geterotsikl. Soedin.*, 1987, 1555
92. M H Mach, A M Baumgartner *Anal. Lett.*, 1979, **12A**, 1063
93. N Viswanathan, A R Sidhaye *Tetrahedron Lett.*, 1979, 5025
94. A Hassner (Editor) *The Chemistry of Heterocyclic Compounds. Vol. 42. Small Ring Heterocycles. Part 1. Aziridines, Azirines, Thiiranes, Thiirenes*, Wiley, New York–Toronto, 1983

95. V A Bespalov *Zh. Org. Khim.*, 1982, **18** 2241
96. M A Lazareva *Teor. Eksp. Khim.*, 1986, **22** 477
97. B V Ioffe, Yu V Artsybasheva, I G Zenkevich *Dokl. Akad. Nauk SSSR*, 1976, **231** 1130
98. B V Ioffe, Yu P Artsybasheva *Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Khimii Karbenov* (Abstracts of Reports at the IV All-Union Conference on the Chemistry of Carbenes), Izd. Nauka, Moscow, 1987, p. 42
99. Yu P Artsybasheva, B V Ioffe *Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Khimii Karbenov* (Abstracts of Reports at the IVth All-Union Conference on the Chemistry of Carbenes), Izd. Nauka, Moscow, 1987, p. 56
100. F A Carey, L J Hayes *J. Org. Chem.*, 1973, **38** 1701
101. Yu P Artsybasheva, B V Ioffe *Zh. Org. Khim.*, 1981, **17** 436
102. A Rüttiman, D Ginsburg *Tetrahedron*, 1976, **32** 1009
103. F V Bagrov, L I Il'ina, L A Vasil'eva *Zh. Obshch. Khim.*, 1977, 47
104. L Hoesch, N Egger, A S Dreiding *Helv. Chim. Acta*, 1978, **61** 795
105. G R Meyer, C A Kellert, R W Ebert *J. Heterocycl. Chem.*, 1979, **16** 461
106. R S Atkinson, B D Judkins, N Khan *J. Chem. Soc., Perkin Trans. 1*, 1982, 2491
107. K Narasimhan, P R Kumar *J. Org. Chem.*, 1983, **48** 1122
108. K Narasimhan, P R Kumar *Heterocycles*, 1984, **22** 1369
109. K Narasimhan, P R Kumar *Indian J. Chem. Sect. B*, 1985, **24** 141
110. P R Kumar *Heterocycles*, 1987, **26** 1257
111. M A Kuznetsov, V N Belov *Zh. Org. Khim.*, 1984, **20** 1768
112. M A Kuznetsov, V N Belov, A Yu Vilyatser *Vestn. Leningr. Univ., Fiz., Khim.*, 1984, (3) 63
113. V N Belov, Abstract of Candidate's Thesis in Chemical Sciences, Izd. Leningr. Gos. Univ., Leningrad, 1984
114. Yu G Loznevaya, V N Belov, M A Kuznetsov *Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Khimii Karbenov* (Abstracts of Reports at the IVth All-Union Conference on the Chemistry of Carbenes), Izd. Nauka, 1987, p. 56
115. R S Atkinson, G Tughan *Chem. Commun.*, 1986, 834
116. R S Atkinson, G Tughan *Chem. Commun.*, 1987, 456
117. R S Atkinson, C M Darrah, B J Kelly *Tetrahedron Lett.*, 1987, **28** 1711
118. R S Atkinson, J Fawcett, D R Russel, G Tughan *Chem. Commun.*, 1986, 832
119. R Milcent, M Guevrekian-Soghomoniantz, G Barbier *J. Heterocycl. Chem.*, 1986, **23** 1845
120. A G Anderson, D R Fegeburg *J. Heterocycl. Chem.*, 1969, **6** 987
121. M Egli, L Hoesch, A S Dreiding *Helv. Chim. Acta*, 1985, **68** 220
122. R S Atkinson, J R Malpass, K L Skinner, K L Woodthorpe *Chem. Commun.*, 1981, 549
123. R S Atkinson, K L Skinner *Chem. Commun.*, 1983, 22
124. R S Atkinson, J R Malpass, K L Skinner, K L Woodthorpe *J. Chem. Soc., Perkin Trans. 1*, 1984, 1905
125. R S Atkinson, M J Grimshire *Chem. Commun.*, 1985, 1218
126. R S Atkinson, M J Grimshire *J. Chem. Soc., Perkin Trans. 1*, 1987, 1135
127. R S Atkinson, J R Malpass, K L Woodthorpe *J. Chem. Soc., Perkin Trans. 1*, 1982, 2407
128. R S Atkinson, N A Gawad, D R Russel, L J S Sherry *Chem. Commun.*, 1983
129. R S Atkinson, N A Gawad *Chem. Commun.*, 1984, 557
130. R S Atkinson, J Fawcett, N A Gawad, et al. *Chem. Commun.*, 1984, 1072
131. R S Atkinson, N A Gawad *J. Chem. Soc., Perkin Trans. 1*, 1985, 335
132. R S Atkinson, N A Gawad *J. Chem. Soc., Perkin Trans. 1*, 1985, 341
133. R S Atkinson, N A Gawad *J. Chem. Soc., Perkin Trans. 1*, 1985, 825
134. D W Jones *Chem. Commun.*, 1973, 67
135. T Miyashi, Y Nishizawa, Y Fujii, et al. *J. Am. Chem. Soc.*, 1986, **108** 1617
136. T L Gilchrist, C W Rees, E Stanton *J. Chem. Soc. C*, 1971, 3036
137. L Hoesch, A S Dreiding *Chimia*, 1972, **26** 629
138. R S Atkinson, J P Malpass *Tetrahedron Lett.*, 1975, 4305
139. D J Anderson, T L Gilchrist, G E Gymer, C W Rees *J. Chem. Soc., Perkin Trans. 1*, 1973, 550
140. R S Atkinson, J Fawcett, M J Grimshire, D R Russel *Chem. Commun.*, 1985
141. R S Atkinson, M J Grimshire *Tetrahedron Lett.*, 1985, 4399
142. R S Atkinson, M J Grimshire *J. Chem. Soc., Perkin Trans. 1*, 1986, 1215
143. V N Belov, V R Denisov, M A Kuznetsov *Khim. Geterotsikl. Soedin.*, 1988
144. A A Suvorov, M A Kuznetsov *Usp. Khim.*, 1987, **56**(8) 1324 [English translation in *Russ. Chem. Rev.*, 1987(8)]
145. L Hoesch, B Köppel *Helv. Chim. Acta*, 1981, **64** 864
146. L Hoesch *Helv. Chim. Acta*, 1981, **64** 890
147. L Hoesch, J H Bieri *Helv. Chim. Acta*, 1981, **64** 905
148. Yu P Artsybasheva, B V Ioffe *Zh. Org. Khim.*, 1982, **18** 1802
149. Yu P Artsybasheva, B V Ioffe *Zh. Org. Khim.*, 1987, **23** 1168
150. P R Kumar *Indian J. Chem., Sect. B*, 1985, **24** 678
151. B V Ioffe, M A Kuznetsov, V A Chernyshev, et al. *Zh. Org. Khim.*, 1976, **12** 2273
152. R Annuziata, M Cinquini *J. Chem. Soc., Perkin Trans. 1*, 1979, 1684

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Vicarious nucleophilic substitution of hydrogen

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ABSTRACT. The reaction involving the vicarious nucleophilic substitution of hydrogen in aromatic nitro-compounds and certain electrophilic heterocycles is discussed. The applications of the reaction, its limitations, the problems concerning its mechanism and mode, as well as the possibilities of the practical application of this new method in organic synthesis are examined.

The bibliography includes 101 references.

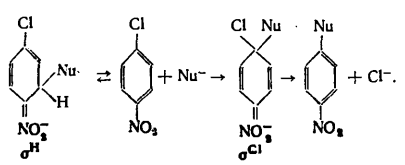
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I. Introduction

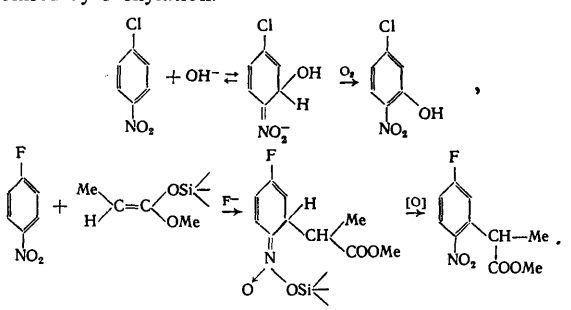
Reactions involving nucleophilic substitution in an aromatic ring[1–5] differ from aliphatic nucleophilic substitution reactions not only by a greater variety of mechanisms but also by the wide variety of groups which can be substituted by nucleophiles. Such a group can be even the hydride ion, but, despite numerous examples,[6,7] the general method for the nucleophilic substitution of hydrogen in aromatic systems has been lacking hitherto, if one disregards the Chichibabin reaction, whose applications are limited to the amination of individual heterocycles.[8] The known instances of the nucleophilic substitution of hydrogen described in the literature are fairly specific and their mechanisms differ very greatly.[7,9–12]

At the end of the 1970s, the present author began to develop a new method for the direct substitution of hydrogen in aromatic nitro-compounds and other electrophilic arenes on the basis of reactions with carbanions. The starting point in our research was the most general reaction involving the nucleophilic substitution of the halogens and other leaving groups in nitroarenes, which proceeds via an addition–elimination mechanism.[1,2] For example, the interaction of a nucleophile with *p*-chloronitrobenzene begins with the addition of the reactant to the carbon atom linked to chlorine whereupon an anionic σ^{Cl}-adduct (frequently called the Meisenheimer complex) is formed and then decomposes rapidly into chloride ion and the nucleophilic substitution product:



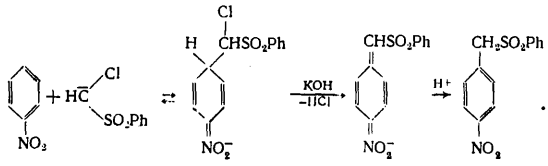
Evidently the formation of the σ^{Cl}-adduct is due to the presence of the nitro-group, which is capable of delocalising effectively the negative charge. For this reason, the nucleophile can also add to the carbon atom in the *ortho*-position relative to the nitro-group. Although the examples of the formation of such σ^{H}-adducts are known,[11,13] the latter are usually incapable of further reactions because of the impossibility of the elimination of the hydride ion.

It follows from the numerous investigations into the chemistry of stable σ-adducts of polynitro-compounds that the addition of nucleophiles to an unsubstituted carbon atom is faster than the addition to one linked to substituents, even substituents such as halogens. On the other hand, the σ-adducts formed in the latter reaction are usually thermodynamically more stable.[14,15] When these observations are extended to the short-lived σ-adducts of mononitro-compounds, one arrives at the conclusion that in most instances of the nucleophilic substitution of a halogen in nitroarenes, the nucleophile adds initially to the carbon atoms linked to hydrogen and σ^{H}-adducts are formed. Since the latter are in general unable to react further because of the impossibility of the elimination of the hydride ion, the formation of such adducts has been unremarked even in the numerous kinetic investigations[1] and the observed reaction is the substitution of the halogen via the slower formation of the σ^{X}-adduct. Hence it follows that the development of a general method for the nucleophilic substitution of hydrogen in nitroarenes is entirely feasible and useful and should be based on the rapid subsequent conversion of the σ^{H}-adducts, including the hydrogen abstraction process. The seemingly most evident approach to this problem, namely the oxidation of the σ^{H}-adducts, cannot have a general importance in view of the reversibility of the addition, the unfavourable equilibrium position, and, usually, the sensitivity of nucleophiles to oxidation. Nevertheless, such a process can be carried out by using non-oxidisable nucleophiles[9] or by ensuring a high concentration of the σ^{H}-adducts. This occurs for polynitro-compounds,[16] in the reactions of organomagnesium compounds with nitroarenes,[17] and also when the resulting σ-adducts of carbanions are stabilised by *O*-silylation:[18]



Our approach to the solution of this problem was based on the hypothesis that the σ^{H}-adducts, formed by carbanions containing a leaving group X (for example, chlorine) at the carbanionic centre,

can undergo further reaction via the elimination of the X^- anion as a result of the 1,2-migration of the hydride ion from the ring to the carbon atom of the entering substituent. This should result in the formation of the product of the substitution of hydrogen by the dehalogenated carbanion residue. The formation of σ-halogenocarbanions is frequently accompanied by autocondensation and in the first attempt to carry out this process we therefore chose as the reagent chloromethyl phenyl sulphone, which is fairly stable in this respect.[19] The reaction of nitrobenzene with this sulphone in the presence of powdered potassium hydroxide in dimethyl sulphoxide occurred with an intense exothermic effect and was accompanied by the development of a very deep blue-violet colour of the reaction mixture. This resulted in the formation of a mixture of *o*- and *p*-nitrobenzyl phenyl sulphones in a satisfactory yield:[20]



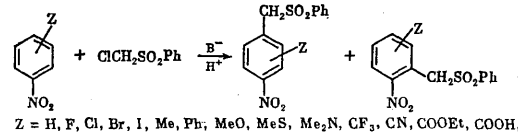
The hydrogen atom in the *o*- and *p*-positions relative to the nitro-group was substituted in this reaction by the carbanion residue, but, from the point of view of the stoichiometry, the halide ion and not the hydride ion was eliminated from the intermediate σ^H-adduct. Thus the halogen plays the role of the leaving group instead of the ring hydrogen, which is incapable of being eliminated in the form of the anion. We therefore designated this process in English as "vicarious nucleophilic substitution of hydrogen (VNS)"†. The study of the reaction mechanism showed that the σ-adducts are converted into the final products not via the hydride complex, as postulated initially, but as a consequence of the β-elimination of hydrogen chloride (or HX in the general case).[21] The earlier important hypothesis of the faster addition of the nucleophile to the unsubstituted rather than the halogen-substituted ring carbon atom has been fully confirmed. In the reactions of *p*- and *o*-chloronitrobenzenes with chloromethyl sulphone in the presence of an excess of a base, hydrogen is substituted exclusively; chlorine substitution products were not detected.[20] The higher rate of the VNS of hydrogen, usually exceeding the rate of the usual substitution of a halogen, is one of the most significant features of this reaction. Here one should note that several examples of VNS had also been known previously. These include the methylation of nitroarenes and certain heterocycles by carbanions derived from DMSO[22–24] and from methyl sulphone[25] and dimethylsulphonium[26] and sulphoxonium[27,28] ylides as well as the dichloromethylation of *p*-halogenonitrobenzenes by trichloromethyllithium.[29] The amination of certain nitroarenes by hydroxylamine in the presence of bases[30,31] also belongs to reactions of this type. However, these few observations were not developed further, since the general character of these reactions was not discovered and the proposed speculative mechanisms were not usually correct.[25,27,31] In our subsequent studies, the general character of this new reaction was demonstrated and its specific features, the principal elements of its mechanism, direction rules, as well as the conditions necessary for its successful performance were found.[32–34]

†Vicarious = substituting another, acting for another.

The carbanion is usually generated directly in the reaction mixture in the presence of an aromatic nitro-compound by treatment of the corresponding CH acid with a base. Since the elimination requires a second equivalent of the base, the base is required in at least a twofold excess relative to the other reactants. The reaction products are formed as intensely coloured nitrobenzyl carbanions derived from strong CH acids. They are protonated only on treating the reaction mixture with an acid. The success of the reaction depends on the nature of the base, the character of the solvent, temperature, and other conditions. The base must ensure the deprotonation of the CH acid and rapid elimination, while the solvent must ensure a high reactivity of the carbanion and the base. Satisfactory results were obtained when the carbanions are present as solvate-separated ion pairs, so that sodium hydroxide, potassium hydroxide, potassium t-butoxide, and sodium methoxide in dimethyl sulphoxide, dimethylformamide, liquid ammonia, and sometimes in tetrahydrofuran are most often used. The carbanions derived from the initial CH acids and the products are frequently unstable, which makes it necessary to carry out the reaction at low temperatures and to neutralise the reaction mixture immediately when the reaction has reached completion.

II. Applications of the reaction

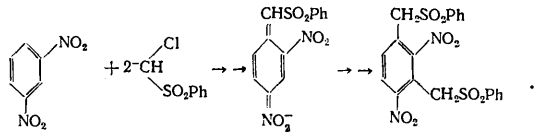
Both reactants participate in the VNS reaction, so that its applications must be determined by their character, namely the electrophilicity of the arenes (usually nitroarenes) and the stability of their carbanions, i.e. ultimately their structure. In order to determine the structural requirements as regards nitroarenes, chloromethyl sulphone has been used. As stated above, it does not undergo autocondensation in the presence of bases[19] and its conjugate carbanion is fairly stable. This sulphone reacts very effectively with nitrobenzene and its substituted derivatives, forming the products of the substitution of hydrogen in the *ortho*- and *para*-positions relative to the nitro-group:[20,35]



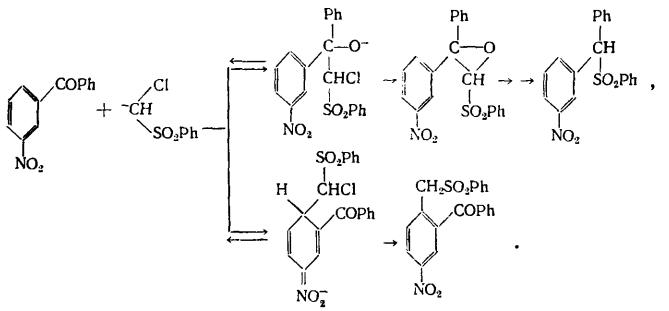
Z = H, F, Cl, Br, I, Me, Ph, MeO, MeS, Me_2N, CF_3, CN, COOEt, COOH, SO_3H, SO_2Me, NO_2, $CH(OR)_2$, COPh, etc.

In the case of *p*-halogenonitrobenzenes (Z = *p*-halogen), only the *ortho*-substitution product is formed. Only when Z = F is the VNS reaction accompanied by the nucleophilic substitution of fluorine. As shown below, this process can be suppressed by carrying out the reaction under special conditions.[21,36] Naturally, when the substituent Z is in the *ortho*- and *meta*-positions relative to the nitro-group, there is a possibility of the formation of two or even three isomeric substitution products. The character of the substituents in the aromatic nitro-substituted ring which do not prevent the reaction is virtually unlimited but there is no doubt about their influence on the rate of the reaction and the site of substitution. The few substituents inhibiting the VNS include also those which are deprotonated under strongly basic reaction conditions with formation of anions containing a free electron pair in the position conjugated with the aromatic ring and the nitro-group, such as, for example, the hydroxy-group in nitrophenols, the mercapto-group in nitrothiophenols, etc. In the case of the substituents COO^- [37] and SO_3^-,[38] where there is no conjugation of this kind, their presence

does not prevent the VNS. Since the VNS products exist in the reaction mixture as nitrobenzyl carbanions, this reaction is very selective in relation to monosubstitution. The inhibiting effect of conjugated negatively charged substituents can be compensated by the presence of a second nitro-group. Whereas nitrophenols do not enter into the VNS reaction, the substitution in dinitrophenols proceeds fairly smoothly.[39] The activating effect of the second nitro-group has also been demonstrated by the reaction of *m*-dinitrobenzene with an excess of a sulphone, which leads to disubstitution products, while in 1,3,5-trinitrobenzene there is even a possibility of trisubstitution:[39]

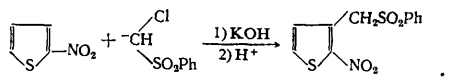


It must be emphasised that the rates of substitution of the first, second, and third hydrogen atoms in polynitroarenes differ greatly, which ensures the process selectivity. Certain limitations in VNS may arise as a consequence of the presence of substituents capable of reacting with carbanions. For example, in the reaction with nitrobenzophenones the mode of reaction is determined principally by the structure of the substrate: the *para*-isomer enters exclusively into the Darzens condensation, the *ortho*-isomer is involved in the VNS reaction, while in the case of the *meta*-isomer the two reactions compete and the conditions ensuring a high concentration of the base promote the substitution of hydrogen:[40]

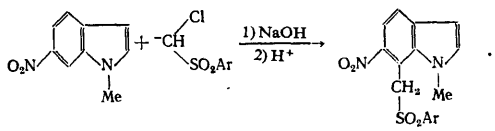


Presumably there is a possibility of the VNS of hydrogen not only in a monosubstituted but also in any nitroarene having at least one hydrogen atom in the *ortho*- or *para*-position relative to the nitro-group. Here it must be emphasised that in all these cases the VNS of hydrogen is faster than the usual nucleophilic substitution of a halogen, as has been observed, for example, in the reactions of chloronitrobenzoic[37] and chloronitrosulphonic acids.[38]

Nitronaphthalenes are distinguished by an especially high reactivity in the VNS reaction, which is undoubtedly associated with the increased stabilisation of the σ-adducts by the second aromatic ring. 1-Nitronaphthalene forms a mixture of 2- and 4-substituted products in which the 2-isomer greatly predominates. The substitution of hydrogen in 2-nitronaphthalene takes place exclusively in the 1-position.[41] VNS reactions are characteristic also of heterocyclic compounds. The nitro-derivatives of aromatic heterocycles are usually very reactive in the reaction with the chloromethyl phenyl sulphone carbanion. Thus the VNS reaction proceeds readily and affords substitution products in satisfactory yields for **2-, 3-, and 4-nitropyridines and also their chloro-, ethyl-, and** methoxy-derivatives.[42] In the case of chloronitropyridines, in which the nucleophilic substitution of chlorine is known to proceed at a high rate, the VNS of hydrogen is observed exclusively.[42] The VNS reaction takes place very smoothly in nitro-derivatives of five-membered heterocycles: 2-nitrothiophen,[43] 2-nitrofuran and its derivatives,[43] *N*-substituted 2- and 3-nitropyrroles,[43] and nitroimidazoles,[44] for example:

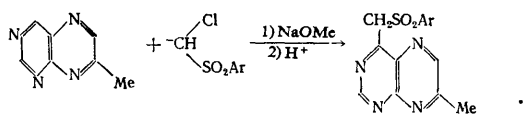


Nitroquinolines are very reactive in the VNS reaction and, as in nitronaphthalenes, mainly or exclusively the hydrogen atom in the *ortho*-position relative to the nitro-group is substituted; for example, in the 6-, 5-, and 7-positions respectively in 5-, 6-, and 8-nitroquinolines.[45] The substitution of hydrogen via the VNS mechanism can also be carried out in *N*-derivatives of nitroindoles:[46]



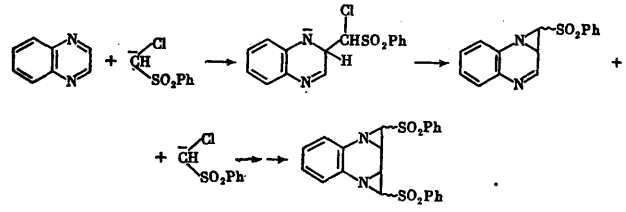
Certain heterocycles are sufficiently electrophilic for the occurrence of the VNS reaction even in the absence of the nitro-group. Thus the methylation of acridine, quinoline, and certain other heterocycles by DMSO and methyl phenyl sulphone anions was noted previously.[23,25]

The chloromethyl phenyl sulphone carbanion is less nucleophilic than the two carbanions used previously, but it is also capable of substituting the hydrogen in acridine, benzothiazole, and benzoxazole.[147] 1,2,4-Triazine and its derivatives are especially interesting, since in this instance nucleophilic attack may be directed to the 5-, 3-, or even 6-positions in the ring, the reactivity of the hydrogen atoms relative to nucleophiles decreasing in the sequence 5-H > 3-H > 6-H.[48] Using the corresponding substituted triazines, it is possible to carry out the VNS reaction in all these positions.[48,49] Pteridine derivatives exhibit a comparatively high reactivity in the VNS reaction. The reaction with unsubstituted pteridine could not be carried out apparently as a consequence of the instability of the ring under the highly basic reaction conditions, but the reaction with 5-methyl- and 5-phenyl-pteridines proceeds fairly readily:[50]

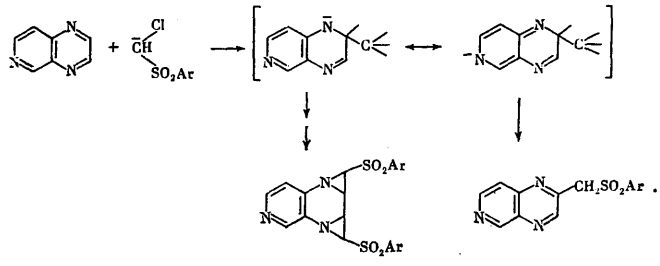


The attempts to extend the VNS reaction to certain other electrophilic heterocycles without the nitro-group, such as quinoxaline and naphthyridines, were unsuccessful: the reaction occurred in a different direction, namely via the bisannelation pathway.[51] The first stage of this process—the formation of a σ-adduct—is undoubtedly common to the VNS, but its subsequent reaction pathway is different. Instead of β-elimination, intramolecular nucleophilic substitution of chlorine takes place and the monoannelation product

formed, containing a reactive aliphatic C=N double bond, reacts rapidly with a second carbanion:

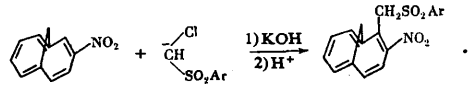


As a consequence of the partial delocalisation of the negative charge in the σ-adduct of quinoxaline, the neighbouring nitrogen atom has fairly pronounced nucleophilic properties promoting substitution and at the same time hindering β-elimination. This situation is absent in quinoxaline *N*-oxide, which forms a σ-adduct with a low negative charge on the nitrogen atom, as a result of which VNS takes place exclusively.[52] The negative charge density on the N(1) atom in the corresponding σ-adduct is reduced as a consequence of the conjugation with the N(6) atom, as a result of which competition is observed between the VNS and bisannelation reactions; the mode of the reaction of the σ-adduct can be controlled by varying the reaction conditions. A high concentration and an excess of the base as well as a low temperature promote bimolecular elimination, leading to VNS, while reduction of the base concentration and an increase in temperature promote bisannelation:[53]



Similar phenomena have been observed when the substituents in the substrate were varied. Thus the interaction of 1-cyanonaphthalene with the chloromethyl phenyl sulphone carbanion leads to the exclusive formation of the bisannelation product. The introduction of a second CN group increases the delocalisation of the negative charge in the σ-adduct, which promotes β-elimination and VNS; thus the mode of reaction is susceptible to control.[52]

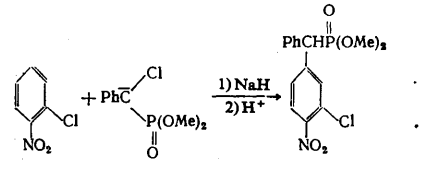
Finally, one should note that sufficiently electrophilic nonbenzenoid aromatic systems are also capable of VNS. The most interesting example is provided by derivatives of 1,6-methano-[10]annulene, which is an analogue of naphthalene as regards properties.[54] Thus in the reactions of 2- or 3-nitro-1,6-methano-[10]annulenes with chloromethyl phenyl sulphone, the hydrogen atom in the 3- and 2-positions respectively is substituted. Cyanomethanoannulenes are less reactive in this reaction. However, cyano-1,6-difluoromethano[10]annulenes undergo VNS, although the yields of the product are low.[55]



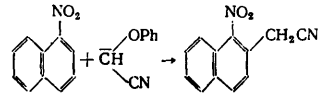
The possibility of VNS in the tropylium cation has been demonstrated in a few instances.[56]

The VNS concept can also be extended to electrophilic alkenes (the so called Michael acceptors). These compounds react with α-halogenocarbanions usually via an addition–intramolecular substitution mechanism with formation of cyclopropane derivatives.[57] By selecting the alkene and the reaction conditions, it is nevertheless possible to induce β-elimination in the adducts and to carry out the VNS of the hydrogen also in aliphatic systems.[58]

The results presented make it clear that the VNS of hydrogen in electrophilic aromatic compounds is of an extremely general character. Similarly, the carbanions of t-butyl chloromethyl, t-butyl *p*-tolyl, and t-butyl chloromethyl sulphones react with various electrophiles like the chloromethyl phenyl sulphone carbanion,[35] but it has to be stated that other alkyl chloromethyl sulphones are not usually employed in this reaction as well as other reactions proceeding via carbanions because they undergo rapid Ramberg–Baecklund rearrangements.[59] Other chloromethanesulphonyl compounds, namely *NN*-dialkylamides[35] and the phenyl or neopentyl ester of chloromethanesulphonic acid,[65] are also satisfactory precursors of carbanions in the VNS reaction. The tertiary carbanions formed from α-chloroalkyl or α-chlorobenzyl sulphone react with nitroarenes in accordance with the VNS mechanism but differ from the chloromethyl derivatives of sulphones by their reactivity and especially by the preferential substitution in the *para*-position.[35] In carbanions stabilised by sulphonyl groups, chlorine is the most convenient leaving group; other halogenomethanesulphonyl compounds are less easily available and undergo side reactions more readily.[35] Not only halogens but also certain other substituents, such as PhS, Me_2NCS_2, or PhO are capable of β-elimination, but the applicability of the corresponding substituted sulphones in VNS reactions is limited as a consequence of the low rate of elimination, which frequently leads to the preferential elimination of benzenesulphonic acid.[53] Chlorine is the most convenient and effective leaving group also in other carbanions stabilised by benzenesulphinyl,[61] diphenylphosphine oxide, and diethoxyphosphonyl[62] groups. For example, dimethyl α-chlorobenzylphosphonate reacts effectively with many nitroarenes, affording esters of *p*-nitrophenyl(phenyl)methylphosphonic acids:[62]



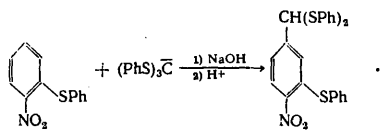
Despite the fact that α-chloronitriles, especially chloroacetonitrile, are fairly unstable in the presence of bases, they are capable of undergoing the VNS reaction but satisfactory results are obtained only in reactions with reactive nitroarenes.[63,64] Thus the cyanomethylation of chloronitrobenzenes or nitronaphthalene by chloroacetonitrile proceeds with a satisfactory yield. In the reaction with nitrobenzene, moderate yields have been achieved, while less reactive alkoxynitrobenzenes do not react with chloroacetonitrile via the VNS mechanism.[63,64] The cyanomethylation of the less reactive nitroarenes can be achieved with the aid of substituted nitriles such as $PhSCH_2CN$ or $PhOCH_2CN$, which are more stable in the presence of bases:[63–65]



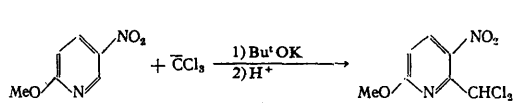
The reaction of α-chloropropionitrile with many nitroarenes usually leads to VNS products in satisfactory yields.[63,64]

The carbanions derived from chloroacetic,[66] dichloroacetic,[67] and α-chloroalkanoic acids[68] are fairly reactive in the alkoxycarbonylalkylation of nitroarenes via the VNS mechanism, but the process is very sensitive to the reaction conditions and the electrophilicity of arenes. Here too the more stable esters containing PhS or Me_2NCS_2 leaving groups have found more general application.[64] An example of the alkoxycarbonylmethylation reaction, in which the leaving group is the ammonium substituent, is known.[69]

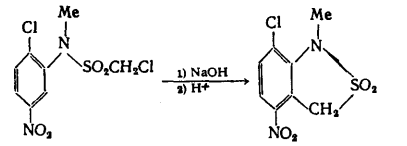
The majority of leaving groups stabilise the corresponding carbanions, so that many of these compounds are fairly strong CH acids capable of being deprotonated on treatment with bases and then reacting further with nitroarenes via the VNS mechanism. For example, PhS is a group of this kind. In fact tri(phenylthio)-methane substitutes the hydrogen atom in the *para*-position relative to the nitro-group in many nitroarenes, forming diphenyl dithioacetals of *p*-nitrobenzaldehydes:[70]



The similar reactions of the diphenyl dithioacetals of aldehydes or of benzyl phenyl sulphides with nitroarenes lead to the formation of nitrobenzyl phenyl sulphides[71] and diarylmethane derivatives.[72] There is no doubt that the VNS reaction with trihalogenomethyl-carbanions is of greatest interest in view of the ready availability of the initial haloforms as well as the possibility of further reactions of the dihalogenomethyl groups introduced. In analysing the possibilities of these reactions, account must be taken of the instability of the trihalogenomethyl anions, which dissociate rapidly with formation of dihalogenocarbenes,[73] and also of the instability of nitrobenzylidene dichloride carbanions.[74] As already mentioned above, McBee et al.[29] carried out the dichloromethylation of *p*-halogenonitrobenzenes by trichloromethyllithium at temperatures in the range −100 to −65 °C and proposed a carbene reaction mechanism.[29] We have found that, when potassium t-butoxide is used in a tetrahydrofuran–dimethylformamide mixture at temperatures in the range −65 to −70 °C, it is possible to achieve the dichloromethylation and even the dibromomethylation of many nitroarenes by the corresponding haloforms frequently in high yields.[75,76] The dihalogenomethylation reaction is very sensitive to the conditions and the reactivity of the nitroarenes. There is no doubt that it proceeds via a mechanism typical for the VNS reaction–the addition of the CX_3^- anions and the elimination of HX from the σ-adduct formed:[76]

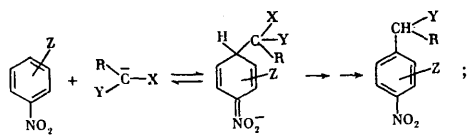


Instances of VNS occurring with ring opening or closure are known. Thus the carbanions of phenylcyanooxirans react with nitronaphthalene to form σ-adducts, the subsequent reaction involving β-elimination from them and being accompanied by the opening of the oxiran ring.[77] Examples of intramolecular processes leading to ring formation are more numerous. They include the intermolecular VNS in chloromethanesulphonamides formed from *m*-nitrobenzylamine and *m*-nitroaniline derivatives:[78]



The synthesis of tetracyclic derivatives of anthraquinone via intramolecular VNS which follows Michael addition is extremely interesting.[79]

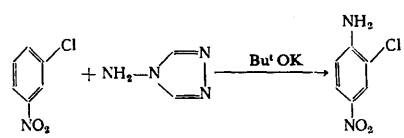
It is evident from the examples quoted above that the range of carbanions suitable for VNS reactions is wide. A necessary requirement which must be met by the structure of the carbanions is the presence at the carbanionic centre of a group X capable of undergoing β-elimination in the form of HX from the intermediate σ-adduct under the influence of bases. Thus carbanions capable of undergoing the VNS reaction can be represented by the general formula X–$\bar{C}$YR, where X is the leaving group, Y the group stabilising the carbanion, and R its substituent. A mechanism of VNS is presented below in a general form (examples of the group Z were presented above):



X = Cl, Br, PhO, PhS, Me_2NCS_2, etc;
Y = SO_2Ar, SO_2OPh, SOPh, CN, COOEt, $P(O)Ph_2$, Cl, PhS, etc;
R = H, Alk, Ar, Cl, PhS, etc.

Virtually any combination of X, Y, and R presented in the scheme gives rise to a carbanion capable of reacting in accordance with the VNS mechanism. Certain limitations in the use of such carbanions are associated with the tendency of some of them to undergo autocondensation ($ClCH_2CP$) or to decompose (CCl_3^-). Such carbanions react smoothly only with reactive nitroarenes. In addition, appreciable stabilisation induces a reduced nucleophilicity of the carbanions, which can also prevent the reaction. Finally, bulky tertiary carbanions (R ≠ H) are frequently incapable of undergoing the hydrogen substitution reaction in the *ortho*-position relative to the nitro-group or to other bulky substituents, principally as a result of the steric hindrance in the elimination stage.

The VNS of hydrogen is not limited to the reactions of carbon-based nucleophilic carbanions. The amination of nitroarenes by hydroxylamine and, especially effectively, by 1-amino- and 1-alkylamino-1,3,4-triazoles takes place via the same addition–β-elimination mechanism:[80,81]



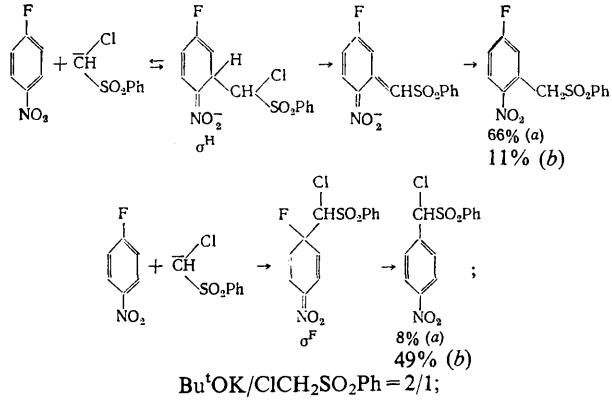
III. The reaction mechanisms

The VNS reaction is undoubtedly a multistage process including, in the first place, the formation of the σ-adduct of the carbanion and the nitroarene and its further reactions. Thus the reaction

mechanism must provide answers to the following questions: how is the σ-adduct formed and in what way is it converted into the product. Furthermore, it is necessary to determine the ratios of the rates of these stages.

σ-Adducts can be formed via two alternative pathways: as a result of the direct nucleophilic attack or in two stages via electron transfer from the carbanion to the nitroarene with subsequent recombination of the radical-anion and the radical formed.[82] The question via which pathway the σ-adducts are formed in the VNS reaction has not been studied in detail but certain observations and preliminary experiments suggest that here we are dealing with direct nucleophilic attack. For example, the *ortho*-directing effect in the VNS reactions, determined by the existence of the carbanions as close ion pairs,[36] while the formation of the σ-adducts of organomagnesium compounds with nitroarenes via one-electron transfer[17,83] usually affords a statistical mixture of the *ortho*- and *para*-isomers, leads to the same conclusion. The hypothesis that the VNS proceeds via the direct addition of the nucleophile and not as a one-electron transfer has been confirmed by the results of studies of reactions using the so called free-radical clocks, because these reactions occur without appreciable competition with free-radical processes.

In our view, the question of the way in which the σ-adducts are converted into the VNS products is more important. Among the various possibilities, the 1,2-hydride shift with the concerted elimination of the X^- anion and the base-induced β-elimination of HX appeared most likely. The study of the influence of the concentration of the base on the rate of reaction led to the conclusion that the VNS proceeds via the elimination pathway.[21] The influence of the base on the rate of reaction was studied by the method of competing reactions—the competition between the fluorine and hydrogen substitution reactions in *p*-fluoronitrobenzene was studied:



$Bu^tOK/ClCH_2SO_2Ph = 2/1$;
(*a*) high concentration of Bu^tOK,
(*b*) low concentration of Bu^tOK.

The rates of formation of the σ^F- and σ^H-adducts as well as the rate of conversion of the σ^F-adduct into the fluorine-substitution product are independent of the base concentration, like the rate of conversion of the σ^H-adduct into the product via hydride transfer, while the rate of conversion of the σ^H-adduct into the product via the β-elimination of HCl should be directly proportional to the base concentration. Thus an increase in the concentration of the base should appreciably increase the fraction of the hydrogen-substitution products, which has in fact been observed. Similarly, when there is intermolecular competition between the substitution of *p*-H in nitrobenzene and *p*-F in *p*-fluoronitrobenzene by the phenylphenoxyacetonitrile carbanion (this tertiary carbanion substitutes only the hydrogen in the *para*-position relative to the nitro-group), the mode of reaction is determined by the base concentration. In the absence of an excess of the base, the usual fluorine substitution has been observed, while in the presence of an excess of the base the exclusive formation of the products of the VNS of hydrogen in nitrobenzene has been observed, while *p*-fluoronitrobenzene remained unaltered[21]!

These results show not only that the conversion of the σ^H-adducts into the VNS products is accelerated by the base and hence that it proceeds via the pathway involving the β-elimination of HX but also that the formation of σ-adducts is a reversible and rapid process compared with β-elimination and that the rate of formation of σ^H-adducts is higher than that of σ^F-adducts. Numerous kinetic studies of nucleophilic aromatic substitution have shown that the rate of substitution of fluorine is much higher than the rate of substitution of chlorine and other leaving groups, which increases still further the ratio of the rates of formationof σ^H-adducts and other corresponding adducts.[1]

On the basis of this ratio, one can control the mode of reaction of chloromethyl phenyl sulphone with *m*-nitrobenzophenone[40] and azaquinoxaline:[53] a high concentration of the base promotes the VNS, while the use of more dilute solutions and the absence of an excess of bases lead to other processes.

Important data concerning the mechanisms of the reactions involving the dissociation of a C–H bond have been obtained in the study of the kinetic isotope effect.[84] For the two-stage VNS process, in which a C–H bond is cleaved (as shown above) in the second stage, which limits the overall rate of reaction, we expected the appearance of a distinct primary effect where the ratio $k_H/k_D > 1$. Unexpectedly, the ratio k_H/k_D for *p*-nitro[D]benzene {determined by comparing the ratios of the *o*- and *p*-isomers in reactions of chloromethyl phenyl sulphone with *p*-nitro[D]benzene and nitrobenzene} proved to be less than unity, amounting to 0.9. Thus a secondary isotope effect is observed. This is possible in the addition stage but not in the elimination stage. These at first sight contradictory results can be accounted for by analysing the energy profile of the process, which in the case of mononitro-derivatives, when the latter are stable, involves the formation of an unstable intermediate (σ-adduct). The subsequent β-elimination of HCl converts this adduct into the highly stabilised nitrobenzyl carbanion and the structure of the early transition state in this stage should therefore be asymmetric.

The difference between the rates of cleavage of C–H and C–D bonds in such processes is known to be insignificant. In other words, in this case $k_H/K_D \simeq 1$ for β-elimination, as a result of which a secondary isotope effect can be manifested in the addition stage. In fact, the addition of the carbanion to the nitrobenzene ring is accompanied by a change in the hybridisation of the ring carbon atom from sp^2 (in the initial nitrobenzene) to sp^3 (in the σ-adduct), which is known to be promoted by the replacement of hydrogen by deuterium. Since the addition is reversible while deuterium retards the dissociation, the equilibrium constant, which determines the concentration of the σ-adducts, is higher for the σ^D-adduct, i.e. $k_D > k_H$.

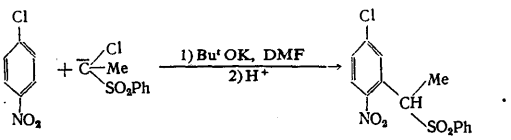
In the absence of the isotope kinetic effect in the elimination stage, the observed rate of substitution of deuterium exceeds the rate of substitution of hydrogen, i.e. $k_H/k_D \simeq 0.9$. These considerations, which are partly speculative, have been confirmed by the results of

the study of the kinetic isotope effect for the VNS reactions in which the elimination proceeds via a symmetrical transition state. The kinetic effects, i.e. the ratios k_H/k_D, reach appreciable values (3–7) in specific examples.[85,86]

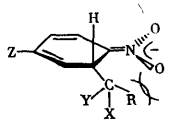
The above conclusions concerning the characteristic features of the VNS mechanism are a result of so far fairly simple studies at a qualitative level. They require further revisions and corrections, especially those based on quantitative measurements. In particular, many observations indicate that the ratios of the rates of addition and elimination found above can vary.

IV. The problem of the reaction site

Although the proposed VNS mechanism is of a preliminary character, nevertheless it indicates effectively the complexity of the problem of the reaction site. As a rule, the reaction proceeds via the rapid and reversible formation of σ-adducts, which then undergo the slower β-elimination. The relative rates of substitution of hydrogen in different positions in the nitroarene therefore depend on the ratios of the rates of formation of the isomeric σ-adducts, the corresponding equilibrium constants, and the elimination rate constants. The overall picture is complicated by the fact that carbanions can also act as bases in the elimination step, while their concentration varies during the reaction. Furthermore, the problem of the reaction site can be approached phenomenologically by analysing the influence of the principal variable parameters on the reaction site: the structure of the carbanions, the structure of the nitroarenes, and the reaction conditions. The ratio of the products of *ortho*- and *para*-substitution, formed in the VNS of the hydrogen atoms in nitrobenzene by the carbanions of α-halogenoalkyl phenyl sulphones depends greatly on the steric effects. Secondary carbanions of the type $X\overline{C}HSO_2Ph$ (X = halogen) substitute the hydrogen atom in the *ortho*- and *para*-positions relative to the nitro-group, the fraction of the *ortho*-isomer diminishing with increase in the size of the halogen, i.e. in the sequence F > Cl > Br > I, whereas tertiary carbanions $Cl\overline{C}RSO_2Ph$ (R = Me, Ph, etc.) give rise exclusively or mainly to *para*-substituted products.[35,87] This does not mean that tertiary carbanions are incapable of substituting hydrogen in the *ortho*-position relative to the nitro-group. In the case of *para*-substituted nitrobenzenes, for example, *p*-chloronitrobenzene, the α-chloroethyl phenyl sulphone carbanion,[87] and certain other tertiary carbanions substitute smoothly the hydrogen atom in the *ortho*-position:[64,66]



The substitution by tertiary carbanions in the *ortho*-position relative to the nitro-group has also been observed in nitrobenzene derivatives having a bulky group in the *meta*-position.[87] Many observations have shown that the VNS is more sensitive to steric hindrance than the classical nucleophilic substitution of a halogen. One can therefore postulate that steric hindrance in the VNS reaction has a greater effect in the elimination stage and not in the addition stage. Since the transition state in the elimination step requires an antiperiplanar disposition of the hydrogen atom and the leaving group, the sensitivity of this process to the size of the groups R and Y is evident.



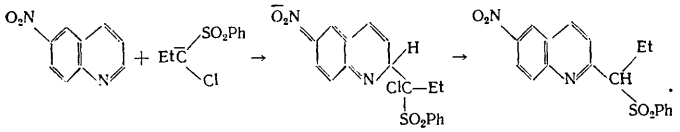
The steric effects in elimination from *ortho*-σ-adducts formed by tertiary carbanions can usually be compensated by the increased nucleophilicity of such carbanions (which increases the equilibrium constants of the addition reactions) and also by the presence of several leaving groups, etc. A good example is provided by the substitution reaction with participation of the tertiary trichloromethyl carbanion, which occurs preferentially in the *ortho*-position relative to the nitro-group even in the interaction with nitrobenzene.[76]

The conditions where the carbanions are present as solvate-separated ion pairs are most favourable for VNS. This happens for the sodium and potassium salts of deprotonated nucleophiles in DMSO, dimethylformamide (DMF), liquid ammonia, etc. in the presence of an excess of a soluble base. Under these conditions, the ratio of the *ortho*- and *para*-substitution products depend little on the nature of the cation and the solvent and is determined mainly by the structure of the carbanion and the nitroarene. The nature of the base can also have a significant influence on the reaction site under these conditions. For example, the NaOH and KOH frequently employed are almost insoluble in these solvents, so that they are used in the powdered state in a large excess. One must postulate that in such cases the elimination occurs mainly on the surface of the solid phase and partly under the influence of the carbanion as a base. It has been demonstrated experimentally that, depending on the character of the base, the ratio of the *ortho*- and *para*-isomers (the products of the VNS of the hydrogen in nitrobenzene by the potassium salt of chloromethyl phenyl sulphone) varies from 1.80 (when the elimination takes place under the influence of the excess Bu^tOK) to 0.86 (when it is induced by the excess carbanion).[88]

The degree of association of the ion pairs has a very powerful influence on the ratio of the *ortho*- and *para*-substitution products in VNS. Thus virtually only *ortho*-substitution is observed in the reaction of chloromethyl phenyl sulphone with nitrobenzene in the Bu^tOK–THF system. The product of the substitution of the second ortho-hydrogen atom is formed exclusively even in the case of *o*-chloronitrobenzene.[36] Similar effects have also been observed in reactions with other carbanions.[89] These phenomena are induced by the intense association of the cation–carbanion ion pairs in a moderately solvating solvent of the type of THF. The K^+ cation in this close ion pair is attracted to the negatively charged oxygen atoms of the nitro-group, which leads to the formation of the *ortho*-σ-adduct and *ortho*-substitution. The solvation character of this effect has been demonstrated by adding to the system an equimolar amount of crown-ether, which strongly binds the K^+ cation in a complex and this entails the formation of a mixture of *ortho*- and *para*-substitution products characteristic of dipolar solvents.[36]

In considering the influence of the structure of nitroarenes on the reaction site, it is necessary to consider the electronic structure of the ring and the influence of substituents. The ratios of the *ortho*- and *para*-substitution products in the VNS reactions with nitrobenzene and nitropyridines differ insignificantly as a consequence of the

similar electronic structures of these aromatic systems. In less symmetrical aromatic systems, the ratio usually changes in favour of the *ortho*-isomer, which happens, for example, in the bicyclic naphthalene and quinoline systems. In the case of 1-nitronaphthalene[41] and 5- and 8-nitroquinolines,[45] the reaction takes place preferentially in the *ortho*-position relative to the nitro-group, i.e. at the C(2), C(6), and C(7) atoms respectively. The *para*-isomers are formed only in small amounts. On the other hand, 2-nitronaphthalene and 6-nitroquinoline react exclusively in the 1- and 5-positions respectively and only with secondary carbanions. The reaction does not take place with tertiary carbanions apparently because of the significant steric hindrance induced by the nitro-group and the hydrogen atom in the *peri*-position. For the same reason, the product of the VNS of the hydrogen atom at the C(2) atom was obtained in a low yield in the reaction of 6-nitroquinoline with α-chloropropyl *p*-tolyl sulphone:[45]

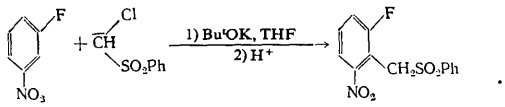


The preferential or exclusive *ortho*-directing effect in the VNS reaction with nitro-derivatives of bicyclic arenes is caused by the significant double bond character of the C(1)–C(2) bonds in naphthalene and also the C(5)–C(6) and C(7)–C(8) bonds in quinoline, which induces the preferential addition of nucleophiles to the positions indicated above in the corresponding *nitro*-derivatives. The addition to the C(3) and C(7) atoms in 2-nitronaphthalene and 6-nitroquinoline is also very much less favourable, because the stabilisation of the σ-adduct by conjugation with the nitro-group would lead to the breakdown of the aromaticity of the second ring. A similar situation arises in five-membered heterocycles such as thiophen, pyrrole, furan, etc. in which the C(2)–C(3) and C(4)–C(5) bonds have an appreciable double bond character. Therefore in 2-nitro-derivatives the VNS takes place preferentially at C(3), while in 3-nitro-derivatives it takes place exclusively at C(2).[43] It must be emphasised that this "*ortho*"-direction occurs also in reactions with tertiary carbanions, which is promoted by the geometry of the five-membered ring in which the steric effects of the neighbouring substituents are weaker than in the six-membered ring.

The question of the influence of the substituent Z in the nitrobenzene ring on the site of the VNS is fairly complex. This problem is naturally absent in the 4-Z-nitrobenzenes and can be solved fairly simply in 2-Z-nitrobenzenes. The ratio of the *ortho*- and *para*-substitution products in the latter case changes mainly as a result of the statistical factor. Sterically bulky substituents can prevent the reaction, hindering the coplanarity of the ring and the group, which is essential for the effective stabilisation of the σ-adduct (the so called secondary steric effect). Nevertheless, the reaction proceeds with a satisfactory yield even with *o*-nitrobenzoic and *o*-nitrobenzenesulphonic acids.[37,38]

The site of the reaction in 3-Z-nitrobenzenes, where one may expect, in principle, the formation of three isomeric products of the substitution of hydrogen in the 2-, 4-, and 6-positions, constitutes the most complex problem. The relative amounts of these isomers depend on the nature of the substituent Z and the carbanion and on the reaction conditions, which leads to a fairly complex picture. In the reaction series with participation of chloromethyl sulphone as the source of the carbanion, the substituents Z promote, regardless of conditions, substitution at either the neighbouring C(2) or C(4) atom (first group) or at the more remote C(6) atom (second group).[35,36,42,90] The halogens, Me, MeO, Me_2, etc. belong to the first group and CF_3, COOEt, NO_2, etc. belong to the second group.

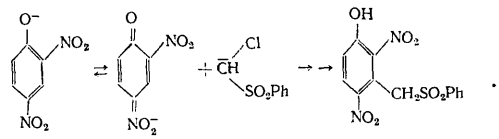
Such influence of the substituents on the reaction site is observed also in reactions with certain other secondary carbanions.[64,89] Bearing in mind that the use of Bu^tOK in THF leads to *ortho*-substitution, it is possible in many cases to synthesise 2,3-disubstituted nitrobenzene derivatives:[36]



The influence of the substituent Z on the reaction site can be determined by its influence on the rate of addition, the equilibrium constant, the rate of elimination, and the electronic and steric factors. The influence of the substituent Z on the electronic effects can be illustrated by a quantum-chemical calculation, which reveals a correlation between the parameters of the lowest unoccupied MO of the substrate and the character of the reaction site; however, better results were obtained when classical electronic effects were resorted to in order to explain this influence.[90] Overall, the effects indicated can account for the influence of the substituent Z on the rate of addition of the nucleophile and, to a lesser extent, on the equilibrium constant, but its influence on the rate of addition of the nucleophile, which can be explained on the basis of steric effects, is less understandable from the standpoint of electronic effects.

The attempts to explain the strong directing effect of the substituents of the first group (Me, MeO) indicated above in terms of the polarisabilities (the so called Bunnett–Reinheimer effect[91]) were unsuccessful, since many non-polarisable substituents (for example, F) have a similar effect.

The influence of substituents with a strong electron-donating activity on the reaction site is very interesting. As already mentioned previously, in contrast to mononitrophenols, dinitrophenols enter into the VNS reaction.[39] Unusual reaction sites are observed in such cases. Thus, substitution in 2,4-dinitrophenol takes place at the C(3) atom, whereas in 2,4-dinitroanisole it occurs at the C(5) atom. In the latter case, the hydrogen atom substituted is in the *para*-position relative to one nitro-group and in the *ortho*-position relative to the other, as for substitution at the C(4) atom in 1,3-dinitrobenzene.[35] The unusual VNS reaction site in 2,4-dinitrophenol is induced by the fact that in a fairly basic medium the phenol reacts as the dinitrophenoxide anion whose negative charge is delocalised, mainly between the oxygen atoms of the nitro-groups:



Hence it is evident that the nucleophilic attack must be directed to the C(3) atom.[35] For the same reason, 1,3-di(benzenesulphonyl)-methyl-2,4-dinitrobenzene is formed in the reaction of *m*-dinitrobenzene with an excess of chloromethyl phenyl sulphone; in this case, the substitution of the second hydrogen atom takes place in the dinitrobenzyl anion whose electronic structure is similar to that of the 2,4-dinitrophenoxide anion.[35] The characteristic features of the VNS reaction sites in the amino-derivatives of dinitrobenzene,

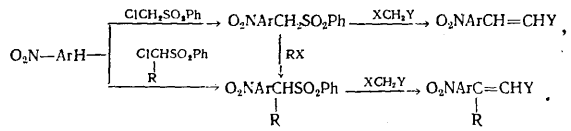
alkoxynitropyridines, *N*-alkyl-2-nitropyrroles, and other structurally related compounds can be explained similarly.

V. Practical applications

The VNS of hydrogen is a new hitherto little investigated reaction in organic chemistry. Our studies were directed mainly towards the elucidation of its applications and the solution of the problems of the mechanism, reaction site, and other general questions. However, certain possibilities for the practical application of the VNS can also be inferred from these results. Readily available starting materials are necessary for the VNS reaction, the reaction does not require any complex conditions, and its result is the direct substitution of the hydrogen atom in the aromatic nitro-substituted ring by alkyl substituents containing functional groups. The prospects for the practical application of the VNS reaction therefore appear very favourable.

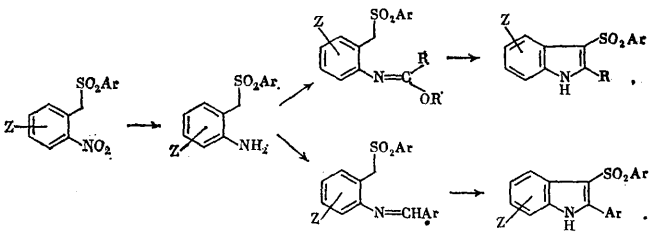
In the first place, the VNS products are fairly strong CH acids; on treatment with bases, they are readily converted into the corresponding carbanions. Despite their moderate nucleophilicity due to the very effective stabilisation, the latter are capable of entering into many reactions characteristic of carbanions. For example, the carbanions derived from nitrobenzyl sulphones and nitriles by the VNS reaction are readily alkylated and add to Michael acceptors.[92] These reactions occur particularly readily under the conditions of phase transfer catalysis.[93]

The possibility of synthesising derivatives of nitrocinnamic acid and other substituted nitrostyrenes by VNS is very interesting. The alkylation of nitrobenzyl sulphones by the esters of carboxylic α-halogenoacids and other alkylating agents containing an electron-accepting group is accompanied by the elimination of benzenesulphonic acid, which leads to the formation of nitrostyrene derivatives.[94] Thus two-stage substitution of a hydrogen atom by the vinyl residue is achieved:



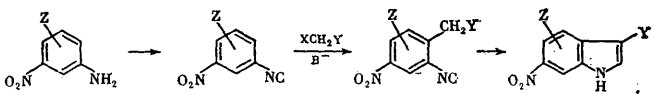
The possibility of introducing carbon-based functional groups into aromatic nitro-substituted rings by means of VNS and the subsequent reactions of the products are of significant interest. Thus the reaction with tri(phenylthio)methane leads to the formation of the dithioacetals of *p*-nitrobenzaldehydes, which afford aldehydes on hydrolysis, whilst their alkylation followed by hydrolysis leads to alkyl nitroaryl ketones.[70] An even more convenient synthesis of nitroarylaldehydes is based on the dihalogenomethylation of nitroarenes by haloforms followed by hydrolysis.[75,76] The VNS products can be readily converted into aromatic nitroacids after oxidation or hydrolytic halogenation and hence one can achieve a two-stage carboxylation of nitroarenes.[95]

By virtue of the possibility of introducing various functional group-containing substituents in the *ortho*-position relative to the nitro-group, the application of the VNS reaction in the synthesis of heterocyclic systems, especially indoles, is very promising. For example, the reduction of substituted *o*-nitrobenzyl phenyl sulphones leads, as a result of the VNS, to the corresponding amino-derivatives, which are converted into substituted indoles as a consequence of the initial conversion into isonitriles, imidates,[96] or Schiff bases[97] and the subsequent condensation in the presence of a base:



The existing method of synthesis of indoles by the catalytic hydrogenation of derivatives of *o*-nitroarylacetonitriles[98] is of limited importance because of the low availability of the initial compounds. The possibility of synthesising various *o*-nitroarylacetonitriles by direct cyanomethylation via the VNS reaction[64,65,89] makes this method of great value. All the isomeric hydroxy- and alkoxy-indoles have been synthesised in this way.[65]

Nitroindoles can be obtained directly by the VNS reaction from *m*-nitroaniline:

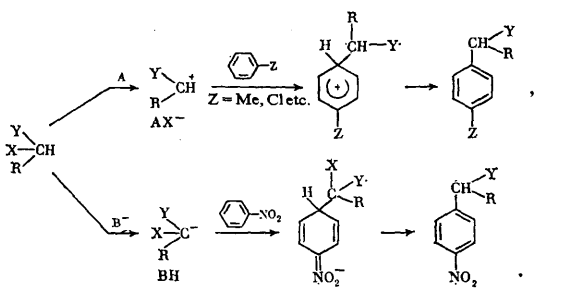


The *m*-nitrobenzoisonitrile obtained is introduced into the VNS reaction with various carbanions; the VNS products formed, in which the functional group-containing methyl substituents are in neighbouring positions relative to the isonitrile group, undergo cyclisation, which leads to nitroindole derivatives.[99]

VI. Conclusion

The data presented in this review permit the conclusion that VNS is an extremely general process for the substitution of hydrogen in electrophilic arenes (predominantly in nitroarenes) by alkyl groups containing functional groups in the α-positions. In this respect, it is possible to deduce a significant similarity between the VNS reaction and the Friedel–Crafts reaction, which takes place via an electrophilic substitution mechanism.

In fact the stoichiometries of the VNS and Friedel–Crafts reactions are similar. Also similar are the types of products obtained, but these processes differ radically in their mechanisms and in the influence of the polarity of the reactants:



Thus, as regards stoichiometry and the results, VNS can be regarded as a process analogous to the Friedel–Crafts reaction but with the reverse polarity of the reactants. It is therefore entirely appropriate to apply the term "umpolung" (reversal of polarity) introduced by Seebach[100] to define the principle of the reversal of the polarity of reactants in organic synthesis. By extending this term to reactions taking place with reversal of polarity, one may say that VNS represents the "umpolung" of the Friedel–Crafts reaction. Apart from these terminological considerations, it must be emphasised that VNS is a process complementary to the Friedel–Crafts reaction, since it makes it possible to substitute a hydrogen atom by carbon-centred substituents in those arenes which are incapable of undergoing electrophilic substitution. Thus a possibility is created for substituting hydrogen by carbon-based residues in virtually any aromatic systems. The general character of the VNS, which is much faster than the usual nucleophilic substitution of the halogens, finally demonstrates the lack of validity of the generally adopted view[1] that the nucleophilic substitution of hydrogen in aromatic systems is a possible phenomenon but is not usual. On the contrary, bearing in mind that the addition of nucleophiles to the carbon atoms of a halogen-substituted aromatic ring takes place at a high rate at the positions containing hydrogen and not halogen atoms and also taking into account the many possibilities for further reactions of the σ^H-adducts obtained in this way, the traditional nucleophilic substitution of the halogen in halogenonitroarenes can be frequently regarded as a side process, developing against the background of the reactions indicated above.[101]

References

1. J Miller *Aromatic Nucleophilic Substitution*, Elsevier, Amsterdam–London, 1968, 374 pp.
2. T J De Boer, J P Dirks *Chemistry of the Nitro and Nitroso Group* (Edited by H Pauer), Intersci. Publ., London, 1969
3. C F Bernasconi *Chimia*, 1980, **34** 1
4. J F Bunnet *Acc. Chem. Res.*, 1978, **11** 413
5. H C van der Plas *Acc. Chem. Res.*, 1978, **11** 462
6. O N Chupakhin, V N Charushin, H C van der Plas *Tetrahedron*, 1988, **44** 1
7. O N Chupakhin, I Ya Postovskii *Usp. Khim.*, 1976, **45**(5) 908 [English translation in *Russ. Chem. Rev.*, 1976(5)]
8. R A Abramovitch, J G Saha *Adv. Heterocycl. Chem.*, 1966, **6** 293
9. E V Malykhin, G A Kolesnichenko, V D Shteingarts *Zh. Org. Khim.*, 1985, **21**, 1150
10. W Danikiewicz, M Makosza *Tetrahedron Lett.*, 1985, 3599
11. G Iwasaki, K Wada, S Saeki, M Hamana *Heterocycles*, 1984, **22** 1811
12. M Makosza, M Jagusztyn-Grochowska, M Ludwikow, M Jawdosiuk *Tetrahedron*, 1974, **30** 3723
13. R B Davis, L C Pizzini *J. Org. Chem.*, 1960, **25** 1884
14. F Terrier *Chem. Rev.*, 1982, **82** 77
15. O A Artamkina, M P Egorov, I P Beletskaya *Chem. Rev.*, 1982, **82** 427
16. T J King, C E Nexal *J. Chem. Soc.*, 1962, 367
17. G Bartoli *Acc. Chem. Res.*, 1984, **17** 109
18. T Rajanßabu, G S Reddy, T J Fukunaga *J. Am. Chem. Soc.*, 1985, **107** 5473
19. F G Bordwell, G D Cooper *J. Am. Chem. Soc.*, 1951, **73** 5184
20. J Golinski, M Makosza *Tetrahedron Lett.*, 1978, 3495
21. M Makosza, T Glinka *J. Org. Chem.*, 1983, **48** 3860
22. P A Argabright, J E Hofmann, A Schriesheim *J. Org. Chem.*, 1965, **30** 3233
23. G A Russel, S A Weiner *J. Org. Chem*, 1966, **31** 248
24. H Nozaki, Y Yamamoto, R Noyori *Tetrahedron Lett.*, 1966, 1123
25. H Nozaki, Y Yamamoto, T Nisimura *Tetrahedron Lett.*, 1968, 4625
26. B Trost *Tetrahedron Lett.*, 1966, 5716
27. M Metzger, H König, K Seelert *Tetrahedron Lett.*, 1964, 867
28. V J Traynelis, J V McSweeney *J. Org. Chem.*, 1966, **31** 243
29. E T McBee, E P Wesseler, T Hodgins *J. Org. Chem.*, 1971, **36** 2907
30. C C Price, S T Voong *Org. Synth.*, 1955, **3** 664
31. N A Pakhomova, Ya D Grudtsyn, S S Gitis *Zh. Org. Khim.*, 1974, **10** 1046
32. M Makosza *Current Trends in Organic Synthesis* (Edited by H Nozaki), Pergamon Press, Oxford, etc. 1983, p. 401
33. M Makosza *Mitt. Chem. Ges. DDR*, 1986, **33** 74
34. M Makosza, J Winiarski *Acc. Chem. Res.*, 1987, **20** 282
35. M Makosza, J Golinski, J Baran *J. Org. Chem.*, 1984, **49** 1488
36. M Makosza, T Glinka, A Kinowski *Tetrahedron*, 1984, **40** 1863
37. M Makosza, S Ludwiczak *Synthesis*, 1986, 50
38. M Makosza, A Kinowski *Bull. Pol. Acad. Sci., Chem.* (in press)
39. M Makosza, S Ludwiczak *J. Org. Chem.*, 1984, **49** 4562
40. M Makosza, J Golinski, J Baran, D Dziewonska-Baran *Chem. Lett.*, 1984, 1619
41. M Makosza, W Danikiewicz, K Wojciechowski *Liebigs Ann. Chem.*, 1987, 711
42. M Makosza, B Chylinska, B Mudryk *Liebigs Ann. Chem.*, 1984, 8
43. M Makosza, E Slomka *Bull. Pol. Acad. Sci., Chem.*, 1984, **32** 69
44. M Makosza, E Kwast *Bull. Pol. Acad. Sci., Chem.*, 1987, **35** 57
45. M Makosza, A Kinowski, W Danikiewicz, B Mudryk *Liebigs Ann. Chem.*, 1986, **34** 69
46. K Wojciechowski, M Makosza *Synthesis* (in print)
47. M Makosza, J Golinski, A Rykowski *Tetrahedron Lett.*, 1983, 3277
48. R G Shepherd, J L Fedrick *Adv. Heterocycl. Chem.*, 1965, **4** 145
49. A Rykowski, M Makosza *Liebigs Ann. Chem.*, 1988, **36** 627
50. M Makosza, S Ostrowski *J. Prakt. Chem.*, 1988, **330** 789
51. J Golinski, M Makosza, A Rykowski *Tetrahedron Lett.*, 1983, 3279
52. M Makosza, T Glinka, S Ostrowski, A Rykowski *Chem. Lett.*, 1987, 61
53. S Ostrowski, M Makosza *Tetrahedron*, 1988, **44** 1721
54. E Vogel *Current Trends in Organic Synthesis* (Edited by H Nozaki), Pergamon Press, Oxford, etc. 1983, p. 379
55. M Makosza, E Vogel, R Moritz, et al. (in preparation)
56. S Ostrowski, M Makosza *Liebigs Ann. Chem.* (in press)
57. L A Yanovskaya, V A Dombrovskii, A S Khusid *Tsiklopropany s Funktsional'nymi Gruppami* (Cyclopropanes with Functional Groups), Izd. Nauka, Moscow, 1980
58. M Makosza, A Kwast *J. Chem. Soc., Chem. Commun.*, 1977, **25** 1
59. L A Paquette *Org. React.*, 1977, **25** 1
60. M Makosza, J Golinski *Synthesis*, 1983, 1023
61. M Makosza, J Golinski, J Pankowski *Synthesis*, 1983, 40
62. M Makosza, J Golinski *Angew. Chem.*, 1982, **94** 468
63. M Makosza, J Winiarski *J. Org. Chem.*, 1980, **45** 1534

64. M Makosza, J Winiarski *J. Org. Chem.*, 1984, **49** 1494
65. M Makosza, W Danikiewicz, K Mojciechiwski *Liebigs Ann. Chem.*, 1988, 23
66. B Mudryk, M Makosza *Synthesis*, 1988, 1007
67. *Polish P. 265645*, 1987
68. G B Stahly, B C Stahly, J Lilje *J. Org. Chem.*, 1984, **49** 578
69. A Tanaka, T Usui *J. Heterocycl. Chem.*, 1979, **16** 1409
70. M Makosza, J Winiarski *Chem. Lett.*, 1984, 1623
71. M Makosza, J Winiarski *J. Org. Chem.*, 1984, **49** 5272
72. M Makosza, A Kinowski, J Pankowski *Synthesis* (in preparation)
73. W Kirmse *Carbene Chemistry*, Acad. Press, New York–London, 1971
74. H Ida, N Ooki, K Takahashi *Nippon Kagaku Kaishi*, 1974, 2127; *Chem. Abs.*, 1975, **83** 27739
75. M Makosza, Z Owczarczyk *Tetrahedron Lett.*, 1987, 3021
76. M Makosza, Z Owczarczyk *J. Org. Chem* (in press)
77. M Makosza, J Pankowski *Bull. Soc. Chim. Belg.*, 1985, **94** 235
78. M Makosza, K Wojciechowski *Tetrahedron Lett.*, 1984, 4791
79. R Murphy, M Cava *Tetrahedron Lett.*, 1984, 803
80. A R Katrizky, K S Laurenzo *J. Org. Chem.*, 1986, **51** 5039
81. A R Katrizky, K S Laurenzo *J. Org. Chem.*, 1988, **53** 3978
82. Z V Todres *Usp. Khim.*, 1978, **47**(2) 260 [English translation in *Russ. Chem. Rev.*, 1978(2)]
83. G Bartoli, M Bosco, R Dal Pozzo, F Ciminale *J. Org. Chem.*, 1982, **47** 5227
84. E Buncel, C C Lee (Editors) *Isotopes in Organic Chemistry*, Elsevier, Amsterdam, 1976, Vol. 2
85. G P Stahly, B C Stahly, J R Maloney *J. Org. Chem.*, 1988, **53** 690
86. T Glinka, B Mudryk, M Makosza *J. Chem. Soc., Perkin Trans. 1* (in press)
87. B Mudryuk, M Makosza *Tetrahedron*, 1988, **44** 209
88. T Glinka *Doctor of Philosophy Thesis*, Institute of Organic Chemistry, Polish Acad. Sci., Warsaw, 1984
89. M Makosza, M Wenall, M Golinski, A Kinowski *Bull. Acad. Pol. Sci., Chim.*, 1985, **33** 427
90. M Makosza, M Golinski *Tetrahedron* (in preparation)
91. J D Reinheimer, J F Bunnett *J. Am. Chem. Soc.*, 1959, **81** 315
92. M Makosza, A Tyrala *Synth. Commun.*, 1986, **16** 419
93. M Makosza, A Fedorynski *Adv. Catal.*, 1987, **35** 375
94. M Makosza, A Tyrala *Synthesis*, 1987, 1142
95. M Makosza, A Tyrala *Synthesis* (in preparation)
96. K Wojciechowski, M Makosza *Synthesis*, 1986, 651
97. K Wojciechowski, M Makosza *Bull. Soc. Chim. Belg.*, 1986, **95** 671
98. I K Stamos *Synthesis*, 1980, 663
99. K Wojciechowski, M Makosza *Tetrahedron Lett.*, 1984, 4793
100. D Seebach *Angew. Chem., Int. Ed. Engl.*, 1979, **18** 239
101. M Makosza *31st IUPAC Congress, Sofia*, 1987, Section 6, p. 118

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Complexes of oligo(poly)nucleotides with structural anomalies

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ABSTRACT. The results of studies on the structure and properties of DNA-RNA hybrids and complexes of oligo(poly)nucleotides containing non-canonical base pairs or unpaired bases both within and at the ends of the double helix are surveyed. The methods used in the study of such systems are briefly characterised: X-ray diffraction analysis, NMR and UV spectroscopy, circular dichroism, scanning microcalorimetry, etc. A comparative analysis of the influence of the non-canonical pairs on the structure and the energetic and kinetic parameters of the formation and dissociation of the oligonucleotide complexes has been carried out. The question of the stability of the non-canonical pairs as a function of their nature and position in the double helix is considered. The mechanisms of the formation of the hydrogen bonds between the bases of non-complementary pairs are discussed.

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I. Introduction

The interest in the double helix complexes of nucleic acids with various structural anomalies arose in connection with the study of the mechanism of the transmission of genetic information. Thus it has been established that hybrid DNA–RNA duplexes are formed as intermediates in key biological processes—replication, transcription, and reverse transcription.[1,2] The correct "reading" of genetic information is known to be ensured by the complementation interactions of the nucleic acid (NA) bases and is controlled by the corresponding enzyme systems. However, the inclusion of "erroneous" nucleotides, forming non-complementary pairs, nevertheless occurs, although extremely rarely, leading to substitutional mutations.[3,4] On the other hand, non-canonical pairs are formed fairly frequently in codon-anticodon interactions (in the third position of the codon triplet)[5] and also on formation of the secondary or tertiary structures of different RNAs.[6–8] The development of the site-specific mutagenesis served as a powerful stimulus to the study of the spatial disposition and energetic parameters of the non-canonical pairs incorporated in the regular double helix structure. The use of the site-mutagenesis technique makes it possible to achieve point substitutions of nucleotides, deletions, and insertions in specified positions in DNA. The appearance of interest in the study of structures of this type coincided with the development of synthetic nucleotide chemistry and the improvement of modern methods for structural studies. This made it possible in recent years to obtain and to study in detail sets of DNA duplexes with non-canonical pairs and "superfluous" nucleotide units in specified positions. Such compounds are convenient models for the investigation of various cell processes—replication, transcription, translation, and mutagenetic processes. In addition, they are of interest as instruments for the study of enzymes of NA metabolism and the structure and conformational possibilities of NA. The available information about the thermodynamics and kinetics of the formation and dissociation of DNA-duplexes with non-canonical pairs is used widely for the diagnosis of genetic diseases.[9]

The data for the geometry of the pairing of certain types of non-complementary bases and their influence on the parameters of the double helix have been analysed in review articles published in 1987.[10,11] This review considers the structure of the DNA–RNA hybrid structures and NA complexes containing all the investigated combinations of the non-complementary pairs and "superfluous" nucleotide units; the influence of structural anomalies on the thermodynamic and kinetic parameters of complex formation and on the secondary structure of the double helices is considered. The structural anomalies induced by minor or modified bases are not included in the review.

II. Methods used to investigate double helix nucleic acids with structural anomalies

X-Ray diffraction analysis of single crystals (XRDA) and X-ray diffraction in oriented fibres (XRDF). The most complete information about the structure of oligonucleotide duplexes independent of conceptual models can be obtained with the aid of XRDA; high-resolution XRDA (~1.5–2 Å) makes it possible to determine the coordinates of all the non-hydrogen atoms, to observe experimentally the influence of modifications of the local and overall structures of the double helix, and to investigate its hydration shell.[10,12–14] XRDF is used to characterise the double and triple helices formed by polynucleotides[15] and yields much less information than XRDA.

High resolution NMR spectroscopy. Such spectroscopy has been widely used recently to investigate oligomeric duplexes.[16] From the ^{1}H NMR spectra, one can infer the local environment of each

proton, which makes it possible to follow the variation of the conformations of the individual nucleotide pairs as the temperature, pH, etc. are varied. Two groups of resonance proton signals are analysed.

(a) The signals of non-exchanging protons—H(5) and H(6) of the pyrimidine bases, H(2) and H(8) of the purine bases, and the protons of the CH_3 group of thymine and the carbohydrate rings. The thermal dissociation of the duplexes leads to a downfield shift of the signals. The thermodynamic parameters of the helix–coil transition can be calculated from the curves for the temperature dependence of the chemical shifts δ of these proton signals and it is possible to follow the dissociation of each nucleotide pair of the duplex.

(b) The signals of the slowly exchanging protons of the imino-groups N(1)–H of guanine and N(3)–H of thymine (uracil), participating in the formation of hydrogen bonds, are recorded in aqueous solutions. The presence of signals in the region of low fields indicates unambiguously the formation of hydrogen-bonded nucleotide pairs. With increase in temperature, an upfield shift, broadening, and disappearance of the signals take place owing to the increase in the relative content of the open-chain forms and the rapid exchange of the imino-group protons in the open-chain forms with water. The temperature of the disappearance of the signals is not related to the thermodynamic stability of the duplexes and merely yields a comparative characteristic of the stability of the individual nucleotide pairs. The study of the kinetics of the exchange of the imino-protons with water makes it possible to estimate the lifetimes τ of the individual base pairs in the helical complex. The activation energies and the rate constants for the dissociation and formation of individual nucleotide pairs are calculated from the temperature variation of τ.[17]

Measurement of the vicinal spin–spin coupling constants of the protons of the C(1′) and C(2′) atoms makes it possible to estimate the conformation of the carbon rings. Information about the distances between the atomic nuclei can be obtained with the aid of the nuclear Overhauser effect (nOe);[18] the nOe is observed for pairs of nuclei separated by distances not greater than 4 Å.

^{31}P NMR spectra contain data about the conformation of the sugar phosphate skeleton of the oligonucleotide constituting the double helix.

Scanning microcalorimetry (SMC). This is used to determine the thermodynamic parameters of the conformational transition.[19] The enthalpy of the helix–coil transitions ΔH^0 can be obtained directly from the curve for the temperature variation for the heat capacity of the system by calculating the area bounded by this curve. The van't Hoff enthalpy $\Delta H^0_{v\text{-}H}$ can be calculated simultaneously from the same experimental data.[20] It has been suggested that $\Delta H^0_{v\text{-}H}$ corresponds to the enthalpy of the helix–coil transition when the two states model is valid. The difference between the experimental ΔH^0 and $\Delta H^0_{v\text{-}H}$ is evidence that on fusion the system passes through a series of partially bound structures and makes it possible to estimate the length of the cooperatively melting section of the duplex.

UV spectroscopy. The curves for the temperature variation of the UV absorption by the system permit the determination of the melting point (T_m) of the double helix and the calculation of the thermodynamic parameters of the complex formation process. The temperature jump method,[21] based on the analysis of the change in the UV absorption after an abrupt increase in temperature, is widely used to obtain the kinetic characteristics of the helix–coil transition.

Circular dichroism (CD) and optical rotary dispersion (ORD). The interpretation of CD (ORD) data, based mainly on the empirical assignment of the spectra to the known conformations of the polymers, permits conclusions concerning the similarity of the geometrical parameters of the double helix structures and their inclusion in a particular study of Na forms ($\overline{A}$, $\overline{B}$, $\overline{Z}$).

Raman spectroscopy (RS). This spectroscopy makes it possible to estimate the secondary structure of double helix oligo(poly)nucleotides both in solution and in the crystalline states.[22]

Theoretical estimation of the conformation of the oligonucleotide duplexes. This is done by calculating the energies of the non-valence interactions by the method of atom–atom potential functions (AAPF).[23] The minimisation of the energy of the non-valence interactions in terms of different variables (parameters determining the geometry of the pairing of bases and the positions of the pairs relative to the axis of the helix, parameters of the helix, torsional angles, etc.) makes it possible to establish the most probable conformation of the non-canonical pairs and of the duplexes containing such pairs. It is noteworthy that the accuracy of calculations of this kind depends on the number of independent variables considered.

III. Hybrid DNA–RNA complexes

1. The secondary structure of the DNA–RNA hybrids

Natural DNA and synthetic polydeoxyribonucleotides are known to exist in aqueous solution and in fibres with a high relative moisture content in the form of the $\overline{B}$ family; forms belong to the $\overline{A}$ family are characteristic of the double helix RNA. Although both conformational families refer to right-hand helices, they differ sharply in their helix parameters. A significant factor determining the type of secondary structure is the conformation of the sugar: C(3′)-endo(*N*) in the $\overline{A}$ family and C(2′)-endo(*S*) in the $\overline{B}$ family. The only form in which the double helix RNA exists is the *A*-form. The conformational possibilities for DNA are much wider: depending on the conditions in the medium and the nucleotide sequence, the DNA duplexes can exist in the form of the $\overline{B}$ and $\overline{A}$ families, the alternating *B*-form, and the left-hand *Z*-form. It has also been shown that the local parameters of the nucleotide pairs vary within wide limits.[24]

By analysing the available literature data, it is possible to conclude that the DNA–RNA hybrids belong most typically to the $\overline{A}$-family of conformations. However, depending on the nucleotide composition and sequence and also on the complex formation conditions, the hybrid complexes can form structures of a new type—*B*- and *Z*-complexes as well as dimorphous complexes containing elements of both forms (Table 1).

We shall consider in greater detail some of the data presented in Table 1. The conformations of the hybrid heptameric complexes†

d(CTTTTTG) (GAAAAAC)r	d(CA_5G) + r(CU_5G)
"rA.dT" complex	"dA.rU" complex

† Here and henceforth the structure of the duplexes is formulated in the direction (5′–3′)–upper strand and (3′–5′)–lower strand.

were analysed simultaneously with the study of their ribo- and deoxyribo-analogues:[29,30]

d(CTTTTTG) r(CUUUUUG)
(GAAAAAAC)d , (GAAAAAAC)r .
"dA.dT" complex "rA.rU" complex

Table 1. The structure of the DNA-RNA hybrid complexes.

Complexes	Form of helix	Method of analysis	Refs.
Polymeric DNA-RNA complexes with an irregular nucleotide sequence	*A*-DNA, *A*-RNA	XRDF, ORD	[25—27]
poly[d(A C)·poly[r(G U)]	closer to *A*-RNA	CD	[28]
poly[r(A C)·poly[d(G T)]	closer to *A*-RNA	CD	[28]
r(C A_8 G)·d(C T_8G)	*A*-RNA	CD, ^{1}H NMR	[29, 30]
d(C A_8 G)·2r(C U_8 G)	*A*-RNA	CD, ^{1}H NMR	[29, 30]
poly (dG)·poly(rC)	*A*-DNA*, *A*-RNA**	XRDF	[15]
poly(rG)·poly(dC)	*A*-DNA	XRDF	[15]
poly(dA)·poly(rU)	*A'*-RNA*, dimorphous structure**	XRDF	[15]
	A-RNA	CD	[31]
poly(dI) ***·poly(rC)	dimorphous structure	XRDF	[15]
poly(rI)·poly(dC)	*A*-DNA*, *A'*-RNA**	XRDF	[15]
poly(rA).poly(dT) (fibres)	*A'*-RNA*, dimorphous structure**	XRDF, ^{31}P NMR	[32, 33]
poly(rA).poly(dT) (in solution)	*B*-DNA,	^{1}H NMR	[34]
	dimorphous structure	CD	[31]
poly(dA)·2poly(rU)	*A*-RNA	XRDF	[35]
poly(rA)·2poly(dT)	dimorphous structure	CD	[31]
d(T C A C A T)·r(A U G U G A)	*B*-DNA	^{1}H NMR	[36]
poly(rG-dC)·poly(rG-dC)	*A*-RNA, *Z*-, *B*-form	CD, ^{31}P NMR	[37—39]
r(GCG)d(CGC)·r(GCG)d(CGC)	*A*-DNA	RS	[22]

*Relative humidity below 80%.
** Relative humidity above 80%.
***I = inosine.

On the basis of the spin–spin coupling constants for the protons of the carbohydrate residues, it has been established that the furanose rings in the "rA.rU" and "rA.dT" complexes are in the *N*-conformation (*A*-form), while the deoxyribose residues in "dA.dT" are in the *S*-conformation (*B*-form). The complex formation reaction between d(C A_5G) and r(C U_5G) leads to the preferential formation of the triple helix d(C A_5G).2r(C U_5G), which belongs to the *A*-family according to CD data.

Under the conditions of a high relative humidity, the polymeric complexes poly(dA).poly(rU) and poly(dI).poly(rC) (in the form of fibres) have unusual diffraction patterns representing a superposition of the reflections corresponding to the *A*- and *B*-forms of the helix.[15] It has been suggested that the carbohydrate residues of the polymeric strands in these complexes have different conformations—of the *N*-type for ribose and of the *S*-type for deoxyribose. A similar dimorphous structure of the DNA–RNA hybrid complex can play an important role in the functioning of the DNA- and RNA-polymerases.

Interesting data have been obtained in studies of poly(rA).poly(dT). This ribo-deoxyribonucleotide hybrid is an analogue of the DNA-duplex poly(dA).poly(dT). The latter retains the *B*-form of the helix even under conditions where the natural non-regular DNA exists in the *A*-form. Apparently the "B affinity" is retained also in the hybrid complex despite the presence in the latter of the conformationally rigid polyribonucleotide chain. The poly(rA).poly(dT) fibres form a helix belonging to the $\overline{A}$ family only for a relative moisture content below 90%.[32] With increase in moisture content, there is a conformational transition to a structure similar to the *B*-form of DNA in terms of geometrical parameters but the structure is dimorphous according to the conformation of the carbohydrate residues.[32,33] It has been shown by ^{1}H NMR, using nOe studies, that in an aqueous buffer solution poly(rA).poly(dT) exists in the *B*-form and the carbohydrate residues in both strands have the same *S*-type conformation.[34] However, owing to the steric hindrance generated by the 2′-hydroxy-group of ribose, the geometry of the hybrid helix differs little from that of the classical *B*-form of the DNA. In particular, the inclination and twist of the bases as well as the distances between the bases and the axis of the helix have increased. It has been found that the *B*-form of the helix in solution is characteristic also of the duplex with the heterogeneous composition d(TCACAT).r(AUGUGA).[36]

The study of the structure of the double helix complexes whose composition includes covalently bound DNA and RNA fragments is of special interest. The mixed composition hybrid with the alternating ribodeoxyribonucleotide sequence poly(rG-dC).poly(rG-dC) is an analogue of the DNA-duplex poly(dG-dC).poly(dG-dC); the latter undergoes a transition into the left-hand *Z*-form at a high ionic strength.[40] At a moderate NaCl concentration, the structure of poly(rG-dC).poly(rG-dC) is analogous to *A*-RNA in terms of geometrical parameters and the conformation of the carbohydrate residues.[37] The transition of the hybrid helix to the *Z*-form occurs, in contrast to its DNA-analogue, both with increase and with decrease in the ionic strength with average *A–Z* transition points at 25 mM NaCl in the low salt region and at 1500 mM NaCl in the high salt region.[37,38] In the presence of tetrabutylammonium ions (> 30 mM) an additional conformational transition of the hybrid complex to the *B*-form is observed.[39]

The hexanucleotide mixed composition duplex

r(G C G)d(C G C)
(C G C)d(G C G)r

forms a helix in the *A*-form in the crystalline state according to RS data[22] and all the carbohydrate residues (both ribose and deoxyribose) have the same *N*-conformation. In aqueous solution, the geometry of the complex is in the main retained, but the deoxyribose rings of the terminal cytidine residues assume an *S*-type conformation, which is associated, according to the authors, with the lower stability of the end pairs and hence their greater conformational mobility.

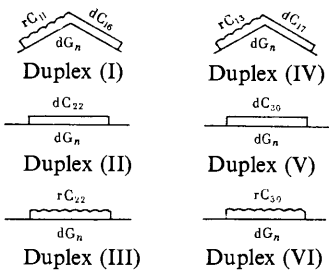
The secondary structure of the decameric duplex

1 2 3 4 5 6 7 8 9 10
r(G C G)d(T A T A—C G C) ,
(C G C—A T A T)d(G C G)r

in which the double helix tetranucleotide DNA fragment (d.d) is flanked by hybrid sections on both sides, has been investigated.[41,42] According to XRDA data, in the presence of a low water content, this duplex forms a helix which is similar, in terms of geometrical parameters, to the *A*-form of DNA with the same *N*-conformation of the carbohydrate ring.[41] According to the authors, the presence of hybrid sections at the end of the duplex stimulates the transition of the central d.d fragment to the *A*-form. In aqueous solution, the situation is somewhat different.[42] According to ^{1}H NMR data, which made it possible to estimate the ratio of the conformers for each nucleotide unit, all the ribose rings of the above duplex have the *N*-conformation. The existence of the *S*- and *N*-conformers is characteristic of all the deoxyribose residues located in both the hybrid and d.d sections of the duplex, the equilibrium constant

depending on the local environment of the individual nucleotide unit (Fig. 1). The carbohydrate residues dC (in the 8-position), dG (in the 9-position), and dC (in the 10-position), belonging to the hybrid fragment, contain respectively 52, 37, and 33% of the *N*-type conformers. This sequence in the variation of the percentage contents of the *N*-conformers is caused by the greater conformational freedom of the terminal deoxynucleotides. The data obtained permit the conclusion that a conformational transmission effect (the influence of the RNA fragment on the conformation of the carbohydrate rings of the DNA sequence linked to it) is observed with covalently bound DNA–RNA hybrid molecules. In the duplex considered, the effect is extended mainly to the two nucleotide residues dT (in the 4-position) and dA (in the 5-position) and to a lesser extent DT (in the 6-position) and dA (in the 7-position). Consequently there is a smooth transition from the *N*-conformation to the predominatly *S*-conformation. The occurrence of the stacking interaction between the bases along the entire molecule, with the predominance of the "stacking" characteristic of the *A*-form in r(GCG) and the "mixed" type in the d(TATACGC) section, has been demonstrated by ^{1}H NMR spectroscopy.

The structures of the hybrid polymeric-oligomeric duplexes $dG_n.rC_{11}dC_{16}$ and $dG_n.rC_{13}dC_{17}$ ($n > 70$) have been investigated.[43,44] The systems investigated are indicated below in a conventional schematic form.



It follows from the analysis of the ^{1}H NMR spectra of the duplexes (I)–(III) that the two fragments of the duplex (I) form helices with different conformations—the hybrid section of the molecule is in the *A*-form characteristic of the duplex (III) and the (d.d) section is in the *B*-form, like the duplex (II).[43] The CD spectra of the duplexes (IV)–(VI) have led to the analogous conclusion that the *A*- and *B*-forms coexist in the hybrid duplex (IV).[44] Analysis of the fusion curves (UV spectroscopy) shows that, despite the presence of two forms, the helix–coil transition in the duplex (IV) is cooperative and single-phase. According to the authors,[44] the existence of two adjoining conformations in the covalently bound hybrid duplexes (I) and (IV) leads to geometrical distortions—the bending of the axis of the helix at the boundary between the two forms; the transitional region between the *A* and *B* forms then includes only one nucleotide pair, belonging to the DNA fragment, and the phosphodiester linkages adjoining it. Analysis of the geometrical structure of the hybrid duplex (Fig. 2), obtained by computer modelling,[44,45] showed that in the region of the bend in the helix the complementation and interplanar interactions between the bases are retained.

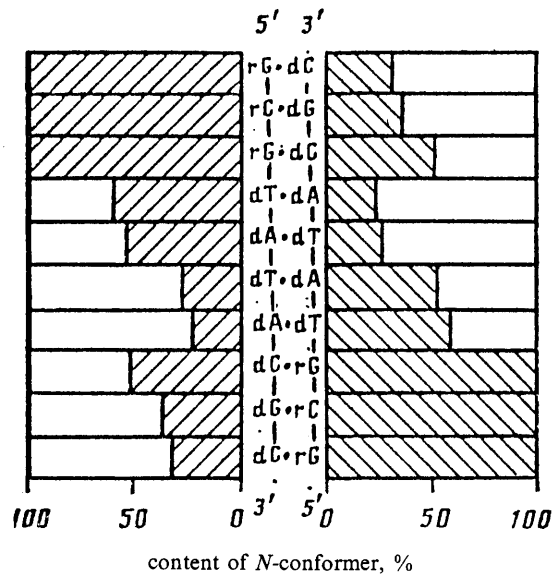


Figure 1. Conformation of the carbohydrate rings of the duplex formed by r(GCG)d(TATACGC) in aqueous solution (according to ^{1}H NMR spectroscopic data).[42]

The conclusions concerning the structure of the covalently bound DNA–RNA hybrid duplexes reached in this series of studies differ from the conclusions arrived at by Mellema et al.[42] for the

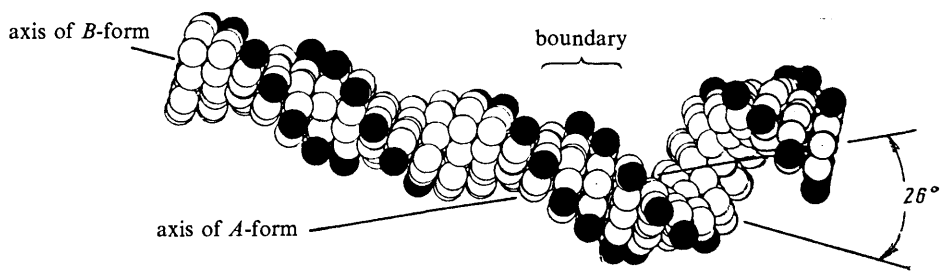


Figure 2. A molecular model of the complex $dG_n.rC_{11}dC_{16}$.[44]

decameric duplex, which can be accounted for by the differences between the lengths of the r.d and d.d sections, the nature of the nucleotide pairs (A.T or G.C) at the "junction" between these sections, and certain assumptions in the interpretation of the data.

2. Thermodynamic and kinetic aspects of the formation of DNA–RNA hybrid complexes

A comparative analysis of the thermodynamics and kinetics of the formation of hybrid double helices and of their DNA and RNA analogues has been performed on the model heptameric complexes "rA.dT", "dA.rU", "dA.dT", and "rA.rU" (see above).[17,30,46] The following duplex stability sequence has been established with the aid of UV and ^{1}H NMR spectroscopy: "dA.dT" > "rA.dT" > "rA.rU" » "dA.rU", which agrees with the stability series for polymeric complexes formed by poly(rA), poly(dA), poly(rU), and poly(dT) in analogous combinations.[47] Comparison of the equilibrium constants ($K_{25°}$) for the formation of the heptameric double helices (Table 2) shows that the duplex "dA.dT" is 10 and 4 times more stable than "rA.rU" and "rA.dT" respectively, while the hybrid duplex "dA.rU" is almost 200 times less stable than "rA.dT". It has been suggested[30] that the *S*-conformation is preferred for the dA clusters and the latter cannot therefore form stable DNA–RNA hybrids. According to the authors, the presence of such clusters facilitates the termination of transcription.

Table 2. Thermodynamic and kinetic parameters of the formation of hybrid oligomeric duplexes and the corresponding ribo- and deoxyribo-nucleotide analogues.

Parameter	«rA·dT»	«dA·rU»	«dA·dT»	«rA·rU»	Refs.
T_m, °C	22.9	<0	27.5	19,1	[30]
$K_{25°}$, litre mol^{-1}	$5,5\cdot10^3$	$<3\cdot10^1$	$1.8\cdot10^4$	$2.2\cdot10^3$	[30]
$\Delta H°$, kcal mol^{-1}	−48	—	−41	−44	[30]
$k_{p,12°}$, litre mol^{-1} s^{-1}	$6.6\cdot10^6$	—	$8.3\cdot10^{-6}$	$6.2\cdot10^6$	[46]
$E_{a,d}$, kcal mol^{-1}	—	—	43	39	[46]
$E_{a,p}$, kcal mol^{-1}	—	—	−0.5	0	[46]
$K_{d,12°}$, s^{-1}	50	—	9.6	38	[46]

Note. Complex formation conditions: 0.01 M phosphate buffer, pH 7, 0.1 mM EDTA, 0.2 M NaCl, $c_0 = 2 \times 10^{-4}$ M; the structures of the duplexes are shown in the text.

Kinetic parameters[17,46] have confirmed the thermodynamic data concerning the stability sequence of the duplexes "dA.dT", "rA.rU", and "rA.dT". The rate constant (K_r) for the formation of the duplex "dA.dT" is a little greater than the approximately equal corresponding constants for the duplexes "rA.rU" and "rA.dT" (Table 2). It has been suggested that this can be accounted for by the slower formation of the stacking-conformation in the ribonucleotide chain.[46,48] On the other hand, the approximate quality of the activation energies ($E_{a,r}$) for the formation of the above duplexes (Table 2) suggests identical mechanisms of the association of the ribo- and deoxyribo-nucleotide strands. The kinetic parameters characterising the dissociation of the double helices differ appreciably (Table 2). The rate constant (K_d) for the dissociation of the duplex "dA.dT" is appreciably lower than the corresponding values determined for the duplexes "rA.rU" and "rA.dT". This feature has been confirmed by the results of studies of the kinetics of the exchange of the imino-protons with water:[17] it has been established that the values of τ for the non-terminal pairs of the duplexes "rA.rU" and "rA.dT" are approximately the same and significantly lower than τ for "dA.dT".

According to ^{1}H NMR data, the end "fraying" effect, i.e. the rapid formation and breakdown of hydrogen bonds between the bases at the end of the duplex under the conditions of the thermodynamic stability of the double helix, is observed for these duplexes. It is essential to emphasise that the "fraying" of the end pairs is characteristic of RNA, DNA, and hybrid duplexes to approximately equal extents.

Overall, the data concerning the comparative stabilities of the hybrid, ribonucleotide, and deoxyribonucleotide complexes are ambiguous. For the majority of systems investigated, it has been shown that the hybrid duplexes are less stable than DNA and RNA of the same composition. For polymeric complexes, the difference is very small and amounts to 2–4 °C.[25,26,28,47,49] In oligomeric systems, the difference is more clear cut. Thus T_m for the complexes $rA_n.pdT_9$ (n = 6–9) is on average lower by 7 °C than T_m for $dA_n.pdT$ with the same n.[50]

On the other hand, other relative stabilities of the hybrid duplexes have been established in a number of studies. For example, the stability of the polymeric complexes, formed by different combinations of poly[d(r)I] and poly[d(r)C], varies in the sequence poly(rI).poly(rC) > poly(rI).poly(dC) > poly(dI).poly(dC) > poly(dI).poly(rC),[51] while for covalently bound DNA–RNA hybrids of the type $dG_n.rC_idC_k$, the following stability series has been determined: $dG_n.dC_{30} < dG_n.rC_{13}dC_{17} < dG_n.rC_{30}$.[44]

Analysis of the rates of exchange of the imino-proton duplexes poly(rA).poly(dT), poly(dA).poly(rU), poly(rA).poly(rU), and poly(dA).poly(dT) for deuterium[52] makes it possible to determine the ratios of the rates of dissociation of these complexes and hence their relative stabilities—poly(dA).poly(dT) > poly(dA).poly(rU) ⩾ poly(rA).poly(rU) > poly(rA).poly(dT). The relative stabilities of the hybrid complexes and their DNA and RNA analogues apparently depend on the nucleotide composition.

Generalising the literature data on the DNA–RNA hybrid complexes, the following conclusions can be reached:

1. The conformationally more rigid ribonucleotide chain has a dominant influence in the majority of systems investigated on the geometrical structure of the duplex as a whole and also on the conformation of the carbohydrate rings of the deoxyribonucleotide residues (complementary with respect to the ribo-fragment or covalently bound to it).

2. A dimorphous structure, i.e. different conformations of the ribo- and deoxyribo-nucleotide strands of the helix, is characteristic of a series of hybrid duplexes and triplexes formed by homopolymers.

3. According to thermodynamic and kinetic properties, the hybrid complexes are closer to the double helix RNA than to the DNA.

IV. Complexes of nucleic acids with non-canonical base pairs

In the analysis of the literature data on complexes of NA containing non-canonical base pairs, attention has been concentrated on the following questions:

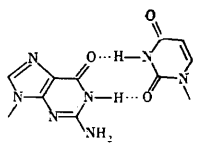
1. The mechanism of the pairing of the bases in the non-canonical pairs.

2. The influence of modification on the interplanar interactions of the bases and on the conformation of the sugar phosphate skeleton; the influence of the non-complementary pair on the secondary structure of the double helix.

3. The thermodynamic and kinetic parameters of the formation and dissociation of the modified oligomeric duplexes.

1. The dG.dT(G.U) pair

The possibility of the existence of the non-canonical G.U pair, stabilised by hydrogen bonds, was first postulated by Crick to account for the degeneracy of the genetic code.[53] He also put forward a mechanism of the formation of hydrogen bonds between the guanine and uracil residues:



G (*anti*) U (*anti*) .

Subsequently the study of various model systems, containing G.U(T) pairs, by modern experimental and theoretical methods confirmed the validity of the proposed mechanism.

Calculation of the conformations with the aid of AAPF and the construction of molecular models[23,54,55] showed that the bases of the dG.dT pair are in the usual tautomeric forms and have the *anti*-orientation relative to the carbohydrate rings. The inclusion of the dG.dT pair in the double helix does not reduce the interatomic contacts and induces only a small increase in the energy of the non-valence interactions and a slight deviation of the angles of the sugar phosphate skeleton from the standard values characteristic of the Watson–Crick helix.

An experimental study of the molecular structure of the dG.dT pair and of its influence on the conformation and the thermodynamic and kinetic parameters of the DNA double helix has been carried out by Patel and co-workers[56–60] in relation to the dodecameric duplex "GT":

```
  1 2  3  4 5 6 6' 5' 4' 3'  2' 1'
d(C G |T| G A A T T C |G| C G)
  G C |G| C T T A A G |T| G C)d
```

duplex "GT" .

The unmodified duplex "GC",[61] formed both in solution and in a crystalline state, having the helix in the *B*-form,[62,63] was used as a control:

```
  1 2 3 4 5 6 6' 5' 4' 3' 2' 1'
d(C G C G A A T T C G C G)
 (G C G C T T A A G C G C)d
```

duplex "GC" .

The presence in the ^{1}H NMR spectrum of the duplex "GT" of two signals due to imino-protons corresponding to the dG.dT pair, which are located in a stronger field than the signals due to the dG.dC pair in the same position in the duplex "GC", indicates unambiguously the existence of two hydrogen bonds with carbonyl acceptor groups between the guanine and thymine residues. This confirms the structure of the dG.dT(G.U) pair presented above and rules out interactions with participation of rare tautomeric forms of the bases. The inclusion of the dG.dT pair leads to the breakdown of the interplanar interactions of the bases of this pair, in particular the thymine residue, with the neighbouring bases. According to ^{31}P and ^{1}H NMR data, the conformational perturbations introduced by the dG.dT pair are localised in the modifcation section and involve only the nearest nucleotide pair from the 3′-end.

The replacement of two dG.dC pairs in the duplex "GC" by the dG.dT pairs induces a decrease in the T_m of the duplex by 20 °C, but the enthalpy of the transition from the double helix state to the single helix state does not then change (see Table 4 below). Accoring to the authors, this is associated with a slight breakdown of the stacking interactions in the duplex "GT". The closeness of the ΔH^0 and the difference between the T_m for the duplexes "GC" suggest that the destabilising influence of the dG.dT pair is entropic in nature. It has been established on the basis of the difference between the values of $\Delta H^0_{v\text{-}H}$ and ΔH^0, determined from the heat absorption curves (SMC), that the cooperatively melting section, both in the duplex "GC" and in the duplex "GT", comprises 9 nucleotide pairs, i.e. it embraces the modification sections. According to ^{1}H NMR data, the end "fraying" effect, involving the nucleotide pairs in the 1- and 2-positions, is observed in the duplexes "GC" and "GT". The presence of the dG.dT pair increases this effect, as a result of which a broadening and disappearance of the signals due to the imino-protons of the dG.dC pairs (in the 1- and 2-positions) in the duplex "GT" takes place at lower temperatures than in the duplex "GC". Comparative analysis of the kinetic data for the exchange of the imino-protons of the duplexes "GT" and "GC" confirms this conclusion that the region corresponding to the spreading of the structural perturbations introduced by the dG.dT pair is limited only by the pair adjoining the non-canonical pair [at 35 °C, τ for the dG.dT pair and the neighbouring dG.dC pair (position 4) of the duplex "GT" are smaller by factors of 10 and 2 respectively than τ for the pairs in the same positions in the duplex "GC"]. The activation energy for the formation of the duplex "GT" has been determined by the temperature jump method[64] and proved to be much higher (22 kcal mol^{-1}) than the same parameter of the unmodified double helix.[65] On this basis, the authors suggested that the formation of the dG.dT and dG.dC pairs (in the 4-position) in the duplex "GT" can be accompanied by conformational adjustments requiring additional energy.

The influence of non-canonical pairs on the thermodynamic and kinetic parameters of the formation of the hexadecameric duplex has been investigated.[66] The hexadecanucleotide d(CAACTTGATATTAATA), which corresponds to the fragment of the bacteriophage ΦX174, was adopted as a basis. Together with the complementary sequence, it forms the protein binding section of the gene *A*. The structure of the initial complementary complex and the studied replacements of the canonical pairs by the dG.dT pair are presented below:

```
   1 2 3 4 5  6 7 8 9 10 11 12 13 14 15 16
d (C A A C T T G A T A T T A A T A)
  (G T T G A A C T A T A A T T A T) d
```

duplex "6TG" duplex "7GT" duplex "12TG" .

All the duplexes containing the dG.dT pair have T_m lower than that of the duplex "O" (see the duplexes 6–8 and 12, Table 4), the destabilising effect being greater for the substitution of the dG.dC pair by a non-complementary pair compared with the analogous substitution of the dA.dT pair and also when the substituted pair is located closer to the centre of the duplex. The dG.dT pair, substituting the dA.dT pair in the 12-position (the duplex "12TG"), indicates the smallest destabilisation. The smaller difference between the free energies of formation (ΔG) of the duplex "O" and the duplexes "6TG", "7GT", and "12TG" ($\Delta\Delta G \simeq 3$ kcal mol^{-1}, Table 4) indicates an insignificant disturbance of the stacking interactions of the bases by the dG.dT pair. The study of the kinetics of the formation and association of the duplexes "O" and "7GT" shows that the perturbations introduced by the G.T pair increase the rate constant for the dissociation of the duplex, while the formation rate constants remain almost the same. The destabilisation of the "7GT" duplex is apparently associated with the increase in the rate of dissociation.

Using the nOe technique, the A.T-rich duplex, containing the inner dG.dT pair, has also been investigated:[67]

d(AAATT|T|TCAAA)
(TTTAA|G|AGTTT)d .

Apart from determining the geometry of the dG.dT pairing, information was obtained in the above study about the degree of hydration of the small groove in the vicinity of the non-complementary pair.

A recent X-ray diffraction study of a synthetic dodecamer in the *B* form with two dG.dT pairs,

d(CGC|G|AATT|T|GCG)
(GCG|T|TTAA|G|CGC)d ,

confirmed that the structural changes induced by these non-complementary pairs are local in character and hardly disturb the overall conformation of the duplex.[68] Nevertheless, precisely this combination of bases (the dG.dT, dA.dC, and dA.dG pairs were compared) forms the most asymmetric pair (a characteristic feature of the Watson–Crick pairs is the presence of a twofold pseudoaxis located in the plane of the bases). This can be the cause of the effective repair of the dG.dT pair by the corresponding enzyme systems "recognising the deviations from the pseudosymmetry.[10,68] It is noteworthy that the dG.dT pair is also effectively discriminated by a restriction enzyme. Thus the replacement of the dG.dC pair by dG.dT or dG.dU in the recognition section of a series of restriction endonucleases leads to a sharp decrease and in some cases to a complete inhibition of the cleavage of the modified DNA duplexes.[69,70]

Two octameric duplexes having identical compositions but differing in the positions of two dG.dT pairs served as the object of study of the influence of the local environment of the dG.dT pairs on the conformation and stability of DNA in the *A* form:[12,71–73]

d(GG|G|GC|T|CC)
(CC|T|CG|G|GG)d
I

d(GGG|G||T|CCC)
(CCC|T||G|GGG)d .
II

A characteristic property of the DNA duplexes containing GG and CC clusters is that in the crystalline state they form a helix in the *A* form.[74] It has been demonstrated by XRDA that the inclusion of the dG.dT pairs leads merely to a slight distortion of the sugar phosphate skeleton of the molecule and that the deformation generated is localised in the modification section and is limited to the nearest phosphodiester linkages. The stacking interactions in the region of the non-canonical pair are disturbed mainly by the decrease in the overlap of the bases of the dG.dT pair with those of the neighbouring pair from the 3′-end, while the "stacking" with the nearest "neighbour" in the 5′-position is retained in almost the same form as in the unmodified duplex. The thermodynamic stabilities of the crystal structures of the duplexes (I) and (II) differ appreciably—the crystals of the duplex (II) are stable at room temperature while those of the duplex (I) melt at 6 °C. According to the authors, one of the causes of the difference between the stabilities of the duplexes is the reduced contribution of the stacking interactions to the stabilisation of the structure of the duplex (I). In the duplex (I), the dG.dT pairs are separated by two dT.dC pairs and the stacking interactions are then disturbed in four out of the seven sites of the interplanar contacts between the base pairs, while in the duplex (II), where the dG.dT pairs are located next to each other, such perturbations occur at only three sites. The different destabilisations of the duplexes (I) and (II) can also be associated with the different states of the hydration shells. In particular, it has been shown that in the duplex (I) there are no bridging hydrogen bonds stabilising the dG.dT pairs. On the basis of these data, it is concluded that the consecutively arranged dG.dT pairs destabilise the double helix less than the isolated pairs.[12,71–73] The influence of the dG.dT pairs on the structure of DNA in the *Z* form has been investigated by the XRDA method in relation to the hexameric duplex[75]

d(C|G|CG|T|G)
(G|T|GC|G|C)d .

Despite the smaller flexibility of the sugar phosphate skeleton of *Z*-DNA compared with *B*-DNA, the non-complementary pair is incorporated in the *Z*-helix virtually without distorting it. It has been shown that the alternation of the conformations of the glycosidic linkage (*syn*-, *anti*-) and of the furanose ring (*N*- and *S*-) is virtually preserved in the nucleotide residues of the duplex, although in the dG.dT pair the deoxyribose of guanosine has the non-characteristic C(4′)-*endo*-conformation. The dG.dT pair, incorporated in the *Z*-helix, not only does not impair the interplanar interactions, but actually stabilises them to some extent, because a more complete overlap of the guanine and thymine residues with the bases of the neighbouring pairs is observed compared with the dG.dC pair located in the same position in the unmodified duplex. It has been established that the hydration shell of the duplex plays an important role in stabilising the dG.dC pair. Bridging hydrogen bonds are formed with participation of water molecules between N(2) and O(6) of guanine and between O(2) and O(4) of thymine respectively, compensating partly for the absence of such a bond in the dG.dT pair compared with the dG.dC pair.

It is noteworthy that the structure of the hydration shell in the vincinity of the non-complementary pair hardly depends on the form of DNA (*A*, *B*, or *Z*).[10,68]

We shall also note briefly certain studies in which the influence of the dG.dT pairs on oligomeric duplexes has been analysed. According to ^{1}H NMR data, the dinucleotides pd(GT) and pd(TG) do not form complexes in solution under conditions where the self-complementary dinucleotides are associated with formation of mini-duplexes.[76,77] On the other hand, the polymer poly[d(GT)] can exist in solution in the form of a double helix.[78–80] This has been demonstrated by UV, CD, and ^{1}H NMR spectroscopy, and also on the basis of the binding of ethidium bromide.

Data characterising the destabilising influence of the dG.dT pairs on oligomeric duplexes have been published.[50,81,82]

A series of studies have been devoted to the ribonucleotide complexes containing the G.U pair. According to XRDA data, the terminal G.U pairs in the tetrameric duplex

r(G GC U)
(U CG G)r

hardly disturb the stacking interactions of the bases.[83]

Table 3. Thermodynamic parameters of the varied nucleotide pair in the octadecameric DNA duplex.[127]

Varied base pair (X.Y)	T_m^* of duplex, °C	ΔH(X.Y), kJ mol^{-1}	ΔS(X.Y), kJ mol^{-1} K^{-1}	Type of structure of X.Y pair
G·C	69.6	70.6	0.208	Watson–Crick
C·G	68.1	68.3	0.208	"
A·T	67.7	67.8	0.208	"
T·A	64.9	55.5	0.208	"
G·T	60.1	30.6	0.116	weak
T·G	60.0	60.8	0.208	bound
A·G	59.3	59.1	0.208	bound
T·T	58.7	0	0.031	open-chain
C·T	58.6	0	0.031	open-chain
G·G	56.7	57.0	0.208	bound
G·A	56.6	30.6	0.128	weak
T·C	56.0	0	0.035	open-chain
A·A	55.6	55.6	0.208	bound
A·C	54.4	30.8	0.133	weak
C·A	53.2	54.1	0.208	bound
C·C	51.5	0	0.045	open-chain

* T_m was measured in 1 mM cacodylate buffer (pH 7.1) containing 0.5 M NaCl, 0.1 M EDTA, and nucleotide at a concentration of 0.3 A_{260}/ml.

The influence of the G.U pair and of its local environment on the stability of pentanucleotide double helices has been investigated.[84,85] The series of duplexes investigated are presented below:

r(C A G U G) (G U U A C)r	r(A G G C U) (U C U G A)r
duplex "5GU"	duplex "5*GU"
r(C A A U G) (G U U A C)r	r(A G A C U) (U C U G A)r
duplex "5AU"	duplex "5*AU"
r(C A G U G) (G U C A C)r	r(A G G C U) (U C C G A)r
duplex "5GC"	duplex "5*GC"
series I	series II .

In the series I duplexes, the central pair is flanked by the A.U pairs, while in the series II duplexes it is flanked by G.C pairs. It has been shown that all the series II complexes are more stable than the corresponding series I complexes. According to ^{1}H NMR data, the T_m of the G.U pair in the duplex "5GU" is lower by 4 °C than the T_m of the remaining pairs, i.e. the G.U pair is a region of local instability of the duplex, while in the duplex "5*GU" the G.U pair has the same T_m as the remaining pairs. The substitution of the central complementary pair by G.U in the series I duplexes reduces their stability the destabilisation being greater on replacing the G.C pair (the T_m of the duplexes "5GU", "5GC", and "5AU" are respectively 23, 38, and 28 °C). In the series II duplexes, the destabilising influence of the G.U pair is much smaller and is manifested solely on substitution of the G.C pair; the replacement of A.U by G.U hardly affects the stability of the double helix (the T_m of the duplexes "5*GU", "5*GC", and "5*AU" are respectively 44, 54, and 45 °C). According to the authors,[85] the different effects accompanying the inclusion of the G.U pair between the A.U or G.C pairs are associated with the fact that the interplanar interactions between the bases of the G.U pair and the pairs flanking it are disturbed to a greater extent in the duplex "5GU" than in the duplex "5*GU".

A comparative analysis of the thermodynamic parameters of the formation of oligomeric duplexes containing G.U pairs and of the unmodified duplexes containing A.U pairs in the same positions (see the duplexes 34–49 in Table 4) has been carried out[86] and it has been established that the substitution of the A.U pair by G.U reduces the stability of the complex, such decrease depending on its composition, nucleotide sequence, and the position of the G.U pair in the oligomer chain and its local environment. The destabilisation of the complexes induced by such substitution is mainly enthalpic in nature, although a decrease in the stability of duplexes containing adjoining G.U pairs is associated with the unfavourable alteration of the entropy of complex formation (Table 4).

The destabilisation effect of the replacement of the canonical pairs by the G.U pair has also been pointed out in a number of others studies.[5,87–89] However, the formation of the G.U pair is thermodynamically more favourable than the appearance of other non-canonical pairs under the same conditions. Thus the pentaribonucleotide AGGCU forms on self-association the duplex "GU" with two G.U pairs and not the duplex "GG" with a single G.G pair:[85]

r(A G GC U) (U CG G A)r	r(A G G C U) (U C G G A)r
duplex "GU"	duplex "GG"

A similar conclusion concerning the preferential formation of the G.U pairs before the G.G pairs was reached by Uhlenbeck et al.[90]

The study of the influence of the terminal G.U pairs on the thermal stability of RNA duplexes showed that the contribution of the free energy of the G.U pair, flanking the tetrameric GC-containing core, is approximately equal to the contribution of the terminal A.U pair and is smaller by ~1 kcal mol^{-1} than the contribution of the G.C pair.[91] Other terminal non-complementary pairs (A.A, A.C, A.G, and U.U) are less stable than the corresponding Watson–Crick pairs. Furthermore, it has been shown that the terminal G.U pair is more stable if it contains 5′-G and 3′-U but not conversely.[91]

The thermal stabilities and conformational characteristics of the polymeric complexes of the ribo- and deoxyribo-series, consisting of the G.U or dG.dT pairs, i.e. poly[r(GU)] and poly[d(GT)], have been compared on the basis of CD data.[79] It was established that the DNA duplex is formed at a higher ionic strength (0 °C, 0.1 M NaCl) than its ribo-analogue (0 °C, 0.02 M NaCl). In the NaCl concentration range from 0.1 to 1 M, the poly[d(GT)]$_2$ helix undergoes conformational rearrangements (within the limits of the *B*-form), which entails a smooth variation of the CD spectrum. The relative stabilities of the duplexes depend on the ionic strength of the buffer: the ribonucleotide duplex is more stable in 0.1 M NaCl, the T_m for poly[r(GU)] and poly[d(GT)] being 14 and 3 °C respectively, while the deoxy-analogue is more stable in 1 M NaCl (the T_m are 23 and 30 °C). However, these duplexes are much less stable than the duplexes formed by the self-complementary polymers—poly[r(AU)] and poly[d(AT)] (the T_m for the latter in 0.1 M NaCl are 65 and 57 °C respectively).

Table 4. Thermodynamic parameters of the formation of oligonucleotide complexes with non-canonical base pairs and unpaired nucleotide units.*

No.	Oligomeric complex	Conventional designation of complex	Complex formation conditions	T_m, °C	$-\Delta H^0$, kcal mol^{-1}	$-\Delta S^0$, e.u.	$-\Delta G^0$ (t, °C) kcal mol^{-1}	$\Delta\Delta G^{0****}$ (t, °C), kcal mol^{-1}	Refs.
1	d(C G C G A A T T C G C G) (G C G C T T A A G C G C)d	«GC»	0.01 M phosphate buffer, pH 7.0, 0.1 mM EDTA, 0.1 M NaCl, c_0^{**} = 0.65 mM	71.3	102 (74)**	—	—	—	[61]
2	d(C G T G A A T T C G C G) (G C G C T T A A G T G C)d	«GT»	ditto	51.3	106 (76)**	—	—	—	[56]
3	d(C G A G A A T T C G C G) (G C G C T T A A C A G C)d	«GA»	»	55.0	—	—	—	—	[99]
4	d(C G C G A A T T C A C G) (G C A C T T A A G C G C)d	«AC»	»	40.0	—	—	—	—	[92]
5	d(C G C A G A A T T C – G C G) (G C G – C T T A A G A C G C)d	«A»	»	52.0	104 (70)**	—	—	—	[129]
6	d(C A A C T T G A T A T T A A T A) (G T T G A A C T A T A A T T A T)d	«O»	0.025 M phopsphate–1 mM cacodylate buffer, pH 7.0, 0.1 mM EDTA, 1 M Na^+, c_0 = 17.5 μM	52.0	102.0	289	15.8 (25°)	—	[66]
7	d(C A A C T T G A T A T T A A T A) (G T T G A G C T A T A A T T A T)d	«6TG»	ditto	45.1	92.6	230	13.2 (25°)	2.6 (25°)	[66]
8	d(C A A C T T G A T A T T A A T A) (G T T G A A T T A T A A T T A T)d	«7GT»	»	42.9	91.3	264	12.7 (25°)	3.1 (25°)	[66]
9	d(C A A C T T G A T A T T A A T A) (G T T G A A C A A T A A T T A T)d	«8AA»	»	42.1	92.0	269	12.6 (25°)	3.2 (25°)	[66]
10	d(C A A C T T G A T A T T A A T A) (G T T G A A C C A T A A T T A T)d	«8AC»	»	40.6	90.9	265	12.1 (25°)	3.7 (25°)	[66]
11	d(C A A C T T G A T A T T A A T A) (G T T G A A C T C T A A T T A T)d	«9TC»	»	43.0	98.4	286	13.1 (25°)	2.7 (25°)	[66]
12	d(C A A C T T G A T A T T A A T A) (G T T G A A C T A T A G T T A T)d	«12TG»	»	46.9	95.5	274	14.0 (25°)	1.8 (25°)	[66]
13	d(C A A A A A A G) (G T T T T T T C)d	—	0.01 M phosphate buffer, pH 7.0 0.1 mM EDTA, 1 M NaCl, c_0 = 0.2 mM	37	59	172	7.8 (25°)	—	[138]
14	d(C A A A C A A A G) (G T T T – T T T C)d	«C»	ditto	22	53	161	4.9 (25°)	—	[138]
15	d(C C C A G G G) (G G G T C C C)d	—	0.01 M phosphate buffer, c_0 = 0.4 mM for self-complementary oligonucleotides and 0.1 mM for non-self-complementary oligonucleotides	48	63	177	10.0 (25°)	—	[103]
16	d(C C C G G G) (G G G C C C)d	—	ditto	43	62	176	9 (25°)	—	[103]
17	d(C C C T G G G) (G G G T C C C)d	—	»	31	60	179	6.7 (25°)	—	[103]
18	d(C C C A G G G) (G G G A C C C)d	—	»	27	60	180	5.9 (25°)	—	[103]
19	d(G A T G G G C A G) (C T A C C C G T C)d	«N»	0.01 M phosphate buffer, c_0 = 11.52 μM	41.53	68.04	191	—	—	[144]
20	d(G A T G G G – C A G) (C T A C C C C G T C)d	«C_N»	c_0 = 10.14 μm	29.21	60.39	174	—	—	[144]
21	d(G A T G G G – C A G) (C T A C C C A G T C)d	«A_N»	c_0 = 7.20 μM	23.15	51.07	146	—	—	[144]
22	d(C A A A C A A A G) (G T T T G T T T C)d	—	0.01 M phosphate buffer, c_0 = 0.4 mM	48	64.5	183	10.1 (25°)	—	[110]
23	d(C A A A G A A A G) (G T T T C T T T C)d	—	ditto	50	62.8	179	9.5 (25°)	—	[110]
24	d(C A A A A A A A G) (G T T T T T T T C)d	—	»	45	68.0	196	9.6 (25°)	—	[110]
25	d(C A A A T A A A G) (G T T T A T T T C)d	—	»	41	58.6	168	8.5 (25°)	—	[110]
26	d(C A A A T A A A G) (G T T T G T T T C)d	—	»	31	55.6	165	6.5 (25°)	—	[110]
27	d(C A A A G A A A G) (G T T T T T T T C)d	—	»	27	46.7	137	5.8 (25°)	—	[110]
28	d(C A A A G A A A G) (G T T T G T T T C)d	—	0.01 phosphate buffer, c_0 = 0.4 mM	30	53.5	158	6.3 (25°)	—	[110]
29	d(C A A A G A A A G) (G T T T A T T T C)d	—	ditto	30	52.6	156	6.2 (25°)	—	[110]
30	d(C A A A A A A A G) (G T T T G T T T C)d	—	»	24	39.9	116	5.3 (25°)	—	[110]
31	d(C A A A C A A A G) (G T T T T T T T C)d	—	»	24	53.2	161	5.3 (25°)	—	[110]
32	d(C A A A T A A A G) (G T T T C T T T C)d	—	»	22	50.0	151	5.0 (25°)	—	[110]
33	d(C A A A A A A A G) (G T T T A T T T C)d	—	»	21	36.9	107	5.0 (25°)	—	[110]

Table 4 (continued)

No.	Oligomeric complex	Conventional designation of complex	Complex formation conditions	T_m, °C	$-\Delta H^0$, kcal mol^{-1}	$-\Delta S^0$, e.u.	$-\Delta G^0$ (t, °C) kcal mol^{-1}	$\Delta\Delta G^{0****}$ (t, °C) kcal mol^{-1}	Refs.
34	r(A U G C A U)p p(U A C G U A)r	—	0.01 M phosphate buffer, pH 7.0, 0.1 mM EDTA, 1 M NaCl, c_0 = 0.1 mM	30.2	38.4	108.4	—	—	[86]
35	r(A U G C G U)p p(U G C G U A)r	—	ditto	20.3	24.3	64.5	—	0.52 (37°)	[86]
36	r(A U G C G C A U)p p(U A C G C G U A)r	—	»	60.5	38.4	108.4	—		[86]
37	r(A U G C G C G U)p p(U G C G C G U A)r	—	»	58.7	54.4	145.8	—	0.88 (37°)	[86]
38	r(A U A C G U A U) (U A U G C A U A)r	—	»	42.0	55.6	158.1	—		[86]
39	r(A U G C G U A U)p p(U A U G C G U A)r	—	»	34.6	44.7	127.1	—	1.3 (37°)	[86]
40	r(A U G U A C A U)p p(U A C A U G U A)r	—	0.01 M phosphate buffer, pH 7.0, 0.1 mM EDTA, 1 M NaCl, c_0 = 0.1 mM	41.8	53.7	152.1	—	—	[86]
41	r(A U G U G C A U)p p(U A C G U G U A)r	—	ditto	39.7	54.2	155.0	—	0.32 (37°)	[86]
42	r(G C U A G C) (C G A U C G)r	—	»	49.3	63.0	177.1	—	—	[86]
43	r(G C U G G C) (C G G U C G)r	—	»	41.7	59.1	169.5	—	1.42 (37°)	[86]
44	r(G A C G U C) (C U G C A G)r	—	»	46.3	57.3	161.0	—	—	[86]
45	r(G G C G U C) (C U G C G G)r	—	»	29.6	37.7	106.1	—	2.58 (37°)	[86]
46	r(C U G C A G)p p(G A C G U C)r	—	»	45.4	54.5	153.0	—	—	[86]
47	r(C U G C G G) (G G C G U C)r	—	»	27.1	38.7	110.5	—	2.72 (37°)	[86]
48	r(C A G C U G)p p(G U C G A C)r	—	»	43.6	50.2	140.0	—	—	[86]
49	r(C G G C U G) (G U C G G C)r	—	»	35.8	44.3	125.0	—	1.08 (37°)	[86]

*The parameters of the formation of the unmodified complexes are quoted for comparison.
**The values of $\Delta H^0_{v\text{-}H}$ are given in brackets.
***c_0 is the concentration of oligonucleotides.
****$\Delta\Delta G^0$ (t, °C) is the difference between the values of ΔG^0(t, °C) for the fully complementary and defective complexes.

2. The A.C pair

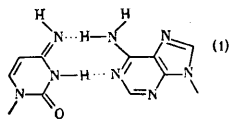
The structure of the dA.dC pair and its influence on the conformation and stability of the DNA duplex "AC"

1 2 3 4 5 6 6′ 5′ 4′ 3′ 2′ 1′
d(C G C | G A A T T C | A C G)
(G C A | C T T A A G | C G C)d

duplex "AC"

have been investigated.[92]

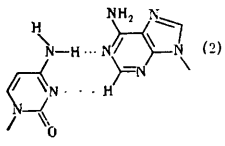
The theoretically possible ways in which the bases can be paired are illustrated below:



(1)

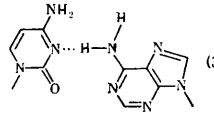
C (*anti*).A (*anti*)

;



(2)

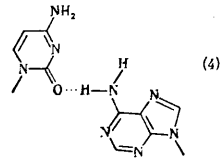
C (*anti*).A (*anti*)



(3)

C (*anti*).A(*anti*)

;



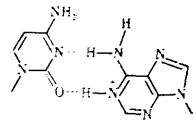
(4)

C (*anti*).A(*anti*)

.

The ^{1}H NMR spectrum of the duplex "AC" contains no signals due to the exchanging protons of the dA.dC pair and Scheme (1), postulating the involvement of the cytosine enolic form in the formation of the hydrogen bond, does not therefore reflect the real structure. The absence of an nOe between the H(2) atom of the adenine in the dA.dC pair and the imino-protons flanking the defect in the dG.dC pairs rules out the orientation of the bases illustrated in Scheme (2). The authors suggest that the dA.dC pair is stabilised by one hydrogen bond between the N(6)-imino proton of adenine and the N(3) atom [Scheme (3)] or the O(2) atom [Scheme (4)] of

cytosine. However, one cannot rule out the possibility of the protonation of the N(1) atom of adenine, which leads to the formation of a second hydrogen bond between the $N^+(1)$–H group of adenine and the O(2) atom of cytosine [Scheme (5)]:



C(*anti*).A^+(*anti*)

The location of the H(6) and H(5) signals of the cytosine in the dG.dC pair adjoining the non-canonical pair (4-position) of the duplex "AC" in a stronger field compared with the signal of the corresponding protons in the duplex "GC" (see above) is evidence of the disturbance of the stacking interactions in the region of the non-canonical pair. It has been suggested that one or both bases of the dA.dC pair are outside the helix. Significant distortions of the sugar phosphate skeleton of the duplex "AC" around the dA.dC pair have been observed by ^{31}P NMR.

The replacement of two dG.dC pairs in the duplex "GC" by the dA.dC pairs reduces the T_m of the duplex by 30 °C (Table 4). According to ^{1}H NMR data, the presence of the dA.dC pair in the third position in the duplex "AC" results in the "fraying" of the dG.dC pairs in the first and second positions of this duplex at lower temperatures than in the duplex "GC". The study of the kinetics of the exchange of the imino-protons of the duplex "AC" with water established τ for the dG.dC pair in the fourth position and for the dA.dT pairs in the fifth and sixth positions are smaller by factors of 3 and 2 respectively than τ for the analogous pairs of the duplex "GC". Consequently, the destabilising influence of the dA.dC pairs is not restricted to the neighbouring pair but involves the entire molecules of the duplex "AC".

However, different conclusions were reached concerning the character of the influence of the non-complementary dA.dC pair on the local and overall DNA structure after a deeper study of the structure of the duplex "AC" and its isomer

d(CG|A|GAATTC|C|CG)
(GC|C|CTTAAG|A|GC)d

by ^{1}H and ^{31}P NMR spectroscopy and after the estimation of the interatomic distances from nOe data.[93] Thus it is clear that the A and C residues are incorporated in the double helix, participating in stacking interactions with the neighbouring bases and inducing only local conformational rearrangements which do not extend to the central AATT segment. The results obtained do not permit a choice between the two A.C pairing schemes (3) and (5).[93]

This interpretation agrees well with the conclusions reached in a study[94] where the defective duplex

d(CGC|C|GC|A|GC)
(CG|A|CG|C|CGC)d

containing two dA.dC pairs was investigated by NMR spectroscopy and studies[95,96] devoted to the XRDA of the duplex "CA" whose nucleotide sequence is similar to that of the duplex "AC":

d(CGC|A|AATT|C|GCG)
(GCG|C|TTAA|A|CGC)d
duplex "CA".

It has been established that, when the dA.dC pair is integrated in the DNA, the stacking interaction with the bases of the neighbouring pairs and the conformation of the sugar phosphate skeleton are only insignificantly disturbed. According to XRDA data, Scheme (5), involving the protonation of adenine, is preferred for the A.C pairing; the important role of bridging hydrogen bonds, with participation of the water molecules incorporated in the hydration shell of the duplex, in the stabilisation of the dA.dC pair has been emphasised.

A comparative analysis of the formation of complexes by 11-, 14-, and 17-unit oligonucleotides with the DNA ΦX174 and a mutant DNA in which a G–A point substitution had been carried out, has been performed.[97] The modified complexes investigated are indicated below:

d(AACA|C|CCTATG)
(...CTTTGT|A|GGATACCC...)d
complex "11AC"

d(AACA|C|CCTATGGGA)
(...CTTTGT|A|GGATACCCTCG...)d
complex "14AC"

d(AACA|C|CCTATGGGAGCG)
(...CTTTGT|A|GGATACCCTCGCTTT...)d
complex "17AC".

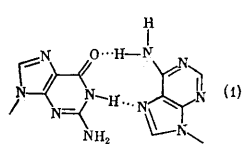
(The complexes with the non-mutant DNA containing the complementary dG.dC pair are designated respectively by "11GC", "14GC", and "17GC".) It was demonstrated that the degree of binding of all three oligonucleotides to the mutant DNA is much weaker than to the natural DNA. Furthermore, the duplexes containing the dA.dC pair are much less stable than their complementary analogues. The replacement of one dG.dC pair by dA.dC is equivalent as regards destabilisation to the removal of three nucleotide pairs (the temperatures of the half-dissociation of the complexes "17AC" and "14GC" and also "14AC" and "11GC" are 43 and 41 °C and 32 and 33 °C respectively).

The destabilising influence of the dA.dC pairs on the DNA duplexes has also been noted in other studies.[66,81,98]

The replacement of dG.dC pair by dA.dC in the recognition section of restriction endonucleases SmaI, KpnI leads to the complete inhibition of these enzymes.[70]

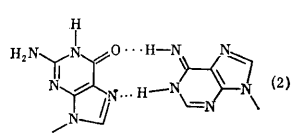
3. The purine–purine pairs

The following schemes for the formation of hydrogen bonds in the dG.dA pairs have been analysed in the literature:



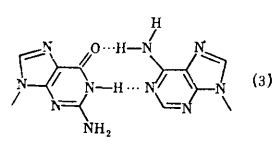
(1)

G (*anti*).A (*syn*)



(2)

G (*syn*).A (*anti*)



(3)

G (*anti*).A (*anti*) .

Theoretical analysis of the conformations of the DNA duplexes showed that the structures (1) and (3) correspond to minimum energies of non-valence interactions.[54,55]

The relative disposition of the bases in the dG.dA pair has been studied experimentally in three model systems. The structure of the dodecameric duplex "GA" has been investigated by NMR spectros-

copy in solution:[99]

1 2 3 4 5 6 6′ 5′ 4′ 3′ 2′ 1′
d(C G | Ā | G A A T T C | Ḡ | C G)
(G C | G | C T T A A G | A | G C)d
duplex "GA".

The nOe between the H(2) atom of the adenine in the dG.dA pair and the imino-protons of the neighbouring dG.dC pairs indicates the *anti*-conformation of adenosine [Scheme (2) and (3)]. The absence of an nOe between the H(2) and H(8) atoms of adenine and guanine respectively rules out the relative disposition of the bases illustrated in Scheme (2). On the basis of these data, the authors conclude that Scheme (3) actually obtains. A similar conclusion concerning the relative orientations of the bases in the dG.dA pair was reached in a study[100] where a decameric duplex containing two adjoining dG.dA pairs was investigated by ^{1}H NMR:

d(C C A A | Ḡ | | Ā | T T G G)
(G G T T | A | | G | A A C C)d .

The same duplex has been investigated by XRDA.[101] It was found that in the crystalline stage too both nucleotide residues of the non-canonical pair are in the *anti*-conformation, the bases being retained by two hydrogen bonds [Scheme (3)]. A distinct propeller disposition of the bases (the bases are rotated relative to one another by 24.8°) is characteristic of the dG.dA pair in this conformation, which facilitates pairing. Despite the fact that the distance between the C(1′) atoms of adenine and guanine is greater by 2 Å than in the Watson–Crick pair, the block consisting of two dG.dA pairs is fairly effectively incorporated in the double helix. The small changes in the individual torsional angles of the sugar phosphate skeleton observed under these conditions are within the limits characteristic of canonical pairs.

A different geometry of the dG.dA pairing with the *syn*-conformation of adenine [Scheme (1)] arises in the dodecameric duplex "AG", whose primary structure is similar to that of the duplex "GA":[13,102]

d(C G C | Ḡ | A A T T | Ā | G C G)
(G C G | A | T T A A | G | C G C)d
duplex "AG".

This investigation was also carried out by XRDA. It is significant that the incorporation in *B*-DNA of the pair dG.dA in which the nucleotide residues have respectively the *anti*- and *syn*-conformations is accompanied by a minimal adjustment of the parameters of the sugar phosphate skeleton. It has been postulated that the realisation of a particular pairing scheme [(1) or (3)] may depend on local conditions, because, according to theoretical calculations, the energy difference between these two states of the dG.dA pair is small.[101]

It has been established that the dG.dA pair, both in the state (1) and in the state (3), is incorporated in the double helix virtually without disturbing the interplanar interactions.[13,99–102]

The destabilising influence of the dG.dA pair is shown by the decrease in the T_m of the duplex "GA" by 17 °C compared with the duplex "GC" (Table 4). Data for the exchange of the imino-protons of the duplex "GA" with water have shown that the perturbations introduced by the dG.dA pair are local in character and involve only the neighbouring dG.dC pair in the fourth position.[99]

Experimental data for the molecular structure of the dA.dA pair have been obtained recently in a NMR study of the DNA duplex:[103]

d(C C C | Ā | G G G)
(G G G | A | C C C)d .

It has been shown that stable hydrogen bonds are not formed between the bases of the non-complementary pair. The incorporation of the dA.dA pair in the double helix is achieved via the stacking interaction of the adenine bases with the neighbouring bases and is accompanied by the displacement of the adenine residues from the plane in order to reduce the overlap of the opposite imino-groups and also by an appreciable distortion of the sugar phosphate skeleton.

The structure of the G.G pair in the NA duplexes has not been investigated by experimental methods.

Purine–purine pairs induce a marked destabilisation of the double helices (Table 4). Comparison of the thermal stabilities of the oligomer-polymeric complexes $dG_n.dC_{12}A_mC_x$ and $dG_n.dC_{10}G_mC_x$ (n = 100, m = 0–6, x = 5–41) having different numbers of consecutively arranged dG.dA or dG.dG pairs shows[104] that the destabilisation of the duplexes is proportional to the number of non-canonical pairs. The inclusion of one dG.dA or dG.dG pair induces a decrease in the T_m complex corresponding to the removal of on average three dG.dC pairs. However, the presence of the dG.dA or dG.dG pairs in the central section of the complex does not disturb the cooperative nature of fusion. Such non-canonical pairs are apparently incorporated in the regular double helix and participate in stacking interactions both with one another and with neighbouring dG.dC pairs.

The influence of the local environment on the destabilising effect of the A.A and G.G pairs has been demonstrated.[84,85] According to ^{1}H NMR spectroscopic data, pentaribonucleotide complexes of the type

r(C A | X̄ | U G)
(G U | X | A C)r

with central A.A and G.G pairs flanked by A.U pairs are not formed. On the other hand, the relatively stable duplex "5*AA" (T_m = 26 °C), in which the A.C pair is surrounded by G.C pairs, is formed:

r(A G | Ā | C U)
(U C | A | G A)r
duplex "5*AA".

4. Pyrimidine–pyrimidine pairs

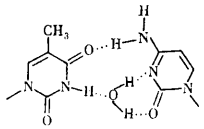
Conformational analysis of the DNA duplexes using AAPF showed that the formation of a dimer stabilised by a hydrogen bond is possible for each pyrimidine–pyrimidine pair.[23,54,55]

The molecular structure of the pyrimidine–pyrimidine pair has been little investigated by experimental methods. The results of a NMR spectroscopic study of the dodecameric duplex "CT"[105]

1 2 3 4 5 6 6′ 5′ 4′ 3′ 2′ 1′
d(C G | C̄ | G A A T T C | T̄ | C G)
(G C | T | C T T A A G | C | G C)d
duplex "CT"

established that the dC.dT pair is retained by two hydrogen bonds: a full hydrogen bond between the NH_2 group of cytosine and the O(4) atom of thymine and a weak hydrogen bond between the

N(3)–H group of thymine and the electron-accepting groups of cytosine with participation of a water molecule:



T (*anti*).C (*anti*).

The replacement of two dG.dC pairs in the duplex "GC" (see above) by the dC.dT pairs reduces T_m by 30 °C (Table 4), the destabilising influence of the dC.dT pair involving all the inner base pairs of the duplex "CT". According to data for the rate of exchange of the imino-protons of the duplex "CT" with water, the lifetimes of the dG.dC (in the 4-position) and dA.dT (in the 5- and 6-positions) pairs are respectively smaller by a factor of 10 and 6 than the values of τ for the analogous pairs in the duplex "GC".

The destabilisation of the oligomeric complexes induced by the replacement of dA.dT by the dC.dT pair is also indicated by the results of other studies[50,66] (see the duplexes 6 and 11 in Table 4).

The existence of U.U pairs stabilised by a hydrogen bond has not been demonstrated experimentally. UV-photohydration and photodimerisation data for the polymeric complexes poly(U).poly(A,U) have led to the conclusion[106] that the uridine residues in poly(A.U) are outside the helix and do not participate in the stabilisation of the secondary structure. It has been demonstrated on molecular models that the formation of such inner loops does not induce appreciable structural changes in the double helix.[107] The increase in the content of uridine residues in the copolymer poly(A.U) diminishes the stability of the complex poly(U).poly(A,U),[88,108,109] while the polynucleotide poly(A,U), containing 49 mol% of uridine does not enter at all into complementation interactions with polyuridylic acid.[107]

The smallest, compared with other nucleotides, capacity of uridine for stacking interactions, which play an important role in the stabilisation of double-stranded structures, is the reason why the pentanucleotide r(AGUCU) does not form a duplex in solution, in contrast to the pentamers containing A, G, or C in the third position.[85]

The geometry of the dT.dT pair has been discussed.[110] According to ^{1}H NMR spectroscopic data, this pair is not stabilised by hydrogen bonds,[103,111] although it is effectively incorporated in the double helix with minimum distortions of the conformations of the bases and of the sugar phosphate skeleton.[103,111,112] The study of the characteristic features of the molecular structure of the dT.dT pair in the duplex

d(CCC|T|GGG)
(GGG|T|CCC)d

showed that equilibrium between two or more conformations is characteristic of thyine residues in the temperature range 10 to 20 °C.[110]

The presence of the dT.dT pair in the duplex "TT"

d(ATCCTA|T|TAGGAT)
(TAGGAT|T|ATCCTA)d

duplex "TT".

reduces its T_m by 11 °C compared with the dodecameric duplex

d(ATCCTATAGGAT)
(TAGGATATCCTA)d

Furthermore the dT.dT pair forms a local unstable section in which the double helix dissociation process is initiated on raising the temperature simultaneously with fusion, which begins at the ends. A similar conclusion was reached[113] in a study of the duplex

d(CGCGA|T|TCGCG)
(GCGCT|T|AGCGC)d .

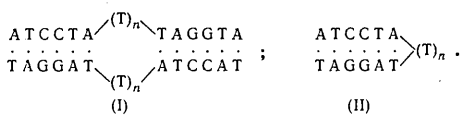
The dependence of the stability of the non-complementary dT.dT pair on the nature of the neighbouring pairs is illustrated by the following data.[103,110] The dT.dT pair has the greatest destabilising effect when it replaces the central dA.dT pair in the

—ATA—
—TAT—

sequence and has the smallest effect on replacement of the dA.dT pair in the sequence

—CAG—.
—GTC—

It has been shown in a series of studies[114,115] by NMR and temperature jump methods that the oligonucleotides d[ATCCTA(T)$_n$.TAGGAT] (n = 0–7), the primary structure of which contains palindrome elements, can form in solution both defective double helices (I) and monomolecular "pins" (II):



(I) (II)

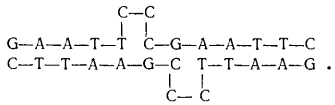
Oligomers containing more than three non-complementary thymine units form "pins" exclusively, while the coexistence of both forms is characteristic of oligonucleotides with $n \leqslant 3$. A decrease in the nucleotide concentration and in the ionic strength of the solution promotes the preferred formation of "pins". According to ^{1}H NMR spectroscopic data, the stabilisation of loops in the "pin" structures containing less than three paired thymine residues is achieved as a result of the decomposition of the nucleotide pairs adjoining the oligo(dT) sequence. The most stable structures are those with loops containing 4–5 nucleotide units. The enthalpies of dissociation of the base pairs in the double-stranded section of the molecule show that the pairs closest to the loop are more stable than the terminal pairs, i.e. the loop stabilises to some extent the double helix fragments. By measuring the nOe, it has been established that the stabilisation is achieved as a result of the "stacking" of the first (from the 5′-end) unpaired thymine residue and the base of the neighbouring nucleotide pair.

The formation of "pin" structures analogous to (II) has also been detected for the oligonucleotides d[CGCGCG(T)$_n$CGCGCG] (n = 4, 5)[116,117] and d(CGCGATTCGCG).[113]

Experimental evidence for the formation of hydrogen bonds between the bases of the C.C pair has not so far been obtained. According to many workers, the absence of hydrogen bonds from the C.C pair and also the incomplete "stacking" of the unpaired cytosine and the bases of the neighbouring nucleotide pairs lead to both cytidine residues "sticking out" from the helix, i.e. to the formation of an inner loop. The destabilising effect of the C.C pair is due to the same factors.[84,85,90,118]

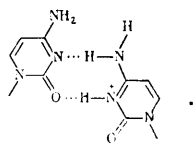
It has been established in the study of the formation of complexes by the oligonucleotides ($A_6C_mU_6$) (m = 1–8)[20,119] that the oligomers with m = 1–3 form a bimolecular helix with an inner loop and that, when m = 4–8, the "pin" structure becomes thermodynamically

more favourable. Among the "pins" formed by oligoribonucleotides, the one whose loop consists of six nucleotide units has the maximum stability. It has been established from ^{1}H NMR and nOe data[120] that the oligonucleotide d(GAATTCCCGAATTC) forms an unusual bimolecular structure containing non-coinciding loops:



The protonation of one of the cytosine residues of the C.C pair promotes the formation of hydrogen bonds between the bases. Thus, according to CD data, the oligomer d($C_4A_4T_4C_4$) forms a duplex with terminal dC.dC$^+$ pairs.[121] The presence of the central d(A_4T_4) section promotes the formation of dC.dC$^+$ pairs between antiparallel chains (in earlier studies[122,123] it was postulated that the C.C$^+$ pairs can arise only between parallel strands) and that this process occurs at higher pH than, for example, the association of dC_8 with $d(C^+)_8$.

The following structure has been proposed for the dC.dC$^+$ pair, which can be incorporated, according to the authors,[81] in the double helix of DA without causing significant changes in the geometrical parameters:



C (*anti*).C$^+$ (*anti*)

It has been suggested that the dC.dC$^+$ pairs are also formed on self-association of poly[d(CT)] and poly[d(AC)].[124]

V. Comparative analysis of the influence of the non-canonical pairs on the structure and energetic parameters of the formation of the oligomeric complexes

(1) The pyrimidine–purine non-complementary pairs as well as the dG.dA pair, incorporated in nucleotide double helices, are retained by two hydrogen bonds. The dA.dA pair is not stabilised by hydrogen bonds. There is no rigorous experimental evidence concerning the molecular structure of the dG.dG pair and the pyrimidine–pyrimidine pairs. The bases in the non-complementary pairs are in the usual tautomeric forms and as a rule in the *anti*-conformation [the dG(*anti*).dA(*syn*) pair is an exception].

(2) The replacement of the A.T and G.C pairs by non-canonical pairs alters the conformation of the sugar phosphate skeleton.

(3) Depending on the nature of the heterocyclic bases in the non-canonical pairs and on their immediate environment, the bases of such pairs can be incorporated in the double helix, participating in the stacking interaction, or can be displaced from the helix, forming a loop.

(4) The smallest perturbations of a local character are induced by the G.U, dG.dT, and dG.dA pairs, which coexist with the complementary pairs within the double helix.

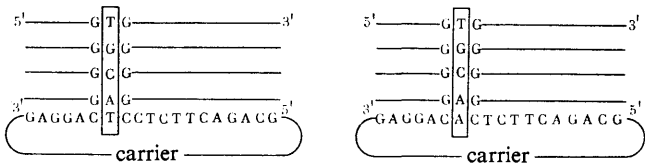
(5) The dA.dA and dC.dT pairs exert the most extensive perturbing influence. The bases of these pairs are arranged, at least partially, outside the double helix.

(6) The replacement of the Watson–Crick pairs by non-canonical pairs reduces the stability of the duplex. The degree of destabilisation depends on the length of the modified duplex, the nature of the non-canonical and replaced (G.C or A.T) pairs, the relative number of "erroneous" pairs and their positions in the duplex, and the local environment, as happens, for example, in the series of DNA duplexes[110]

d(C A A A $\boxed{\text{X}}$ A A A G)
(G T T T $\boxed{\text{X}'}$ T T T C)d

X, X′ = A, C, G,T .

The study of their melting profiles yielded the following stability series (the X.X′ pairs are indicated): dG.dT > dG.dG > dG.dA > dC.dT > dA.dA = dT.dT > dA.dC = dC.dC. Computer analysis of 100 t-RNA made it possible to estimate the relative stabilities of the non-complementary pairs in DNA: G.U ≃ G.G > C.C, U.U, C.A, A.A > G.A, U.C.[125] Measurement of the rates of dissociation of a series of oligomer–polymer DNA duplexes fixed on a dry agarose gel, i.e.



led to the derivation of the following series based on decreasing thermal stabilities as a function of the nature of the varied nucleotide pair: dT.dA ≃ dA.dT > dG.dT ⩾ dG.dA > dA.dA ≃ dT.dT ≃ dC.dA > dC.dT.[126] The thermodynamic parameters of the formation of oligomeric complexes with non-canonical base pairs are summarised in Table 4.

(7) In the general case, the destabilisation of the modified duplex compared with the "regular" duplex is associated with a decrease in the enthalpy of complex formation (as a result of the disturbance of the stacking interactions in the region of the non-canonical pair) overlapping the favourable change in entropy (as a result of the greater conformational mobility of the "erroneous" pairs).

The comparative characteristics of the influence of all the possible combinations of non-canonical pairs on the thermodynamic parameters of the complex formation process have been obtained[127] in relation to the DNA duplex

d(C G T C G T T T $\boxed{\text{X}}$ A C A A C G T C G)
(G C A G C A A A $\boxed{\text{Y}}$ T G T T G C A G C)d

X, Y = A, C, G, T .

Only the components of ΔH^0 (X.Y) and ΔS^0 (X.Y) (calculated per nucleotide pair) characterising the stacking interactions of the non-canonical pair with neighbouring pairs (the "virtual stacking" approximation) were analysed (Table 3).

The data obtained led to a hypothesis concerning the structural features of the non-complementary pairs. Three main types of conformations of such pairs have been considered.

(a) Bound pairs (the so called "wobble" pairs). They are characterised by the same value of ΔS and somewhat reduced values of ΔH compared with the Watson–Crick pairs, they have paired bases, and are incorporated in a double helix.

(b) Open chain pairs. They are characterised by low values of ΔH and ΔS; such pairs form loops.

(c) Weak nucleotide pairs. They have intermediate (between extremum values) thermodynamic parameters and form intermediate

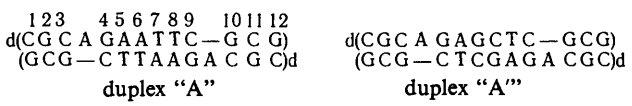
structures of different types. A direct correspondence has not been found between the structural features of the pairs and their destabilising influence. It is of interest that the T_m of duplexes with the non-canonical pairs X.Y and Y.X, differing only in the relative disposition of the bases in the complementary chains, are not the same although the environment of these pairs and hence the interplanar contacts are not altered. This is apparently associated with the effect of the long-range interactions of the non-canonical pairs.

Consideration of the formation and reparation of the non-complementary pairs has led to the conclusion that the reparation systems eliminate with the greatest efficiency the most frequently encountered pairs. Thus the repair system of *E. coli* effectively "mends" the dT.dG, dG.dG, and then dC.dA pairs and to a much lesser extent the dG.dA, dA.dG, dT.dT, dC.dC, dT.dC, and dC.dT pairs.[128] It has been suggested that the recognition of the "erroneous" pairs by reparation enzymes is not associated with the degree of destabilisation but is determined by the orientation of the bases relative to the sugar phosphate residue and the profile of the functional groups in the grooves within the double helix.[10,127]

VI. Complexes of nucleic acids containing unpaired nucleotide residues

1. Inner unpaired units

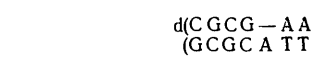
Analysis of the structure of the DNA duplexes "A" and "A'",[14,57–59,64,129,130] whose composition includes adenosine residues without a partner on the complementary chain, i.e.



showed that the unpaired purine base is incorporated in the helix and particpates in the stacking interaction with the neighbouring dG.dG pairs. However, the inclusion of a "superfluous" unit is acompanied by an increase in the distance between the G.C pairs and hence leads to the disturbance of the "stacking" of the bases of the unmodified strand of the duplex. Furthermore, a distortion of the sugar phosphate skeleton as well as a change in the length and torsional angles of the P–O bonds of the phosphate section opposite the "superfluous" adenosine have been observed in the modification section (^{1}H NMR spectroscopic data).

The presence of an unpaired residue greatly destabilises the duplex (Table 4). The similarity of the values of ΔH^0 for the duplexes "GC" (see above) and "A" [the disturbance of the stacking interactions between the G(3) and C(4) bases on the unmodified strand is compensated by the additional interplanar interactions of the "superfluous" adenosine] indicates the entropic nature of the destabilising effect. On the basis of the difference between $\Delta H_{v\text{-}H}$ and ΔH^0, determined by the SMC method for the duplex "A", it has been established that the cooperatively melting section comprises 9 ± 1 nucleotide pairs, i.e. includes the "superfluous" unit. According to data for the rate of exchange of the imino-protons of the duplex "A" with water, the destabilising influence of the unpaired adenosine involves all the inner pairs of the duplex.

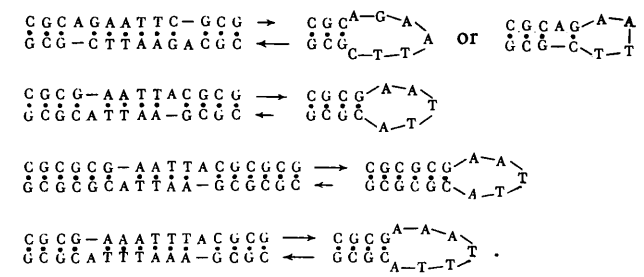
An NMR spectroscopic study of a longer sequence containing the unpaired adenosine residue, i.e.



also showed that the "superfluous" base is integrated in the double helix.[131] However, this entails not an increase in the distance between the bases on the opposite strand, as in the case of the duplex "A", but some bending of the helix. Since the defects are arranged symmetrically on different strands of the duplex, the helix acquires an S shape. The bases of the unmodified strand opposite the unpaired residue are then in fairly effective contacts.

It is of interest that in the crystalline state the conformation with the disposition of the unpaired adenosine outside the helix is characteristic of both duplexes—"A"[132] and "A'".[133,134] Despite the palindrome sequence, both "superfluous" bases are oriented in different ways (probably owing to the influence of the crystal packing). Furthermore, the local structure in the region of the defect is different for the "A" and "A'" duplexes. Thus in solution the unpaired adenosine residue is incorporated in the double helix, while in the crystalline state it "sticks out". The data obtained indicate the conformation flexibility of DNA duplexes modified in this way and their ability to pass from one conformational state to another when the external conditions are altered.

The study of the conformational transitions in a series of imperfect palindromes with inserts comprising superfluous adenosine residues has shown[135,136] that the distance between the insert and the "central symmetry" determines the equilibrium between the duplex and the single-stranded "pin". The theoretically possible conformations of the oligodeoxyribonucleotides investigated are illustrated in the scheme below:



It has been established on the basis of UV and NMR spectroscopic and SMC data that the introduction of additional adenosine units does not induce a change in the enthalpy of complex formation regardless of their positions in the sequence.

The DNA duplex[137]



served as a model of a double helix with a "superfluous" guanosine residue.[137] A three-dimensional model of the duplex "G" has been constructed from ^{1}H NMR spectroscopic data and by means of computer modelling (incremental approach). The series of structures differing in the length of the double helix sequence flanking the defect proved to be very similar. The duplex "G" is a double helix belonging to the $\overline{B}$-family; the axis of the helix is bent by 18–23°. As was to be expected, the unpaired residue is incorporated in the double helix.

The structure and stability of the DNA duplex "C", containing a superfluous cytidine residue, have been investigated:[138]

1 2 3 4 5 6 7 8
d(C A A A C A A A G)
(G T T T — T T T C)d
duplex "C".

The occurrence of an nOe duplex "C" between the imino-protons of the dA.dT pairs (in the 4- and 5-positions) and also the absence of an upfield shift of the signls of the non-exchanging protons of the unpaired cytosine as the temperature reduced indicate that the "superfluous" cytosine residue "sticks out" from the helix and does not participate in the stacking interaction with the bases of neighbouring pairs. Cytosine is apparently "expelled" by the neighbouring purine bases, which are known to possess an enhanced capacity for stacking interactions. The position of cytosine outside the helix destabilises the duplex (the duplexes 13 and 14 in Table 4 and in the paper of Aboul-Ela et al.[110]), the destabilising effect being enthalpic in nature in this instance.

The question arises whether the unpaired cytosine always occupies a position outside the helix. It has been found that its conformation depends on temperature. Thus a study by two-dimensional NMR spectroscopy and the analysis of nOe parameters of the DNA duplex

d(C C G C G A A T T C — C G G)
(G G C — C T T A A G C G C C)d

showed[139] that at low temperatures (0 °C) the "superfluous" cytosine is outside the helix, while the adjoining bases participate in the stacking interaction. With increase in temperature, the conformational equilibrium shifts towards the formation of structures in which the cytosine residue is built into the duplex (> 40 °C). It is noteworthy that the disturbances in the sugar phosphate skeleton extend to a region remote from the site of the defect.

Even more interesting results have been obtained in a study of the conformational characteristics of other unpaired pyrimidine bases—thymine and uracil—in the duplexes "T"[140] and "U":[141]

d(C T G G T G C G C)	r(C U G G U G C G C)
(G A C C — C G C G)d	(G A C C — C G C G)r
duplex "T"	duplex "U" .

These duplexes, which have a similar sequence, differ only in the nucleotide residues belonging to the deoxyribo- or ribo-series. The set of NMR spectroscopic data, the nOe parameters, the temperature dependence of the chemical shifts of the proton signals, etc. show that the unpaired thymine residues are built into the duplex "T". According to the results of computer modelling, the insertion of the "superfluous" thymine does not induce appreciable changes in the structure of *B*-DNA under these conditions: the base pairing is not disturbed and there are no appreciable distortions in the torsional angles. We may note that, when the more bulky adenine residue is intercalated, the structural perturbations are much more pronounced.

In contrast to thymine residues, the uracil in the duplex "U" is preferentially located outside the helix. The regular structure of *A*-RNA is then hardly disturbed. The authors suggest that the difference in the behaviour of these bases in the DNA and RNA duplexes can be accounted for by the different tendencies of thymine and uracil to participate in stacking interactions.

If the unpaired thymine residues are not unique but are encountered regularly and frequently in the duplex, then a position outside the helix is more characteristic of them. Such a conformation has been postulated for the polymeric duplex poly[d(GGAA)].poly[d(TC)][142] from data for the formation of cytosine photodimers:

—G—G—A—G—G—A—
—C C—T—C C—T— .
T T

It has been established that the "superfluous" thymine residues do not disturb the cooperative nature of the fusion but diminish greatly the stability of the defective helix compared with the regular poly[d(GGA)].poly[d(TCC)].

A similar conclusion that the unpaired thymine residues are located outside the helix has been reached on the basis of a study of the duplex poly[d(GA)].poly[d(TTC)].[143]

Interesting data for the stability and dynamics of a series of duplexes with a nucleotide sequence corresponding to the mutation "hot spot" with a shift of the frame have been obtained by NMR spectroscopy:[144]

d(G A T G G G C A G)	d(G A T G G G — C A G)	d(G A T G G G — C A G)
(C T A C C C G T C)d	(C T A C C C C G T C)d	(C T A C C C A G T C)d .
duplex "N"	duplex "C_N"	duplex "A_N"

It was found that the unpaired adenine exerts a mainly local influence on the stability of the nucleotide pairs (the duplex "A_N"), while the delocalisation of the destabilising effect along the G.C track of the duplex "C_N" as a result of the migration of the defect is characteristic of the unpaired cytosine:

d(G A T G G G — C A G) → d(G A T G G — G C A G) →
(C T A C C C C G T C)d ← (C T A C C C C G T C)d ←
→ d(G A T G — G G C A G) → d(G A T — G G G C A G)
← (C T A C C C G T C)d ← (C T A C C C C G T C)d
duplex "C_N" .

The greater thermal stability of the duplex "C_N" compared with the duplex "A_N" (ΔT_m = 5.7 °C) has been explained by the authors in terms of the positional degeneracy of the defect (unpaired cytosine) and the associated increase in entropy. It is noteworthy that the results of the above study[144] conflict with the results and conclusions of a number of other studies[57,64,129] as regards a series of aspects associated with the character of the influence of the "superfluous" adenosine on the stability of the duplex pairs and the enthalpy of complex formation.

In the next study of the above series, the conformational dynamics of the "superfluous" guanine residue, located in the G.C track of the analogous duplex, was investigated.[145] The presence of free imino-protons of the unpaired guanine made it possible to follow the migration of the defect. It was discovered that the "superfluous" unit occupies all possible positions, although it occurs more frequently at the ends of the track. One cannot say with certainty that the rate of migration of the defect is the same for oligopurine and oligopyrimidine sequences. As regards the location of the "superfluous" base relative to the duplex, experimental data show that the unpaired purine bases are incorporated in the double helix, while the pyrimidine bases are involved in equilibrium between the *endo*-helical and *exo*-helical conformations.

Overall, one can say that the ways in which DNA neutralises perturbations induced by unpaired bases are fairly varied and depend on the local "stacking" of the bases, the nature of the superfluous unit, the flexibility of the sugar phosphate skeleton, and the nucleotide sequence.

2. Oligonucleotide duplexes flanked by unpaired units

The influence of the terminal unpaired nucleotides on the stability of the NA double helices has been investigated mainly on short ribonucleotide duplexes.[146–159] Analysis of the available literature (Table 5) permits the following conclusions.

Table 5. Thermodynamic parameters of the formation of oligonucleotide complexes flanked by unpaired nucleotide residues.*

No.	Complex	Complex formation conditions	T_m °C	$-\Delta H^{0}$**, kcal mol^{-1}	$-\Delta S^0$, e.u.	$-\Delta G^0(t, °C)$, kcal mol^{-1}	Refs.
1	r(C C G G) (G G C C)r	0.01 M cacodylate buffer, pH 7.0, 1 mM EDTA, 1 M NaCl, c_0=0.1 mM	27.1	34.7	97.1	4.41 (39°)	[152]
2	r(A C C G G)p p(G G C C A)r	ditto	36.4	39.7	109.9	5.44 (39°)	[152]
3	r(C C G G U)p p(U G G C C)r	»	37.8	42.8	119.3	5.60 (39°)	[152]
4	r(C C G G A)p p(A G G C C)r	»	44.6	47.3	130.4	6.57 (39°)	[152]
5	r(G C C G G)p p(G G C C G)r	0.01 M phosphate buffer, pH 7.0, 0.5 mM EDTA, 1 M NaCl, c_0=0.1 mM	31.0	34	93	—	[158]
6	r(U C C G G)p p(G G C C U)r	ditto	29.7	37	104	—	[158]
7	r(C C G G C)p p(C G G C C)r	»	34.4	40.3	113	—	[154]
8	r(C C G G G)p p(G G G C C)r	»	46.5	48.3	133	—	[154]
9	r(G G C C) (C C G G)r	»	35.0	36.0	98	—	[154]
10	r(A G G C C)p p(C C G G A)r	»	38.3	37.9	103	—	[158]
11	r(C G G C C)p p(C C G G C)r	»	39.3	35.1	94	—	[158]
12	r(U G G C C)p p(C C G G U)r	»	34.5	35.6	97	—	[158]
13	r(G G C C C)p p(C C C G G)r	»	47.5	41.7	112	—	[154]
14	r(G G C C U)p p(U C C G G)r	»	51.5	48.3	130	—	[154]
15	r(G G C C G)p p(G C C G G)r	»	57.5	52.3	140	—	[154]
16	r(G G C C A)p p(A C C G G)r	»	58.0	51.5	137	—	[154]
17	r(G C G C) (C G C G)r	0.005 M phosphate buffer, pH 7.0, 0.5 mM EDTA, 1 M NaCl, c_0=1 mM	27.4	32.3	89.0	—	[157]
18	r(G G C G C)p p(C G C G G)r	ditto	28.8	35.3	98.7	—	[157]
19	r(U G C G C) (C G C G U)r	»	31.5	29.2	77.6	—	[157]
20	r(G C G C A)p p(A C G C G)r	»	51.9	50.0	135.7	—	[157]
21	r(G C G C C)p p(C C G C G)r	»	41.3	39.2	106.2	—	[157]
22	r(G C G C G)p p(G C G C G)r	»	50.7	47.9	129.5	—	[157]
23	r(G C G C U)p p(U C G C G)r	»	45.5	45.5	124.6	—	[157]
24	d(G A A T T C G C G) (G C G C T T A A G)d	0.01 M phosphate buffer, pH 7.0, 0.1 mM EDTA, 1 M NaCl, c_0=0.7 mM	46.3	60 (35)	—	—	[155]
25	d(G G A A T T C C) (C C T T A A G G)d	ditto	52.5	59 (59)	—	—	[155]

* Data for the fully complementary complexes are quoted for comparison.

** The values of ΔH^0_{v-H} are given in brackets.

*** c_0 is the oligonucleotide concentration.

The flanking of the double helix by an unpaired terminal residue increases the stability of the duplex.

Stabilisation is achieved as a result of additional interplanar interactions of the unpaired residue with the terminal paired base of the opposite strand; this entails a decrease in the end pair "fraying" effect.

The increase in stability is due to the favourable change in the enthalpy of complex formation (the contribution by additional "stacking") which exceeds the unfavourable entropic effect (the decrease in the degree of "freedom" of the pendant residue) compared with the fully complementary duplex.

The following sequence in the stabilisation by unpaired residues has been established: G ≃ A > U ≃ C, i.e. purine bases are more effective than pyrimidine bases. A similar dependence of the stability of the duplexes also on the nature of the base involved in overlapping with the unpaired residue has also been observed.

In helices of the ribo-series, the 3'-terminal base increases stability to a greater extent than the base located at the 5'-end. On the other hand, in deoxyribonucleotide duplexes, the 5'-terminal unit makes a greater contribution to stabilisation,[112] which is apparently associated with the differences between the structures of the *A*- and *B*-forms.

Conversely, the presence of more than one unpaired residue at the ends of the duplex reduces the stability of the double helix.[155]

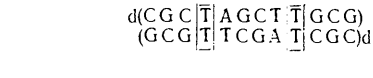
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During the preparation of the manuscript for the press, a number of communications on the subject of the review were published.

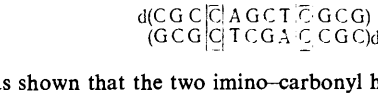
It was shown that[160] by the RS method that the non-complementary G.T pair induces a greater disturbance of *B*-DNA (solution) than of *Z*-DNA (crystalline state). Arguments are put forward in support of the hypothesis that this method in fact yields most information required to determine the geometry of the phosphodiester linkages near the non-complementary pairs.

A comparative study of the fine structure of the DNA duplexes in the *A*-form, one of which contains two adjacent G.T pairs while the others are unmodified analogues, has been carried out by XRDA (1.7 Å).[161] The thermal stability of imperfect and fully complementary double helices has also been studied (UV spectroscopy).

The structural features of the pyrimidine–pyrimidine non-complementary pairs C.C and T.T forming part of the composition of the 12-unit DNA duplexes have been studied by NMR spectroscopy:[162]



and



It was shown that the two imino–carbonyl hydrogen bonds, stabilising the T.T pair, are weaker than the corresponding bonds in the G.T pair. As regards the C.C pair, the experimental data did not permit a correct choice between several pairing schemes. It was only evident that one of the bases of the pair must be protonated.

A study has been made[163] of the stability of the formation of the $C.C^+$ pairs in 2-, 3-, or 6-unit cytosine tracts localised within an antiparallel DNA duplex. It had been shown earlier that such pairs are formed at the ends of an antiparallel duplex.[121] According to CD data, the pairing of cytosine residues does not occur in any of the duplexes studied.

The interrelation between the thermodynamic parameters of the fusion of defective duplexes, formed by the matrix DNA and decanucleotide primers containing non-complementary bases at the 3'-end (variants of the non-complementary pairs—G.T, C.T, and T.T), on the one hand, and the accuracy of the DNA replication, on the other, has been analysed.[164] The causes of the ambiguous relation are discussed.

The influence of the nucleotide sequence of the matrix DNA on the type of the non-complementary pair has been observed in the DNA-polymerase reaction.[165] The frequency of errors counted was artificially increased by using only three out of the four deoxyribonucleotide triphosphates.

The additional possibility of the formation of non-canonical pairs has been discussed in a theoretical study.[166] According to calculations of the energies of the intermolecular interactions (AAPF), in alternative pairing schemes one of the bases is in the *syn*-orientation and a water molecule participates in the formation of hydrogen bonds. According to the authors, such pairs are closer to the Watson–Crick pairs in terms of geometrical parameters.

The influence of the terminal non-complementary pairs (A.C, A.A, and A.G) on the thermal stability of oligoribonucleotide duplexes has been discussed.[167]

The dimorphous structure of poly(rA).poly(dT) has been confirmed by Raman spectroscopy.[168]

Comparative studies have been made of the thermal stabilities and of the secondary structures (by UV and CD spectroscopy) for a series of oligomeric DNA, RNA, and hybrid RNA.DNA duplexes.[169] It has been shown that the ribonucleotide duplex is the most stable, the hybrid duplexes occupying an intermediate position. The *A*-form of the double helix is characteristic of the latter but it is not fully identical with *A*-RNA.

The influence of two unpaired thymine residues, flanking the hexanucleotide duplexes $[d(GC)_3]_2$ or $[d(CG)_3]_2$ at the 3'- or 5'-end, on the thermodynamic and structural characteristics of the double helices has been studied.[170] It has been observed with the aid of UV, NMR, and CD spectroscopy and by computer modelling that the presence of thymidine residues stabilises the double helix as a result of the stacking interaction of the unpaired bases, the effect being greater in the case of 5'-terminal substituents.

The individual thermodynamic contriution of the four-unit loop and of the unpaired base in the double helix section has been determined for 14-pin ribonucleotide structures.[171] It has been shown that the destabilising effect of the unpaired purine is greater than that of pyrimidine and depends on the nucleotide sequence of the section adjoining the defect.

References

1. A Sugino, S Hirose, R Okazaki *Proc. Nat. Acad. Sci. USA*, 1972, **69**(7) 1863
2. J D Watson *Molecular Biology of the Gene* (Translated into Russian from English), Izd. Mir, Moscow, 1978, p. 276
3. L L Gerchman, D B Ludlum *Biochim. Biophys. Acta*, 1973, **308** 310
4. R S Lasken, M F Goodman *J. Biol. Chem.*, 1984, **259**(18) 11491
5. O C Uhlenbeck, J Baller, P Doty *Nature*, 1970, **225**(5232), 508
6. G J Quigley, N G Seeman, A H-J Wang, et al. *Nucleic Acids Res.*, **1975, 2(12)** 2329
7. **R Mikelsaar *J. Theor. Biol.*, 1981, 92** 163
8. W Taub, J L Sussman *Nucleic Acids Res.*, 1982, **10**(8) 2701
9. R B Wallace, A B Studencki, A Murasugi *Biochimie*, 1985, **67** 755
10. O Kennard *Nucleic Acids and Molecular Biology* (Edited by F Eckstein, D M J Lilley), Springer-Verlag, Berlin–Heidelberg, 1987, Vol. 1, p. 25
11. D J Patel, L Shapiro, D Hare *Nucleic Acids and Molecular Biology* (Edited by F Eckstein, D M J Lilley), Springer-Verlag, Berlin–Heidelberg, 1987, Vol. 1, p. 70
12. T Brown, O Kennard, G Kneale, D Rabinovich, *Nucleosides, Nucleotides*, 1985, **4**(1–2) 255
13. T Brown, W N Hunter, G Kneale, O Kennard *Proc. Nat. Acad. Sci. USA*, 1986, **83**(8) 2402
14. M A Saper, H Eldar, K Mizuuchi, et al., *J. Mol. Biol.*, 1986, **188**(1) 111
15. S Arnott, R Chandrasekaran, R P Millane, H-S Park *J. Mol. Biol.*, 1986, **188**(4) 631
16. N G Dolinnaya, E S Gromova *Usp. Khim.*, 1983, **52**(1) 138 [English translation in *Russ. Chem. Rev.*, 1983(1)]
17. A Pardi, I Tinoco *Biochemistry*, 1982, **21**(19) 4686
18. J Tropp, A G Redfield *Biochemistry*, 1981, **20**(8) 2133
19. S V Matveev, V V Filimonov, P L Privalov *Mol. Biol.*, 1982, **16**(6) 1234
20. J Gralla, D M Crothers *J. Mol. Biol.*, 1973, **73**(4) 483
21. M E Craig, D M Crothers, P Doty *J. Mol. Biol.*, 1971, **62**(2) 383
22. J M Benevides, A H-J Wang, A Rich, et al. *Biochemistry*, 1986, **25**(1) 41
23. V P Chuprina, V I Poltev *Nucleic Acids Res.*, 1983, **11**(15) 5205
24. V L Florent'ev *Bioorg. Khim.*, 1982, **8**(7) 885
25. G Milman, R Langridge, M J Chamberlin *Proc. Nat. Acad. Sci. USA*, 1967, **57**(6) 1804
26. S Heguchi, M Tsuboi, Y Iitaka *Biopolymers*, 1969, **7**(6) 909
27. M-I B Tunis, J E Hearst *Biopolymers*, 1968, **6**(8) 1218
28. D M Gray, R L Ratliff *Biopolymers*, 1975, **14**(3) 487
29. A Pardi, F H Martin, I Tinoco *Biochemistry*, 1981, **20**(14) 3986
30. F H Martin, I Tinoco *Nucleic Acids Res.*, 1980, **8**(10) 2295
31. H T Steely, D M Gray, R L Ratliff *Nucleic Acids Res.*, 1986, **14**(24) 10071
32. S B Zimmerman, B H Pheiffer *Proc. Natl. Acad. Sci. USA*, 1981, **78**(1) 78
33. H Shindo, U Matsumoto *J. Biol. Chem.*, 1984, **259**(14) 8682
34. G Gupta, M H Sarma, R H Sarma *J. Mol. Biol.*, 1985, **186**(2) 463
35. S Arnott, P J Bond, E Selsing, P J C Smith *Nucleic Acids Res.*, 1976, **3**(10) 2459
36. D G Reid, S A Salisbury, et al. *Eur. J. Biochem.*, 1983, **135**(2) 307
37. H-Y Wu, M J Behe *Proc. Nat. Acad. Sci. USA*, 1984, **81**(23) 7284
38. M J Behe *Biopolymers*, 1986, **25**(3) 519
39. S D Jayasena, M J Behe *Nucleic Acids Res.*, 1987, **15**(9) 3907
40. R E Dickerson, H R Drew, B N Conner, et al. *Science*, 1982, **216** 475
41. A H-J Wang, S Fujii, J H van Boom, et al. *Nature*, 1982, **299**(5884) 601
42. J-R Mellema, C A G Haasnoot, G A van der Marel, et al. *Nucleic Acids Res.*, 1983, **11**(16) 5717
43. E Selsing, R D Wells, T A Early, D R Kearns *Nature*, 1978, **275**(5677) 249

44. E Selsing, R D Wells *J. Biol. Chem.*, 1979, **254**(12) 5410
45. E Selsing, R D Wells, C I Alden, S Arnott *J. Biol. Chem.*, 1979, **254**(12) 5417
46. J W Nelson, I Tinoco *Biochemistry*, 1982, **21**(21) 5289
47. M Riley, B Maling, M I Chamberlin *J. Mol. Biol.*, 1966, **20**(2) 359
48. T G Dewey, D H Turner *Biochemistry*, 1979, **18**(26) 5757
49. M Chamberlin, P Berg *J. Mol. Biol.*, 1964, **8**(2) 297
50. S Gillam, K Waterman, M Smith *Nucleic Acids Res.*, 1975, **2**(5) 625
51. E J O'Brien, A W MacEwan *J. Mol. Biol.*, 1970, **48**(2) 243
52. H Takashima, M Nakanishi, M Tsuboi *Biochemistry*, 1985, **24**(18) 4823
53. F H C Crick *J. Mol. Biol.*, 1966, **19**(2) 548
54. J W Keepers, P Schmidt, T L James, P A Kollman *Biopolymers*, 1984, **23**(12) 2901
55. V P Chuprina, V I Poltev *Nucleic Acids Res.*, 1985, **13**(1) 141
56. D J Patel, S A Kozlowski, L A Marky, et al. *Biochemistry*, 1982, **21**(3) 437
57. A Pardi, K M Morden, D J Patel, I Tinoco *Biochemistry*, 1982, **21**(25) 6567
58. D J Patel, A Pardi, K Itakura *Science*, 1982, **216**(4546) 581
59. L A Marky, S A Kozlowski, K J Breslauer *Biophys. J.*, **33**(2), Pt. 2 318a
60. D Hare, L Shapiro, D J Patel *Biochemistry*, 1986, **25**(23) 7445
61. D J Patel, S A Kozlowski, L A Marky, et al. *Biochemistry*, 1982, **21**(3) 428
62. R E Dickerson, H R Drew *J. Mol. Biol.*, 1981, **149**(4) 761
63. D R Hare, D E Wemmer, S-H Chou, et al. *J. Mol. Biol.*, 1983, **171**(3) 319
64. Y G Chu, I Tinoco *Biopolymers*, 1983, **22**(4) 1235
65. D Porschke, M Eigen *J. Mol. Biol.*, 1971, **62**(2) 361
66. N Tibanyenda, S H de Bruin, C A G Haasnoot, et al. *Eur. J. Biochem.*, 1984, **139**(1) 19
67. E Quignard, G V Fazakerley, G van der Marel, et al. *Nucleic Acids Res.*, 1987, **15**(8) 3397
68. W N Hunter, T Brown, G Kneale, et al. *J. Biol. Chem.*, 1987, **262**(21) 9962
69. P J Greene, M S Poonian, A L Nussbaum, et al. *J. Mol. Biol.*, 1975, **99**(2) 237
70. S Shenoy, K Daigle, K C Ehrlich, et al. *Nucleic Acids Res.*, 1986, **14**(11) 4407
71. T Brown, O Kennard, G Kneale, D Rabinovich *Nature*, 1985, **315**(6020) 604
72. G Kneale, T Brown, O Kennard, D Rabinovich *J. Mol. Biol.*, 1985, **186**(4) 805
73. W N Hunter, G Kneale, T Brown, et al. *J. Mol. Biol.*, 1986, **190**(4) 605
74. M McCall, T Brown, O Kennard *J Mol. Biol.*, 1985, **183**(3) 385
75. P S Ho, C A Frederick, G J Quicley, et al. *Embo J.*, 1985, **4**(13A) 3617
76. T R Krugh, M A Young *Biochem. Biophys. Res. Commun.*, 1975, **62**(4) 1025
77. M A Young, T R Krugh *Biochemistry*, 1975, **14**(22) 4841
78. A G Lezius, E Domin *Nature New Biology*, 1973, **244**(136) 169
79. D M Gray, R L Ratliff *Biopolymers*, 1977, **16**(6) 1331
80. T A Early, J Olsmted, D R Kearns, A G Lezius *Nucleic Acids Res.*, 1978, **5**(6) 1955
81. T A Millican, G A Mock, M A Chauncey, et al. *Nucleic Acids Res.*, 1984, **12**(19) 7435
82. S A Salisbury, N A Anand *J. Chem. Soc., Chem. Commun.*, 1985, 985
83. H Mizuno, K Tomita, E Nakagawa, et al. *J. Mol. Biol.*, 1981, **148**(1) 103
84. P J Romaniuk, D W Hughes, R J Grégoire, et al. *Biochemistry*, 1979, **18**(23) 5109
85. D Aikema, P A Hader, R A Bell, T Neilson *Biochemistry*, 1982, **21**(9) 2109
86. N Sugimoto, R Kierzek, S M Freier, D H Turner *Biochemistry*, 1986, **25**(19) 5755
87. S K Podder *Nature New Biology*, 1971, **232**(30) 115
88. K F Bautz, F A Bautz *Proc. Nat. Acad. Sci. USA*, 1964, **52**(6) 1476
89. T Ackermann, V Gramlich, H Klump, et al. *Biophys. Chem.*, 1979, **10**(3) 231
90. O C Uhlenbeck, F H Martin, P Doty *J. Mol. Biol.*, 1971, **57**(2) 217
91. S M Freier, R Kierzek, M H Caruthers, et al. *Biochemistry*, 1986, **25**(11) 3209
92. D J Patel, S A Kozlowski, S Ikuta, K Itakura *Biochemistry*, 1984, **23**(14) 3218
93. X Gao, D J Patel *J. Biol. Chem.*, 1987, **262**(35) 16973
94. M H Sarma, G Gupta, R H Sarma, et al. *Biochemistry*, 1987, **26**(24) 7707
95. W N Hunter, T Brown, O Kennard *Nucleic Acids Res.*, 1987, **15**(16) 6589
96. W N Hunter, T Brown, N N Anand, O Kennard *Nature*, 1986, **320**(6062) 552
97. R B Wallace, I Shaffer, R F Murphy, et al. *Nucleic Acids Res.*, 1979, **6**(11) 3543
98. D H Evans, A R Morgan *Nucleic Acids Res.*, 1986, **14**(10) 4267
99. D J Patel, S A Kozlowski, S Ikuta, K Itakura *Biochemistry*, 1984, **23**(14) 3207
100. L-S Kan, S Chandrasegaran, S M Pulford, P S Miller *Proc. Nat. Acad. Sci.* USA, 1983, **80** 4263
101. G G Privé, U Heinemann, S Chandrasegaran, et al., Science, 1987, **238**(4826) 498
102. W N Hunter, T Brown, O Kennard *J. Biomol. Struct. Dynam.*, 1986, **4**(2) 173
103. F N Arnold, S Wolk, P Cruz, I Tinoco *Biochemistry*, 1987, **26**(13) 4068
104. J B Dodgson, B D Wells *Biochemistry*, 1977, **16**(11) 2367
105. D J Patel, S A Kozlowski, S Ikuta, K Itakura *Fed. Proc.*, 1984, **43**(11) 2663
106. A J Lomant, J R Fresco *J. Mol. Biol.*, 1973, **77**(3) 345
107. J R Fresco, M B Alberts *Proc. Nat. Acad. Sci. USA*, 1960, **46**(3) 311
108. R F Steiner *J. Biol. Chem.*, 1960, **235**(10) 2946
109. A J Lomant, J F Fresco *Biopolymers*, 1973, **12**(8) 1889
110. F Aboul-ela, D Koh, I Tinoco, F H Martin *Nucleic Acids Res.*, 1985, **13**(13) 4811
111. A G Cornelis, J H J Haasnoot, J F den Hartog, et al. *Nature*, 1979, **281**(5728), 235
112. J-R Mellema, R van der Woerd, G A van der Marel, et al. *Nucleic Acids Res.*, 1984, **12**(12) 5061
113. M F Summers, R A Byrd, K A Gallo, et al. *Nucleic Acids Res.*, 1985, **13**(17) 6375
114. C A G Haasnoot, J H J Hartog, J F M de Rooij, et al. *Nucleic Acids Res.*, 1980, **8**(1) 169
115. C W Hilbers, C A G Haasnoot, S H de Bruin, et al. *Biochimie*, 1985, **67** 685

116. S Ikuta, R Chattopadhyaya, H Ito, et al. *Biochemistry*, 1986, **26**(17) 4840
117. L E Xodo, G Manzini, F Quadrifoglio, et al. *Nucleic Acids Res.*, 1986, **14**(13) 5389
118. F H Martin, O C Uhlenbeck, P Doty *J. Mol. Biol.*, 1971, **57**(2) 201
119. O C Uhlenbeck, P N Borer, B Dengler, I Tinoco *J. Mol. Biol.*, 1973, **73**(4) 483
120. R V Hosur, A Sheth, K V Chary, et al. *Biochem. Biophys. Res. Commun.*, 1986, **139**(3) 1224
121. D M Gray, T Cui, R L Ratcliff *Nucleic Acids Res.*, 1984, **12**(19) 7565
122. K A Hartman, A Rich *J. Am. Chem. Soc.*, 1965, **87**(9) 2033
123. R B Inman *J. Mol. Biol.*, 1964, **9**(3) 624
124. D M Gray, M Vaughan, R L Ratcliff, F N Hayes *Nucleic Acids Res.*, 1980, **8**(16) 3695
125. J Ninio *Biochimie*, 1979, **61** 1133
126. S Ikuta, K Takagi, R B Wallace, K Itakura *Nucleic Acids Res.*, 1987, **15**(2)
127. H Werntges, G Steger, D Riesner, H-J Fritz *Nucleic Acids Res.*, 1986, **14**(9) 3773
128. B Kramer, W Kramer, H-J Fritz, *Cell*, 1984, **38**(3) 879
129. D J Patel, S A Koslowski, L A Marky, et al. *Biochemistry*, 1982, **21**(3)
130. D Hare, L Shapiro, N J Patel *Biochemistry*, 1986, **25**(23) 7456
131. S Roy, B Sklenar, E Appella, J S Cohen *Biopolymers*, 1987, **26**(12)
132. L Joshua-Tor, D Rabinovich, H Hope, et al. *Nature*, 1988, **334**(6177) 82
133. M Miller, R Wlodawer, E Appella, J L Sussman *J. Mol. Biol.*, 1987, **195**(4) 967
134. M Miller, R W Harrison, A Wlodawer, et al. *Nature*, 1988, **334** 85
135. M Miller, W Kirchhoff, F Schwarz, et al. *Nucleic Acids Res.*, 1987, **15**(9)
136. S Roy, S Weinstein, B Borah, et al. *Biochemistry*, 1986, **25**(23) 7417
137. S A Woodson, D M Crothers *Biochemistry*, 1988, **27**(9) 3130
138. K M Morden, Y G Chu, F H Martin, I Tinoco *Biochemistry*, 1983, **22**(24) 5557
139. M W Kalnik, D G Norman, M G Zagorski, et al. *Biochemistry*, 1989, **28**(1) 294
140. Y T van den Hoogen, A A van Beuzekom, H van den Elst, et al. *Nucleic Acids Res.*, 1988, **16**(7) 2971
141. Y T van den Hoogen, A A van Beuzekom, E de Vroom, et al. *Nucleic Acids Res.*, 1988, **16**(11) 5013
142. D H Evans, A R Morgan *J. Mol. Biol.*, 1982, **160**(1) 117
143. D H Evans, A R Morgan *Nucleic Acids Res.*, 1986, **14**(14) 4267
144. S A Woodson, D M Crothers *Biochemistry*, 1987, **26**(3) 904
145. S A Woodson, D M Crothers *Biochemistry*, 1988, **27**(1) 436
146. T E England, T Neilson *Can. J. Biochem.*, 1975, **55** 365
147. D Alkema, R A Bell, P A Hader, T Neilson *J. Am. Chem. Soc.*, 1981, **103**(10) 2866
148. P L D'Andrea, D Alkema, R A Bell, et al. *J. Am. Chem. Soc.*, 1983, **105**(3) 636
149. P J Romaniuk, D W Hughes, R J Gregoire, et al. *J. Am. Chem. Soc.*, 1978, **100**(12)
150. D Alkema, R A Bell, P A Hader, T Neilson *FEBS Lett.*, 1981, **136**(1) 70
151. T Neilson, P J Romaniuk, D Alkema, et al. *Nucleic Acids. Res., Symp. Ser.*, 1980(7) 293
152. M Petersheim, D H Turner *Biochemistry*, 1983, **22**(2) 256
153. M Petersheim, D H Turner *Biochemistry*, 1983, **22**(2) 269
154. S M Freier, B J Burger, D Alkema, et al. *Biochemistry*, 1983, **22**(26) 6198
155. D J Patel, S A Kozlowski, L A Marky, et al. *Biochemistry*, 1982, **21**(3) 451
156. J W Nelson, F H Martin, L Tinoco *Biopolymers*, 1981, **20**(12) 2509
157. S M Freier, N Sugimoto, A Sinclair, et al. *Biochemistry*, 1986, **25**(11)
158. S M Freier, D Alkema, A Sinclair, et al. *Biochemistry*, 1985, **24**(17) 4533
159. M Petersheim, D H Turner *Biochemistry*, 1983, **22**(2) 264
160. J M Benevides, A H-J Wang, G A van der Marel, et al. *Biochemistry*, 1989, **28**(1)
161. D Rabinovich, T Haran, M Eisenstein, Z Shakked *J. Mol. Biol.*, 1988, **200**
162. M Kouchakdjian, B F L Li, P F Swann, D J Patel *J. Mol. Biol.*, 1988, **202** 139
163. E L Edwards, R L Ratcliff, D M Gray *Biochemistry*, 1988, **27**(14) 5166
164. J Petruska, M F Goodman, M S Boosalis, et al. *Proc. Nat. Acad. Sci. USA*, 1988, **85** 6252
165. M-D Lai, K L Beattie *Biochemistry*, 1988, **27**(5) 1722
166. S V Shteinberg, V I Poltev *Biofizika* 1988, **33**(6) 922
167. D R Hickey, D H Turner *Biochemistry*, 1985, **24**(15) 3987
168. J M Benevides, G J Thomas *Biochemistry*, 1988, **27**(10) 3868
169. R T Walker *Nucleic Acids Res.*, 1988, **16**(7) 3091
170. M Senior, R A Jones, K J Breslauer *Biochemistry*, 1988, **27**(10) 3879
171. D R Groebe, O C Uhlenbeck *Biochemistry*, 1989, **28**(2) 742

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Photoionisation detection in gas chromatography

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ABSTRACT. Problems of the design and application in gas chromatography or photoionisation detectors with separated and non-separated ionisation and detection compartments are examined. The characteristics of the detectors of both types are described and specific problems of their construction are discussed. The mechanism of the signal generation and the factors determining the magnitude of the response are examined.

Extensive experimental data concerning the use of photoionisation detectors with separated detection and ionisation compartments in gas-chromatographic analysis are presented. The application of such detectors in multi-detector schemes in combination with flame-ionisation, electron-capture, and other detectors is discussed. The employment of such combinations of detectors for the purposes of identification is analysed.

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I. Introduction

Among the numerous detection methods used in gas chromatography, ionisation methods based on the use of a non-independent discharge have come to be widely used. Depending on the type of the external source of ionisation in the measuring compartment, it is possible to distinguish radioionisation and photoionisation detection. Both methods have been used successfully for the solution of various analytical problems. They possess advantages such as high sensitivity and a virtually non-disruptive character of their effect on the compounds analysed.

Photoionisation detection is technically more complex than radioionisation detection because it requires the use of a stable source of emission of vacuum UV radiation. The development of the technique of photoionisation detection is determined to a large extent by the improvement of the emission sources. Therefore, despite the fact that the first photoionisation detector (PID) was described as early as 1960,[1] the industrial production of chromatographs with PID did not begin until the end of the 1970s when it became possible to incorporate adequate sources of UV radiation.

The use as ionisation sources of resonance UV lamps working stably over long periods of time made it possible to simplify significantly the design of the apparatus. In particular, there is no need for an auxiliary gas, the open flame is eliminated, and there is no need for the use of radioisotopes. It becomes possible to employ air as the carrier gas. These properties combined with high sensitivity, selectivity, and the large linear range promoted the use of PID in laboratory and portable chromatographs.[2–5]

The use of PID in the gas-chromatographic analysis has led to the appearance of a whole series of studies devoted to the design, operating conditions, and practical use of this detector (see, for example, Refs. 6–8). The available literature data (for the last 15 years) concerning the design, characteristics, and analytical applications of the photoionisation detector are analysed in the present review.

II. Signal generation in the photoionisation detector

The essential feature of the operation of the PID is that a flux of photons emitted by the source in the far ultraviolet ionises the substance to be analysed. The motion of the charges produced in the ionisation chamber generates a current signal characterising the concentration of the substance analysed.

The ionisation of the molecules AB can occur as a result of direct ionisation with formation of an ion and an electron:

$$AB + h\nu \rightarrow AB^+ + e + \text{energy},$$

direct ionisation with formation of an ion pair:

$$AB + h\nu \rightarrow A^+ + B^- ,$$

or with preionisation:

$$AB + h\nu \rightarrow AB^* \rightarrow AB^+ + e .$$

The contribution of each of these processes to the formation of charged species is determined both by the characteristics of the radiation (its spectrum and its monochromatic nature) and by the characteristics of the substance irradiated (the distribution of molecules with respect to energies in the ground state, the distribution of the energy level density in the excited state, and the distribution of the probability of ionisation transitions).

In the range of energies close to the ionisation threshold, the direct ionisation processes predominate. With increase in the energy of photons, the contribution of the preionisation processes rises. Preionisation can occur with appearance of fragment ions, formed

from excited molecular ions. The fraction of fragment ions increases for energies exceeding the second ionisation potentials of the molecules.[9]

Apart from the processes mentioned, molecular excitation and dissociation processes are also important when molecular gases are acted upon by UV light.[10]

The overall cross-section of the processes enumerated determines the overall absorption cross-section. The photoionisation cross-section is only a fraction of the absorption cross-section, which depends on the radiation energy.

The absorption of photons in the ionisation chamber of the detector obeys the Beer–Lambert–Bouguer law:

$$I = I_0 \exp\left(-\sigma N_A c l \frac{P}{760}\frac{273}{T}\right), \quad (1)$$

where I_0 and I are the intensities of the entering and emerging light fluxes respectively, σ is the overall absorption cross-section, N_A the Loschmidt number, c the concentration of the test substance, l the length of the absorption path, and P and T are respectively the pressure and temperature in the ionisation chamber.

The absolute photoionisation quantum yield is

$$\eta = i/(I_0 - I), \quad (2)$$

where i is the ion current.

The dependence of the current on the concentration of the ionised component is determined from Eqns. (1) and (2). If the exponent in Eqn. (1) is less than unity, then we have, for P = 760 mmHg and T = 273 °C,

$$\eta = i/(I_0 \sigma N_A c l). \quad (3)$$

Multiplication of the right- and left-hand sides of Eqn. (3) by σ yields the expression

$$i = I_0 N_A c l \sigma_i, \quad (4)$$

where $\sigma_i = \eta\sigma$ is the effective photoionisation cross-section. It has been noted[11] that equations of type (4) are valid for low pressures of the test substance and for a short length of the ionisation chamber. When applied to the PID under gas-chromatographic conditions, this expression holds at normal pressure P owing to the low value of c.

For a cross-sectional area of the ionisation chamber S and a light flux density $j_0 = I_0/S$, the current is given by

$$i = j_0 N_A c V \sigma_i, \quad (5)$$

where V is the volume of the chamber.

Thus the current in the ionisation chamber is proportional to the concentration of the substance analysed and the sensitivity of the PID is proportional to the volume of the ionisation chamber.†

The ion current is also linearly related to σ_i but the latter quantity itself depends as a rule on the wavelength of the radiation in a complex manner. Since mainly non-monochromatic sources are used currently for photoionisation detection several emitted lines of different intensity are involved in signal generation. In many cases fragment ions with different masses are produced in the ionisation chamber together with molecular ions under these conditions. The fraction of particular ions in the overall ion current depends on the characteristics of the source of the UV radiation.

† The mechanisms of the current limitation, inducing deviations from linearity, are not discussed here.

Fig. 1 presents curves for the efficiency of the photoionisation (the ratio of the current of ions with the selected mass to the photon flux) of a methanethiol with formation of the molecular ions CH_3SH^+ and the fragment ions CH_3S^+.[12] The most intense lines in the argon, krypton, and xenon line spectra are also indicated. Fig. 1 shows that, when the argon emission is used for ionisation, the photoionisation efficiency can increase as a result of the appearance of fragments ions, while part of the xenon line spectrum makes no contribution at all to the current flowing in the ionisation chamber.

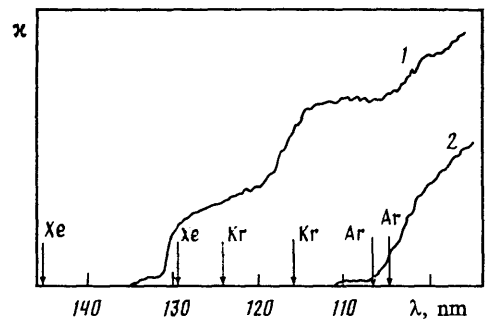


Figure 1. Photoionisation efficiency curves for methanethiol: *1*, the CH_3SH^+ molecules ion; *2*, the CH_3S^+ fragment ion.

III. Detectors with non-separated emission and detection compartments

Vigorous investigations of detectors with non-separated emission and detection compartments began in the middle 1960s. In these detectors, the radiation emitted by the electric discharge in an inert gas or hydrogen is introduced via a light conducting channel into the ionisation chamber. The chamber is not then separated from the emitter by any partition preventing the movement of the gas from one compartment to the other. The gas pressures in the source of radiation and in the ionisation chamber are the same. Eqn. (4) quoted above is not suitable for this detector, because some of the charged and metastable species from the radiation source also enter the ionisation chamber.

Such detectors make it possible to detect both organic and inorganic substances depending on the working medium in the radiation sources—the gas involved in the discharge. The use of helium, for example, makes the detector universal because of the presence in the spectrum of this gas of an intense continuum up to 50 nm (photon energy 24.3 eV). A d.c. discharge[1,13–20] and HF and UHF discharges[21–24] are used to excite the emission. There is a possibility of devices of two types: detectors in which the gas is present at low[1,15–17,21] and high (not more than atmospheric) pressures.[13,14,18–20] Table 1 shows that the characteristics of the different detectors in general agree with one another.

Despite the high sensitivity and universality of detectors of this type, they have not found applications in commercial instruments, since, firstly, detectors operating at reduced pressures require a vacuum system and, secondly, the spectroscopic characteristics of the radiation, influencing the sensitivity, vary as a function of the

Table 1. The working characteristics of PID with non-separated emission and detection compartments.

Carrier gas	Discharge gas	Type of discharge	Pressure, mmHg	Ionisation efficiency	Background current, nA	Detection limit and substance determined	Linear dynamic range	Refs.
Ar	Ar	Glow	<760	10^{-4}	0.1		10^4	[1]
He	He	»	760	—	0.1—1	2.8×10^{-11} g ml^{-1} (O_2)	10^3	[14]
						6.8×10^{-11} g ml^{-1} (C_3H_8)	10^3	[14]
Ar, He, N_2	Ar, He, N_2	»	<120	$6\cdot10^{-5}$	0.5	2×10^{-10} g (C_3H_8)	10^5	[16]
H_2, N_2, Ar	H_2, N_2, Ar	»	<100	10^{-3}	0.2	5×10^{-13} g s^{-1} (C_3H_8)	10^5	[17]
He	He	UHF	<25	$3\cdot10^{-3}$	6	1.3×10^{-11} g ml^{-1} (Ar)		
						4×10^{-10} g ml^{-1} (O_2)	10^4	[21]
He	He	Glow	760	$0.14\cdot10^{-3}$ (O_2)	0.5	4.9×10^{-11} g ml^{-1} (O_2)	10^4	[19]
				$1.1\cdot10^{-3}$ (Ar)		9×10^{-13} g ml^{-1} (Ar)		
Ar	Ar	UHF	760	—	—	7.7×10^{-11} g s^{-1} (C_6H_6)	10^5	[23]

pressure in the detector. Although the detectors operating at atmospheric pressure are in fact incorporated at the outlet from the chromatographic column without auxiliary devices, nevertheless they too suffer currently from a series of disadvantages retarding their application. In the first place one must include among such disadvantages the increased noise level caused by the instability of the discharge and the transfer of charged species from the emitting to the detecting compartment.

In order to ensure the stability of a d.c. discharge with $i < 1$ A, it is desirable to use a gas with a high thermal conductivity—hydrogen or helium.[25] In practice, helium is used, since the short-wavelength part of its spectrum makes it possible to determine inorganic gases. Since the presence of impurities in helium affects the emission spectrum, it is essential to use pure gas and to take special precautions to reduce the erosion of the electrodes and to prevent the diffusion of the substances analysed into the emitting compartment.

In order to increase the stability of the discharge in detectors with a d.c. discharge, measures are taken to optimise the electrode system. As a result, it has been possible to reduce the noise from 10^{-12} A [26] to 10^{-13} A and below.[15] It has been noted [15] that an increase in the discharge current increases the noise and does not always reduce the detection threshold. The detector described by Roesler[15] has been used[27] to analyse organic and inorganic compounds.

The employment of an electrodeless discharge makes it possible to solve the problem of erosion and to increase the power injected and the sensitivity of the detector. Thus the sensitivity of a PID in a UHF discharge amounting to 1.57 K g^{-1} has been reported,[22] which is probably the maximum value at the present time (the power injected into the discharge was 20 W).

For the wide-scale practical use of the PID considered, the maximum working temperature must be increased. The question of the stability of the temperature (owing to its influence on the discharge current) is also important in this respect.[15] The maximum working temperature of PID with non-separated emission and detection compartments is at present 200 °C.[21]

IV. Detectors with separated emission and detection compartments

The difficulties in the practical use of PID with a reduced pressure in the detection compartment stimulated not only the development of sources operating stably at atmospheric pressure but also the appearance of photoionisation detectors of a new type, with separated emission and detection compartments. The first suggestion to separate these compartments was made in Ref. 28 and was then additionally justified by Locke and Meloan.[16] The first descriptions of the design of PID with an optical window between the source of vacuum UV radiation (VUV) and the ionisation chamber soon appeared.[29–31] The window is normally part of the design of the hermetically sealed UV source in which the pressure does not exceed tens of millimetres of mercury. This technical solution proved extremely promising and the manufacture of chromatographs with built in PID was initiated.[32] This was promoted by the development and manufacture of stable sources emitting vacuum UV radiation.

Metal halides and certain oxides can be used as materials for the transmission of the radiation. The dependence of the transmittances of some of these compounds on wavelength in the VUV is illustrated in Fig. 2.[33] Thin SiO films fixed on a metallic grid also have a satisfactory transmittance in the range 60–90 nm (20–70%). However, their mechanical strength is inadequate. A SiO window 100 nm thick and 10 mm in diameter can withstand a pressure difference not greater than 1000 N m^{-2}.[33]

In terms of the combination of optical and mechanical properties, lithium and magnesium fluorides are the most acceptable materials. However, lithium fluoride, which has the lowest transmittance limit (106 nm) among all the halides, has not come to be used as widely as magnesium fluoride because of its high hygroscopicity which alters the emission spectrum. The transmittance of lithium fluoride is also impaired on VUV irradiation owing to the formation of colour centres.[34] Magnesium fluoride has a fairly low short-wavelength limit (113 nm), which makes it able to transmit photons with the energy required for the ionisation of the majority of organic

substances. Some decrease in the transparency of magnesium fluoride is observed when it is heated to 200–400 °C with simultaneous exposure to the VUV radiation.[35] The decrease in the transmittance of magnesium fluoride windows can be associated with the absorption by the film (including the substance to be analysed) present on the surface of the crystal.[36,37] Organic films can be removed from the surface by employing VUV radiation in the presence of oxygen.[38] In chromatographic practice, the transparency of windows is restored mechanically (by wiping).[4]

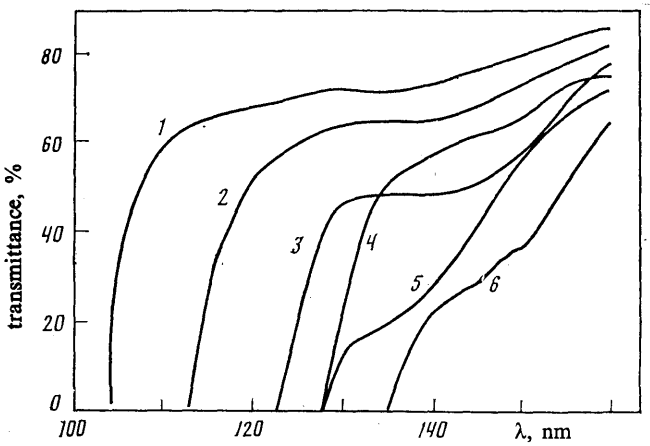


Figure 2. The transmittances of certain metal halides as a function of wavelength in the VUV region: *1*, LiF; *2*, MgF_2; *3*, CaF_2; *4*, NaF; *5*, SrF_2; *6*, BaF_2.

The characteristics of the materials which can be used to transmit VUV radiation have been specified in detail.[39]

Sources, with a line spectrum, capable of operating for a long time under continuous conditions,‡ have come to be most widely used for the generation of the VUV radiation in photoionisation detectors. For a discharge in a rarefied gas, there are lines at 104.82 (11.8 eV) and 106.67 nm (11.6 eV) in the argon spectrum, at 116.49 nm (10.64 eV) and 123.58 nm (10.03 eV) in the krypton spectrum, and at 129.55 nm (9.57 eV) and 146.96 nm (8.44 eV) in the xenon spectrum (the energy is indicated in brackets).[41]

Fairly reliable resonance lamps, filled with different substances and working in glow or arc discharge regimes, are currently widely used in PID designs. Inert gas (krypton and xenon) resonance lamps each emit virtually two resonance lines, the intensity of the long-wavelength lines being higher by 1–2 orders of magnitude than that of the short-wavelength lines.[42] The emission quantum yield for such sources is $10^{14}-10^{16}$ quanta s^{-1} behind the window of the lamp. He–Kr on He–Xe gas mixtures at a Kr or Xe pressure of 0.12–0.06 mmHg are used in such lamps, which makes it possible to obtain non-self-reversed Kr and Xe resonance lines, in the presence of which He is not excited.[43] Modern modifications of the krypton and xenon resonance lamps, developed in the USSR, have been described.[44] The power required by such lamps does not exceed 1–2 W.

Resonance lamps manufactured by the HNU Systems Company filled with krypton, xenon, and argon are used in chromatographs produced by a series of foreign manufacturers and fitted with photo-ionisation detectors. These lamps differ in the values of so called nominal energy. The nominal energies do not determine the energy of the photons emitted by the lamp but represent a conventional designation defining the type of the lamp. Lamps with nominal energies of 8.3, 9.5, 10.0, 10.2, 10.9, and 11.7 eV are known. Detectors with the corresponding lamps are designated by PID-8.3, PID-10.0, etc. The distribution of the emission energy in the line spectra of lamps with nominal energies of 8.3, 9.5, 10.2, and 11.7 eV, obtained using a vacuum UV spectrometer, has been published.[45] Only the lamp with a nominal energy of 8.3 eV produces monochromatic radiation. The remaining lamps emit not less than two lines. The intensity of the emitted lines in the range of the working currents is independent of the current in the lamp. The lamp with a nominal energy of 11.7 eV has a lithium fluoride optical window. Its operating life is several hundreds of hours.[46]

It has been suggested[47] that electrodeless UHF discharge lamps be used as radiation sources in PID. A portable chromatograph, fitted with a PID incorporating a UHF discharge lamp was later constructed.[48,49]

In the development of PID ionisation chambers, serious specific problems frequently arise. They are associated with the hermetic seal in the chamber, the reduction of the influence of the photoeffect, the elimination of the contamination of the window, etc. The question of the volume of the detector in a capillary chromatograph is of fundamental importance. The first, commercially produced PID had an ionisation chamber with a volume of 50 μl [32] (Fig. 3). The volume of the modified detector of the same series was 175 μl.[50] Such a volume is not optimal when used in conjunction with capillary columns, although it does make it possible to ensure a high sensitivity of detection.

Studies designed to reduce the detector volume are being prosecuted both to reduce the physical (total) volume and to reduce the effective volume responsible for the signal generation.

The decrease in the physical volumes of the ionisation chamber involves difficulties arising from the need to ensure a hermetic seal and a high sensitivity, but such reduction makes it possible to operate at lower potentials on the polarising electrode and with low flow rates of the make-up gas. The latter is important because the PID is a concentration detector.

A detector with a physical volume of 50 μl operating with a make-up gas flow rate of 2–3 ml min^{-1} has been reported.[51] There are data concerning the operation of PID altogether without a make-up gas flow. Thus the experimental results of a study of the influence of the volume of the photoionisation detector on the spreading of the chromatographic peaks of acetone have been published.[52] Fig. 4 reproduces these data,[52] obtained for detectors with volumes of 225, 150, and 50 μl and also for a flame-ionisation detector (FID). The figure shows that spreading could not be eliminated completely even in the detector with a volume of 50 μl.

The efficiency of the chromatographic system in which a PID with a volume§ of 50 μl and a FID were connected in series has been estimated. The loss of efficiency compared with the direct inclusion

‡ It is essential to note that the use of laser multistep ionisation, ensuring a high selectivity, is undoubtedly promising.[40]

§ The 50 μl volume was referred to as effective in the relevant study although a make-up gas was not supplied to the detector.

of the FID at the outlet from the chromatographic system after recalculation in terms of the number of theoretical plates is less than 10%.[53] A detector with a volume of 37 μl not requiring a make-up gas has also been reported.[45] In one of the variants of fluid chromatography, the designs of PID with volumes of 70 and 7 μl were investigated.[54]

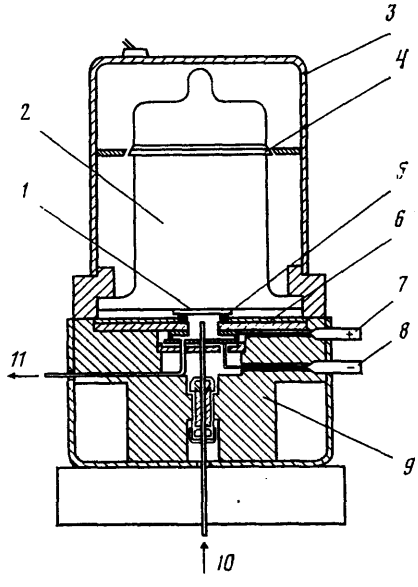


Figure 3. The design of the photoionisation detector based on the system of the HNU Systems Company: *1*, window for the transmission of radiation; *2*, vacuum UV lamp; *3*, lamp shell; *4*, electrode; *5*, Kalrez seal; *6*, graphite seal; *7*, measuring electrode; *8*, polarising electrode; *9*, heating block; *10*, gas inlet; *11*, gas outlet.

A decrease in the effective detector volume is achieved by reducing the irradiated region and by organising a "shielding" gas flow. The effective detector volumes were 1 and 10 μl respectively in the studies of Nutmagul et al.[55] and in Ref. 56. In the study of Gmür et al.,[54] the make-up gas flow rate was maintained at the level of 8–10 ml min^{-1}, which is close to the make-up flow rates of 10–15 ml min^{-1} used in a commercial detector with a volume of 150 μl.[57,58]

The shell of the ionisation chamber is made of a material with the highest possible specific resistance and the lowest porosity: PTFE,[47,59] boron nitride,[53] and a special glass.[55] In order to ensure a background current at the level of 10^{-11} A at a detector supply potential of ~100 V, the specific resistance of the insulators must be of the order of 10^{13} Ω cm. At temperatures up to 200 °C, PTFE is suitable. Ceramics are more heat resistant, but their electrical resistances fall significantly on raising the temperature to 300–400 °C, which increases the background current and the noise level and hence impairs the characteristics of the detector. The specific resistances ρ_V of several types of ceramics at 20° and 500 °C have been published in a monograph.[60] The ceramic based on Al_2O_3, which also has a low porosity, is the most suitable (Table 2).

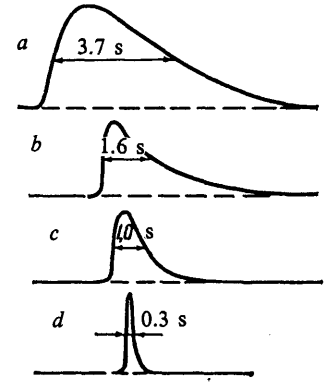


Figure 4. Chromatographic peaks of acetone obtained with PID having a chamber with different volumes (μl): *a*, 225; *b*, 150; *c*, 50; *d*, obtained with a FID.

Table 2. Specific resistances of various types of ceramics.[60]

Type of ceramic	ρ_V, Ω cm	
	20° C	500° C
Al_2O_3	10^{14}	10^{12}
$2MgO \cdot SiO_2$	10^{14}	10^{10}
$MgO \cdot Al_2O_3$	10^{14}	10^{11}
MgO	10^{14}	10^{12}
BeO	10^{14}	10^{12}

When the PID is series-connected to other detectors, the problem of its hermetic seal becomes important. It is solved mainly in the traditional manner using the seal between the ionisation chamber and the lamp. The limiting temperature for this design using perfluorinated rubber is 300 °C.[45] It has been suggested[61] that an additional window, glued to the shell of the ionisation chamber, be introduced into the PID design to ensure a hermetic seal. A disadvantage of this design is the weakening of the radiation flux in the chamber and also the impossibility of cleaning the additional window. It has likewise been suggested that the MgF_2 window be sealed to the chamber with the aid of a conical sealing arrangement.[62] A hermetically sealed junction between the shell and the window and also between the ceramic shell and the electrode can be achieved with the aid of diffusionally hardening solders.[63] In order to increase the maximum working temperature of the detector, it has been suggested[64] that the hermetic seal in the ionisation chamber be abandoned so that the release of gas through the gap between the detector shell and the optical window can be ensured.

A coaxial electrode system is most often employed in the ionisation chamber of the PID. In this system, the central electrode is generally subjected to VUV radiation, which increases the background current. The shielding of the electrode from the direct effect of the radiation made it possible to reduce the background current by three orders of magnitude.[53]

The optimum configuration of the electrodes for which the highest signal is attained has been sought.[55] The possibility of achieving such a configuration may be associated with the fact that the chamber operates under conditions far from saturation. Optimisation implies the attainment of maximum sensitivity for low detector supply potentials when the gas-induced intensification processes are absent and the leakage through the insulator is small.

It is shown below how the nature of the carrier gas affects the sensitivity of the PID with a 10.2 eV lamp in the detection of benzene:[65]

Carrier gas	Air	Ar	CO_2	N_2	CF_4	He	CO
Response, rel. units	0.542	1.401	0.285	1.00	1.01	0.987	1.07

It has been suggested that the following processes are responsible for the decrease in the response of the PID; the capture by the carrier gas of the electrons formed as a result of photoionisation; the absorption of the UV radiation by the carrier gas; the de-excitation of the components analysed on their collision with the molecules of the carrier gas having vibrational and rotational levels. The fact that the response of the PID is greatest when argon is used has been explained[65] by the high rate of drift of the electrons (v_e) in this gas, which lowers the losses in recombination compared with He or N_2. However, in argon v_e is greater than in He or N_2 only for $E/P < 10^{-2}$ V cm^{-1} (mmHg)$^{-1}$ (E is the strength of the electric field between the electrodes of the ionisation chamber).[66] Under real conditions, where $E/P > 10^{-1}$ V cm^{-1} (mmHg)$^{-1}$, the quantity v_e in argon is smaller than in He or N_2. The increased values of v_e in argon may be caused by its greater sensitivity to molecular impurities.[66] The presence of the latter (including ionisable impurities) diminishes the electron temperature and increases v_e.

Table 3. Characteristics of PID with separated emission and detection compartments.

Gas filling the lamp	Background current $10^{11}I_b$, A	Noise $10^{14}I_n$, A	Detection limit w.r.t. benzene	Maximum working temperature, °C	Detector volume, μl	Linear dynamic range	Refs.
H_2, Ar, Kr, Xe	1.4	4	2×10^{-12} g	300	175 50	10^7	[50]
H_2	2	—	0.6×10^{-12} g	200	1	—	[55]
H_2	—	2	0.5×10^{-12} g	220	10	10^5	[56]
H_2	2	5	0.67×10^{-14} g s^{-1}	300	—	10^6	[68]

The fluctuation noise in PID constitutes a serious problem. The nature of the noise is determined mainly by the variation of the photocurrent with the composition of the gas in the detector and by the contamination of the insulating elements, causing leakage.[45,67] The increased level of PID noise (compared with FID) precludes the full utilisation of its greatest advantage—its high sensitivity.[67]

Certain characteristics of PID with separated emission and detection compartments are presented in Table 3. It follows from Table 3 that, in terms of their characteristics, the detectors are similar. The PID produced by the HNU Systems Company is outstanding as regards its long linear range. The detection threshold and the linear range of the PID are illustrated in Fig. 5, which includes for comparison the analogous data for FID and the electron capture (ECD), flame-photometric (FPD), and ultraviolet (UVD) detectors.

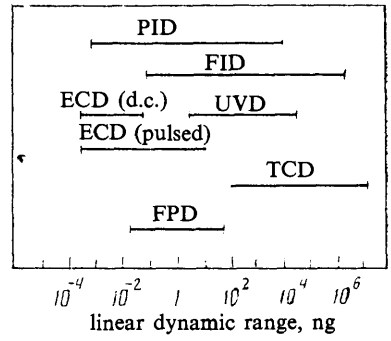


Figure 5. The linear dynamic range for certain detection methods[7] [TCD = thermal conductivity detection (Ed. of Translation)].

V. The response of the photoionisation detector

The magnitude of the response of the PID depends on the effective photoionisation cross-section σ_i, which is determined by the energy of the photoionising photons and by the characteristics of the substance analysed. The dependence of σ_i on the energy of the ionising photons E_{ph} is complex. It can be estimated using the photoionisation efficiency curves (PEC) $\eta(E_{ph})$, obtained, for example, with the aid of photoionisation mass spectrometry.[9] These relations have been resorted to in order to explain qualitatively the influence of the energy of the photons on the response.[69] However, the PID responses cannot be estimated quantitatively with the aid of the PEC because of the different intensities of the lamps and the non-monochromatic nature of the radiation.

The PID response can be estimated to a first approximation with the aid of the quantity $E_{ph} - E_i$, where E_i is the ionisation energy of the test substance. For non-monochromatic lamps, one must take into account not only the most intense line but also other lines. If the quantity $E_{ph} - E_i$ is fairly large (1–2 eV and more), ionisation occurs along the PEC section remote from the threshold value, where the $\eta(E_{ph})$ relation has a plateau for many substances. The response is then independent of E_i.[69] On the other hand, if the difference $E_{ph} - E_i$ is small (a fraction of an electron-volt), then ionisation occurs in the pre-threshold region on the PEC, and the response therefore also depends on the closeness of the E_i to the photoionisation threshold or, for a given E_{ph}, on E_i. A greater difference $E_{ph} - E_i$ obtains when a lamp with a nominal energy of 11.7 eV is used, 71.1% of its radiation corresponding to photons

with an energy of 11.62 eV. The PID responses to alkanes, alkenes, and aromatic hydrocarbons are in this case approximately the same. A small difference $E_{ph} - E_i$ is characteristic of a large number of compounds of different classes when a lamp with a nominal energy of 10.2 eV is used (the spectrum contains photons with energies of 10.03 and 10.64 eV). It is essential to note that, when $(E_{ph} - E_i) < 0$, a signal due to the removal of electrons from vibrationally excited molecules may be observed and may increase with increasing temperature in proportion to $\exp[-(E_{ph} - E_i)/kT]$, where k is the Boltzmann constant. An attempt has been made[70] to relate the PID response to the number of electrons participating in the formation of multiple carbon–carbon bonds, but the conclusions reached[70] were subjected to serious criticism.[37]

Table 4. The relative sensitivities of the PID-10.2 to organic compounds.[71]

Substance	$K_{i,M}$
n-Alkanes	
Heptane	0.032
Octane	0.080
Nonane	0.14
Decane	0.23
Undecane	0.30
Dodecane	0.37
Tridecane	0.46
Tetradecane	0.53
Pentadecane	0.59
Hexadecane	0.71
Heptadecane	0.72
Octadecane	0.79
Nonadecane	0.86
Eicosane	0.93
Heneicosane	1.03
Docosane	1.13
Isoalkanes and Cycloalkanes	
2,2-Dimethylbutane	0.037
2,3-Dimethylbutane	0.032
2-Methylpentane	0.011
3-Methylpentane	0.027
2,4-Dimethylpentane	0.080
2,3-Dimethylpentane	0.10
3-Methylhexane	0.075
2,4- and 2,5-Dimethylhexane	0.15
2,2,4-Trimethylpentane	0.21
2,3,4-Trimethylpentane	0.22
3-Methylheptane	0.13
2,2,5-Trimethylhexane	0.26
Cyclohexane	0.18
Methylcyclohexane	0.28
Decahydronaphthalene	1.04
Alkenes, Dienes, and Alkynes	
3-Methylbut-1-ene	0.52
n-Hept-1-ene	0.54
n-Hept-2-ene	0.51
n-Hept-3-ene	0.58
n-Oct-1-ene	0.55
n-Non-1-ene	0.58
n-Dec-1-ene	0.67
n-Undec-1-ene	0.70
n-Dodec-1-ene	0.73
n-Tridec-1-ene	0.81
n-Tetradec-1-ene	0.87
n-Pentadec-1-ene	0.92
n-Hexadec-1-ene	0.99
n-Heptadec-1-ene	1.06
n-Octadec-1-ene	1.10
n-Nonadec-1-ene	1.17
Deca-1,9-diene	1.07
n-Oct-2-yne	2.75
Halogeno-derivatives of aliphatic hydrocarbons	
1-Bromobutane	0.066
1-Iodobutane	1.93
1,2-Dibromobutane	0.081
Hexachlorocycloyhexane	0.027
Hexachlorocyclopentadiene	0.88
Hexachlorobuta-1,3-diene	1.34
Ketones	
Acetone	0.35
2-Butanone	0.40
2-Pentanone	0.45
3-Pentanone	0.54
2-Hexanone	0.52
2-Heptanone	0.59
3-Heptanone	0.68
4-Heptanone	0.70
2-Octanone	0.71
3-Octanone	0.73
2-Nonanone	0.78
5-Nonanone	0.82
3-Methyl-2-butanone	0.58
3-Methyl-2-pentanone	0.60
2-Methyl-3-pentanone	0.62
4-Methyl-2-hexanone	0.62
5-Methyl-2-hexanone	0.65
3-Methyl-2-heptanone	0.72
5-Methyl-3-heptanone	0.75
3,3-Dimethyl-2-butanone	0.65
2,4-Dimethyl-3-pentanone	0.70
2,6-Dimethyl-4-heptanone	0.81
Cyclopentanone	0.57
Cyclohexanone	0.62
2-Methylcyclohexanone	0.66
3-Methylcyclohexanone	0.66
4-Methylcyclohexanone	0.63
Butane-2,3-dione	0.45
Aldehydes	
Butanal	0.30
Pentanal	0.36
Hexanal	0.41
Heptanal	0.45
Octanal	0.49
Nonanal	0.53
Alcohols	
1-Butanol	0.023
1-Pentanol	0.053
1-Hexanol	0.086
1-Heptanol	0.12
1-Octanol	0.16
1-Nonanol	0.20
1-Decanol	0.25
1-Undecanol	0.29
1-Dodecanol	0.36
Isobutyl alcohol	0.029
Isopentyl alcohol	0.057
t-Pentyl alcohol	0.054
Hex-3-en-1-ol	0.46
Butane-1,4-diol	0.10
Esters	
Methyl propionate	0.010
Methyl butanoate	0.039
Methyl pentanoate	0.082
Methyl hexanoate	0.096
Methyl heptanoate	0.14
Methyl octanoate	0.15
Methyl nonanoate	0.26
Methyl decanoate	0.33
Methyl dodecanoate	0.48
Methyl tetradecanoate	0.66
Methyl hexadecanoate	0.82

Table 4 cont'd.

Substance	$K_{i,M}$
Esters	
Ethyl acetate	0.020
Ethyl butanoate	0.15
Ethyl hexanoate	0.24
Ethyl octanoate	0.32
Ethyl decanoate	0.51
Ethyl dodecanoate	0.70
Propyl acetate	0.025
Propyl butanoate	0.21
Butyl acetate	0.044
Aromatic hydrocarbons	
Benzene	1.00
Toluene	1.09
o-Xylene	1.14
m-Xylene	1.15
p-Xylene	1.20
Cumene	1.22
p-Cymene	1.27
Mesitylene	1.27
Ethylbenzene	1.16
n-Propylbenzene	1.21
n-Butylbenzene	1.27
n-Hexylbenzene	1.29
n-Octylbenzene	1.52
n-Decylbenzene	1.69
Naphthalene	1.97
Biphenyl	1.88
Anthracene	2.44
Phenanthrene	2.50
1,2-Benzoanthracene	2.46
p-Terphenyl	2.20
Pyrene	3.02
Chrysene	2.96
Triphenylene	3.08
Fluorene	2.08
Fluoranthene	2.85
Acenaphthene	3.06
Halogenobenzenes	
Chlorobenzene	1.30
1,3-Dichlorobenzene	1.42
1,4-Dichlorobenzene	1.39
1,2-Dichlorobenzene	1.30
1,3,5-Trichlorobenzene	1.26
1,2,4-Trichorobenzene	1.20
1,2,3-Trichlorobenzene	1.44
1,2,4,5-Tetrachlorobenzene	1.28
1,2,3,4-Tetrachlorobenzene	1.40
Pentachlorobenzene	1.32
Hexachlorobenzene	1.25
Bromobenzene	1.82
Iodobenzene	2.50
1-Chloro-2-fluorobenzene	0.98
Polychlorobiphenyls	
2,3-Dichlorobiphenyl	2.18
4,4'-Dichlorobiphenyl	2.47
2',3,4-Trichlorobiphenyl	2.40
2,2',5,5'-Tetrachlorobiphenyl	2.43
2,3',4',5-Tetrachlorobiphenyl	2.39
Polychlorobiphenyls	
3,3',4,4'-Tetrachlorobiphenyl	2.96
2,2',4,5,5'-Pentachlorobiphenyl	2.45
2,2',3,4,5'-Pentavchlorobiphenyl	2.80
2,2',3,4,5,6'-Hexachlorob iphenyl	2.55
2,2',4,4',5,5'-Hexachlorobiphenyl	2.60
Phthalates	
Dimethyl phthalate	0.56
Diethyl phthalate	0.87
Di-n-butyl phthalate	1.06
Di-(2-ethylhexyl) phthalate	1.78
Benzyl butyl phthalate	1.78
Phenols	
Phenol	1.05
p-Cresol	1.07
2,4-Dimethylphenol	1.10
2-Chlorophenol	1.19
3-Chlorophenol	1.32
4-Chlorophenol	1.30
2,3-Dichlorophenol	1.34
2,4-Dichlorophenol	1.34
2,5-Dichlorophenol	1.34
2,6-Dichlorophenol	1.33
3,4-Dichlorophenol	1.37
3,5-Dichlorophenol	1.35
2,3,4-Trichlorophenol	1.28
2,3,5-Trichlorophenol	1.28
2,3,6-Trichlorophenol	1.47
2,4,5-Trichlorophenol	1.32
2,4,6-Trichlorophenol	1.30
3,4,5-Trichlorophenol	1.20
2,3,4,5-Tetrachlorophenol	1.14
2,3,4,6-Tetrachlorophenol	1.43
2,3,5,6-Tetrachlorophenol	1.38
Pentachlorophenol	1.18
2-Chloro-5-hydroxytoluene	1.20
Organic compounds with different functional groups	
Nitrobenzene	0.29
4-Nitrophenol	0.29
1-Fluoro-4-nitrobenzene	0.15
2,4-Dinitrophenol	0.094
2,4-Dinitrotoluene	0.062
Aniline	1.13
Pyridine	0.50
Benzoic acid	0.50
Benzaldehyde	0.96
Mesityl oxide	0.61
Acetophenone	0.94
1,2-Dimethoxybenzene	1.19
Diphenyl ether	2.10
Dibenzofuran	0.86
Dibenzo-*p*-dioxin	0.93
Dibenzothiophen	1.31
2-Bromophenyl phenyl ether	3.30
2-Chloronaphthalene	2.04
Tetrahydrofuran	0.39
Diethyl ether	0.36

It has been established experimentally that PID is highly sensitive to aromatic hydrocarbons with low ionisation potentials. In practice, it is convenient to determine the absolute sensitivity and the PID detection limit with respect to benzene (Tables 4 and 5). The molecular sensitivity coefficients $K_{i,M}$ have been measured[71] for a large number of organic compounds relative to benzene (Table 4):

$$K_{i,M} = (S_i/S_{st})(c_{st}/c_i),$$

where S_i and S_{st} are the peak area of the ith substance and benzene and c_i and c_{st} are the concentrations (in nmol ml^{-1}) of the ith substance and benzene in the model mixture respectively. A model P1-51-02 PID from the HNU Systems Company, fitted with a UV lamp having a nominal energy of 10.2 eV, was used for the measurements.

Table 4 shows that the molar sensitivity of the PID increases with increasing number of carbon atoms in the molecule within the limits of the homologous series. The linear equation

$$K_{i,M}=0.715n-0.475.$$

is valid for n-alkanes. The following sequence in the variation of the $K_{i,M}$ is characteristic of normal aliphatic compounds with different functional groups and having the same numbers of carbon atoms: alkanes < alcohols < methyl ethers < ethyl ethers < aldehydes < 2-ketones < 3-ketones. Branches in the carbon chain of the molecule and the presence in the latter of saturated rings or double bonds tend to increase the PID response, whilst the presence of nitro-groups tends to decrease it.

Table 5. Detection limits of the PID.

Compound	Detection limit		Lamp energy, eV	Type of column*	Company manufacturing the PID**	Refs.
	pg	fmol				
1	2	3	4	5	6	7
Propane	200	$4.5\cdot10^3$	11.7	P	«HNU Systems»	[46]
n-Butane	260	$4.5\cdot10^3$	10.2	C	»	[76]
	181	$3.1\cdot10^3$	10.2	MP	»	[74]
	26	446	11.7	MP	»	[74]
n-Pentane	161	$2.2\cdot10^3$	10.2	C	»	[76]
n-Hexane	15	171	10.2	C	—	[55]
n-Heptane	9.0	90	10.2	C	—	[55]
n-Octane	7.5	66	10.2	C	—	[55]
	458	$4.0\cdot10^3$	10.2	C	«HNU Systems»	[76]
n-Nonane	6.7	52	10.2	C	—	[55]
n-Decane	5.1	36	10.2	C	—	[55]
Propene	5.6	134	10.2	MP	«HNU Systems»	[74]
	37	839	11.7	MP	»	[74]
	22	536	10.2	C	»	[76]
Butene	30	536	10.2	C	»	[76]
Hex-1-ene	1.6	19	10.2	C	—	[55]
Hept-2-ene	1.3	13	10.2	C	—	[55]
Oct-1-ene	2.1	19	10.2	C	—	[55]
Non-1-ene	2.7	21	10.2	C	—	[55]
Dec-1-ene	2.1	15	10.2	C	—	[55]
Butadiene	1.7	31	10.2	MP	«HNU Systems»	[74]
	12	224	11.7	MP	»	[74]
Methyl bromide	10	105	10.9	P	«Photovac Jnc.»	[77]
Methyl chloride	11	224	11.7	MP	«HNU Systems»	[74]
Methylene chloride	190	$2.2\cdot10^3$	10.2	C	»	[76]
1,1,1-Trichloroethane	60	446	11.7	MP	»	[74]
Trichloroethylene	18	137	10.2	MP	»	[74]
	90	685	11.7	MP	»	[74]
	30	228	10.2	C	»	[76]
Vinyl chloride	4	64	10.2	P	»	[31]
	50	800	10.2	P	»	[77]
Tetrachloroethylene	37	223	10.2	C	»	[76]
Formaldehyde	300	$1\cdot10^3$	11.7	P	»	[46]
Methanethiol	20	417	10.2	P	»	[7]
Ethanethiol	20	323	10.2	P	»	[78]
Propanethiol	20	263	10.2	P	»	[78]
t-Butanethiol	20	222	10.2	P	»	[78]
s-Butanethiol	20	222	10.2	P	»	[78]
n-Butanethiol	60	667	10.2	P	»	[78]
Dimethyl sulphide	20	323	10.2	P	»	[7]
Dimethyl sulphide	22	234	10.2	P	»	[7]
Methylamine	5	161	10.2	P	»	[31]
Dimethylnitrosoamine	100	$1.3\cdot10^3$	10.2	C	»	[79]
Ethylbutynylnitrosoamine	100	769	10.2	C	»	[79]
Nitrosopyrrolidinone	50	500	10.2	C	»	[79]
Nitropentane	$>10^6$	$>8.5\cdot10^6$	10.2	P	»	[80]
Nitrocyclohexane	$>10^6$	$>7.8\cdot10^6$	10.2	P	»	[80]
Benzene	5	64	10.2	P	—	[81—82]
	0.6	7.7	10.2	C	—	[55]
	0.8	10	10.9	P	«Photovac Jnc»	[83]
	20	256	10.9	C	»	[84]
	0.7	9.0	10.2	MP	«HNU Systems»	[74]
	1.1	14	10.2	P	»	[85]
	2.0	26	10.2	P	»	[31]
	2.0	26	10.2	P	»	[73]
	7.0	90	11.7	MP	»	[74]
	18	225	10.2	C	»	[76]
Toluene	1.2	13	10.2	P	»	[85]
	1.2	13	10.9	P	«Photovac Jnc.»	[83]
	0.8	8.7	10.2	C	—	[55]
Ethylbenzene	1.3	12	10.2	C	—	[55]
	4.2	40	10.9	P	«Photovac Jnc.»	[83]
o-Xylene	4.2	40	10.9	P	»	[83]

Table 5 cont'd.

Compound	Detection limit		Lamp energy, eV	Type of column*	Company manufacturing the PID**	Refs.
	pg	fmol				
1	2	3	4	5	6	7
o-Xylene	1.3	12	10.2	C	—	[55]
m-Xylene	4.3	41	10.9	P	«Photovac Jnc.»	[83]
p-Xylene	4.3	41	10.9	P	»	[83]
	2.8	26	10.2	P	«HNU Systems»	[85]
Isopropylbenzene	1.8	15	10.2	C	—	[55]
Anthracene	25	140	10.2	C	—	[53]
Naphthalene	10	78	10.2	P	«HNU Systems»	[86]
C_{10}–C_{15} poloyarenes and their monochloro-derivatives	50—100		10.2	P	»	[36]
C_{10}–C_{18} polyarenes	$(0.2—1)\cdot10^3$		10.2	MP	»	[87]
Phenol	80	851	10.2	P	»	[88]
Aniline	900	$9.7\cdot10^3$	10.2	C	»	[89]
	700	$7.5\cdot10^3$	9.5	C	»	[89]
2-Chloroaniline	100	787	10.2	C	»	[89]
	600	$4.7\cdot10^3$	9.5	C	»	[89]
4-Bromoaniline	600	$3.5\cdot10^3$	10.2	C	»	[89]
	$1.4\cdot10^3$	$8.1\cdot10^3$	9.5	C	»	[89]
2,4,5-Trichloroaniline	200	$1\cdot10^3$	10.2	C	»	[89]
	800	$4.1\cdot10^3$	9.5	C	»	[89]
2-Nitroaniline	900	$6.5\cdot10^3$	10.2	C	»	[89]
	$1.3\cdot10^3$	$9.4\cdot10^3$	9.5	C	»	[89]
3-Nitroaniline	$2\cdot10^3$	$1.4\cdot10^4$	10.2	C	»	[89]
	$1\cdot10^4$	$7.2\cdot10^4$	9.5	P	»	[89]
o-Nitrotoluene	400	$2.9\cdot10^3$	10.2	P	»	[80]
2,6-Dinitrotoluene	$2.8\cdot10^3$	$1.5\cdot10^4$	10.2	C	»	[80]
2,4-Dinitroaniline	$2.1\cdot10^4$	$1.1\cdot10^5$	10.2	C	»	[89]
	$1\cdot10^5$	$5.5\cdot10^5$	9.5	C	»	[89]
Androsterone	33	114	10.2	C	»	[90]
Testosterone	55	191	10.2	C	»	[90]
Oestrone	62	228	10.2	C	»	[90]
Oestradiol	69	253	10.2	P	»	[90]
Barbital	150	815	10.2	P	»	[91]
Secobarbital	400	$1.7\cdot10^3$	10.2	P	»	[91]
Hexobarbital	200	847	10.2	P	»	[91]
Phenobarbital	950	$4.1\cdot10^3$	10.2	P	»	[91]
Butethal	500	$2.4\cdot10^3$	10.2	P	»	[91]
Pentobarbital	450	$2\cdot10^3$	10.2	P	»	[91]
Tetraethyllead	150	464	10.2	P	»	[32]
Hydrogen sulphide	15	442	10.2	P	»	[31]
	15	442	10.2	P	»	[7]
Phosphine	25	735	10.2	P	»	[31]
	20	588	10.2	P	»	[91]
Ammonia	200	$1.2\cdot10^4$	10.2	P	»	[31]
	200	$1.2\cdot10^4$	10.2	P	»	[91]
Arsine	25	321	10.2	P	»	[91]
Nitrogen oxide	52	$1.7\cdot10^3$	10.2	P	»	[91]
Iodine	25	98	10.2	P	«HNU Systems»	[91]
Chlorine	$1\cdot10^4$	$1.4\cdot10^5$	11.7	P	»	[46]
Carbon disulphide	3.4	45	10.2	MP	»	[74]
	6.8	89	11.7	MP	»	[74]
	30	395	10.2	P	»	[7]

* The following abbreviations have been adopted: P = packed column; C = capillary column; MP = micropacked column.
** The dash denotes the author's own design.

The high sensitivity of the PID with respect to the characteristic features of the carbon skeleton of organic compounds is very important for the practical purposes of group identification. It is noteworthy that, since the PID selectivity varies with the quantity $E_{ph} - E_i$, it can be regulated by using UV lamps with different nominal energies.

For example, when a lamp with a nominal energy of the 11.7 eV was used, the molar sensitivity coefficients for benzene, cyclohexane, and cyclohexene were approximately the same[72] and, when a 10.2 eV lamp was employed, the PID responses to cyclohexane and cyclohexene were respectively 15 and 30% of the response to benzene.[57] According to the results of Locke and Meloan,[16] the signal of the PID with an 11.7 eV lamp in response to arenes exceeded on average by 30% the signal in response to alkanes. When a 10.2 eV lamp was used, the sensitivity of the PID to arenes was found to be higher by a factor of 5.[73]

The non-monochromatic radiation from certain lamps, the probable change in the distribution of the emission energy as the temperature of the PID is varied, and the marked difference between the emission intensities of lamps having different nominal energies have an interfering effect on detailed studied of the relation between $E_{ph} - E_i$ and the relative sensitivity coefficients and on the development of methods for the determination of the required compound against the background of large amounts of other substances. An idea may be obtained about the last interfering factor by comparing the sensitivities of PID with 8.3, 9.5, 10.2, and 11.7 eV lamps of polyalkylated arenes and benzenes, which are in the proportions 1 : (10–20) : (100–400) : 20 respectively.[51,57] The high intensity of the emission proved to be decisive in reducing the benzene, butadiene, carbon disulphide, and trichloroethylene detection limits in a PID with a 10.2 eV lamp compared with one fitted with an 11.7 eV lamp. The sensitivity of the PID to n-butane depends mainly on the quantity $E_{ph} - E_i$ and it is therefore seven times greater for the PID with an 11.7 eV lamp.[74] One should also bear in mind the influence of the change in the emission intensity of the same lamp on the relative sensitivity coefficients of the PID. It has been found[75] that an increase in the emission intensity of 10.2 eV lamp by a factor of 1.6 led to an increase in the ratios of the responses to C_4-C_5 alkenes to the response to toluene by 30–40%. For alkanes and alkylbenzenes, these changes are significantly smaller.

The threshold sensitivity of the detector or the detection limit (DL) is important for the determination of microimpurities. In practice, the threshold sensitivity of the detector is usually expressed in terms of the amount of the substance (in grams or moles) generating a detector signal (the height of the chromatographic peak) greater by a factor of 2–5 than the noise of the zero line. Although this quantity is determined by the characteristics of the entire chromatographic system and the analytical conditions (namely the volume of the chromatographic peak at the outlet from the column, the rate of its passage through the detector, the make-up gas flow rate, etc.), nevertheless the data in Table 5 contain useful information about the real results obtained with PID in the analysis of trace amounts of substances. To facilitate the comparison of the data in Tables 5 and 4, the detection limits in Table 5 are expressed in grams and moles. Table 5 shows that the DL has been reached at the level of picograms for light aromatic hydrocarbons, alkenes, and amines and at the level of tens of picograms for mercaptans, sulphides, chloroalkanes and chloroalkenes, nitrosoamines, steroids, certain polyarenes, and inorganic gases. For barbiturates and aniline derivatives, with the exception of nitroanilines, the DL can apparently be reduced by improving the efficiency of the gas-chromatographic separation.

The choice of the lamp with a specific nominal energy depends on the sample composition and the purposes and conditions of the analysis. For example, in the determination of substances with comparatively short retention times in mixtures with a large amount of a polar solvent (methanol, Freon 11, methylene chloride, acetonitrile), it is useful to employ a PID with a 10.2 eV lamp, which is only slightly sensitive to solvents of this type. As a result the solvent tail is diminished and the accuracy of the determination of the substances eluted in the vicinity of the solvent peak is increased.

The photoionisation detector can be used under conditions where the useful signal is generated as a result of electron capture[92,93] or the absorption of radiation.[94] A specific feature of experiment under these conditions is that a large background current ($10^{-8}-10^{-9}$ A) is generated by virtue of the ionisation of the make-up gas introduced into the ionisation chamber and ionised by the radiation from the lamp. The useful signal is generated at the expense of the decrease in the background current.

Table 6. Characteristics of the analytical methods using PID.

Object of analysis and sample size	Compounds determined, detection limits (DL), PID efficiency	Preparation of sample	Column characteristics	Temperature regime in separation	Carrier gas, flow rate	PID characteristics	Refs.
1	2	3	4	5	6	7	8
Air (20 litres)	Benzene, C_7–C_9 alkylbenzenes, halogenobenzenes; DL 5 μg m^{-3}	Enrichment on a tube with Poropak N, desorption with methanol	2.7 m × 2 mm packed column, 15% SF-96 + 6% OV-225 on Chromosorb WAW DMCS; 100/120 mesh	Heating from 65° to 80 °C (10 min) at a rate of 3 K min^{-1}	N_2, 30 ml min^{-1}	"HNU Systems", model P-101, 250 °C	[96]
Air (1 litre)	Benzene, n-butane and trichloroethylene; DL 2×10^{-7}, 7×10^{-9}, and 3×10^{-10}% respectively (for the 10.2 eV lamp) and 2×10^{-10}, 1×10^{-9}, and 1.5×10^{-9}% respectively (for the 11.7 eV lamp). Other hydrocarbons and halogenohydrocarbons	Cryogenic concentration in a tube with glass beads at –173 °C	9 m × 0.2 mm micropacked column, Duropak n-C_8/Porasil-C; 100/120 mesh	Heating from –103 ° to 47 °C at a rate of 25 K min^{-1} and then to 127 °C at a rate of 2 K min^{-1}		"HNU Systems", model PI 52, 10.2 eV 187 °C lamp. 11.7 eV 87 °C lamp; N_2 make-up gas flow at a rate of 13 ml min^{-1}	[74]
Air	Benzene and chlorobenzene; DL 6.5×10^{-8}% and 2.5×10^{-7}% respectively. Chloroalkenes	Enrichment in passive traps with activated charcoal, desorption with 5% CS_2 solutions in methanol	2.4 m × 3 mm packed column, 1% SP 1000 on Carbopack B	Heating from 100° (10 min) to 180 °C at a rate of 4 K min^{-1}	N_2, 30 ml min^{-1}	"HNU Systems", 10.2 eV lamp	[97, 98]
Air	Mono-, di-, tri-, tetra-, penta-, and hexa-chlorobenzenes: DL $(0.7–1.2)\times10^{-7}$%	Enrichment on a tube with Amberlite XAD-2; desorption with CCl_4	3 m × 3 mm packed column; 0.5% PEG 20 M + 5% Synerg C on Chromosorb WAW; 80/100 mesh	Heat6ing from 50° (3 min) to 200 °C (6 min) at a rate of 10 K min^{-1}	N_2, 18 ml min^{-1}	"HNU Systems" 10.2 eV, 250 °C	[99]
Air (1 ml)	Benzene, toluene, ethylbenzene, and xylenes: DL 2.5×10^{-8} 3.2×10^{-8}, 9.4×10^{-8}, and 9.7×10^{-8}% respectively	Without enrichment	1.5 m × 3.1 mm packed column, 5% SE-30 on Chromosorb G; 100/120 mesh	Room temperature	Air, 15 ml min^{-1}	"Photovac" 10A10, 10.9 eV lamp, room temperature	[83]
Air (1 ml)	Dibromoethylene and epoxyethane: DL 5×10^{-7} and 1×10^{-3}% respectively	Without enrichment	Packed column	Room temperature	Air	"Photovac" 10A10, 10.9 eV lamp, room temperature	[100]

Table 6 cont'd.

Object of analysis and sample size	Compounds determined detection limits (DL), PID efficiency	Preparation of sample	Column characteristics	Temperature regime in separation	Carrier gas, flow rate	PID characteristics	Refs.
1	2	3	4	5	6	7	8
Air	Methyl bromide (the sensitivity of its determination with a FID is ~100 times higher than with a PID)	ditto	2 m × 3 mm packed column, Carbopack; 40/60 mesh	32 °C	Air, 10 ml min^{-1}	"Photovac" 10A10, 10.9 eV lamp	[101]
Air	Formaldehyde (the sensitivity of its determination with a FID is 33 times higher than with a PID)	"	1.2 m × 3 mm packed column, Carbopack BHT	25 °C	Air, 12 ml min^{-1}	"Photovac" 10A10, 10.9 eV lamp	[102]
Air (5 ml)	Ethane-, t-butane-, propane-, and s-butanethiols: DL 4 μg m^{-2} (12 μg m^{-3} for butanethiol)	"	Packed column 2.7 m long 15% SF-96 + 6% OV-225 on Chromosorb WAW DMCS	60 °C	N_2, 30 ml min^{-1}	"HNU Systems", 10.2 eV lamp, 200 °C	[78]
Air (10 litres)	Carbon disulphide: DL 1×10^{-5}%	Enrichment on a tube with activated charcoal, desorption with acetonitrile	0.75 m × 2.1 mm packed column, Chromosorb 108; 80/100 mesh	105 °C	N_2, 30 ml min^{-1}	"HNU Systems", 210 °C	[103]
Water	Benzene, toluene, xylene, and vinyl chloride: DL 1 μg $litre^{-1}$	Gas extraction from 100 ml of H_2O at 45 °C, enrichment on a tube with Porapak N, desorption with methanol	For arenes: 2 m × 2 mm packed column, 20% SE-30 on Gas Chrom Q; for vinyl chloride: 2 m × 2 mm packed column, Porapak T; 80/100 mesh	Heating from 40° to 60 °C at a rate of 3 K min^{-1}; 90 °C for vinyl chloride	He, 30 ml min^{-1}	"HNU Systems", 200 °C	[104]
Water	Vinyl chloride: DL 0.01 μg $litre^{-1}$	Analysis of 5 ml from 60 ml of equilibrium vapour over 100 ml of water at 56 °C	0.9 m × 2 mm packed column, Chromosorb 104	90 °C	He, 20 ml min^{-1}	"HNU Systems", model PI-52-02, 10.2 eV lamp, 250 °C	[77]
Water (18 litres)	Bicyclic and tricyclic arenes and their chloroderivatives: DL at the level of ng $litre^{-1}$ and mg $litre^{-1}$	Concentration by the HPLC method on a column with C_{18}-Corasil II with elution of fractions by a mixture of H_2O and acetonitrile	2.4 m × 2 mm packed column, 1.5% SP 2250 + 1.95% SP 2401 on Supelcort; 100/120 mesh	182 °C	N_2, 23 ml min^{-1}	"HNU Systems", model PI 51, 250 °C; N_2 make-up gas flow at a rate of 10–75 ml min^{-1}	[36]
Sewage water (1 litre)	Aniline and halogeno-, halogenonitro-, nitro-, and dinitro-anilines [the quantitative analysis is difficult owing to the complexity of the chromatogram. The (N/P)-detector is recommended]	Extraction with CH_2Cl_2, purification by the LC method on a column with Florisil	30 m × 0.25 mm glass capillary column, SE-52	Heating from 80° to 230 °C at a rate of 4 K min^{-1}	He, 30 cm s^{-1}	"HNU Systems", model PI 50, 10.2 and 9.5 eV lamps, He make-up gas flow	[89]
Blood serum (10 ml)	Barbiturates and other medicinal drugs (the sensitivity of the determination with a FID is 8–16 times higher than with a PID	Extraction with CCl_4, distillation of solvent, dissolution of residue in acetonitrile	1.8 m × 2 mm packed column, 3% OV-17 on Gas Chrom Q deactivated with H_3PO_4	Heating from 200° to 285 °C at a rate of 12 K min^{-1}	N_2, 19 ml min^{-1}	"HNU Systems", model PI 52-02, 10.2 eV lamp	[105]
Blood (5 g) and urine (20 g)	Mono-, di-, tri-, tetra-, penta-, and hexa-chlorobenzenes: DL 3–19 ng g^{-1} in blood and 0.7–4.9 ng g^{-1} in urine	Extraction with CCl_4, purification by the LC method on a column with silica gel	1.8 m × 3 mm packed column, 0.2% PEG 40 M + 0.5% synerg C on Chromosorb WAW	Heating from 60° (2 min) to 180 °C at a rate of 12 K min^{-1}	N_2, 18 ml min^{-1}	"HNU Systems", 10.2 eV lamp, 250 °C	[99]
Deposit (15 g)	Benzene, alkylbenzenes, chloroalkenes, and halogenobenzenes: DL 7 ng g^{-1}	Gas extraction at 120 °C with concentration on a tube with Porapak N, desorption with methanol	60 m × 0.25 mm quartz capillary column, DV-5	Heating from 50° to 170 °C (156 min) at a rate of 4 K min^{-1}	He, 60 cm s^{-1}	"HNU Systems", 10.2 eV lamp, 220 °C, He make-up gas flow at a rate of 8 ml min^{-1}	[106]
Atmospheric dust (9.8 mg)	Tri-, tetra-, and pentacyclic arenes (the more selective FID with an 8.3 eV lamp is recommended)	Vacuum sublimation at 260 °C with cryogenic concentration in a trap	30 m × 0.32 mm quartz capillary column, DV-5	Heating from 55° (10 min) to 225 °C (30 min) at a rate of 10 K min^{-1}	He, 6 ml min^{-1}	"HNU Systems", model PI 52-02, 9.5 eV lamp, 230 °C, He make-up gas flow	[107]
Meat products	Nitrosoamines (owing to the complexity of the chromatogram, the determination of low concentrations is difficult)	Extraction, purification by the LC method on a column with silica gel	50 m × 0.32 mm glass capillary column, Triton X-305	Rapid heating from room temperature (4 min) to 60 °C followed by heating to 160 °C at a rate of 5 K min^{-1}	He	"HNU Systems", 9.5 and 10.2 eV lamps, 250 °C, He make-up gas flow	[79]

In the operation of the PID under electron conditions, a threshold level of detection of heptachlorodicyclopentadiene (heptachlor) of 10^{-12} g was attained.[93]

Light hydrocarbons, having large absorption coefficients *in vacuo* in the UV region of the spectrum, have been determined with the aid of PID.[94] The detection limit with respect to methane was 8×10^{-7}%.

The operation of the detector under conditions corresponding to the generation of a negative signal by the diminution of the background current improves the selectivity and extends the scope of the photoionisation detection method, since it makes it possible, for example, to detect certain substances whose ionisation energies exceed significantly the energy of the emitted photons.

VI. The application of the photoionisation detector in the gas-chromatographic analysis of mixtures of organic and inorganic compounds

The high sensitivity and selectivity of the PID promoted its application primarily for the determination of impurities in complex multicomponent systems. The PID is particularly promising in the

analysis of substances in the environment: air, natural and waste water, soils, marine and lake deposits, etc.

Table 6 presents the characteristics of certain practical methods employing PID. It shows that the main components of air and water determined with the aid of PID are benzene, C_7-C_9 alkylbenzenes, halogeno-derivatives of these compounds, halogenoalkenes, and polycyclic aromatic hydrocarbons. The lowest detection limit of benzene in air using cryogenic concentration is 2×10^{-11}% (HNU Systems Detector with a 10.2 eV lamp),[74] while without concentration it amounts to 2.5×10^{-8}% (Photovac detector with a 10.9 eV lamp).[83] These figures are satisfactorily correlated, since the volume of the sample in the former case was 1 litre, while in the latter case it was 1 ml. The employment of high performance capillary columns and PID in which the volume of the working chamber was 30–40 μl for a minimal make-up gas flow rate or even in its absence made it possible to reduce still further the DL. The use of PID for the determination in air and aqueous media of alkylbenzenes, chloroalkenes, chlorobenzenes, mercaptans, carbon disulphide, and formaldehyde as microimpurities is effective. A DL of 10^{-8}% has been attained for formaldehyde on a HNU Systems microprocessor gas chromatograph 301D fitted with a PID having an 11.7 eV lamp.[95]

At the same time, the increased sensitivity of the PID to compounds of certain classes sometimes does not compensate for the non-clear-cut gas-chromatographic separation. Thus the use of PID with a 9.5 eV lamp for the determination of polyarenes in atmospheric dust without preliminary fractionation of the sample components gives rise to difficulties. The background due to alkanes, cycloalkanes, ethers, etc. is too large to analyse reliably trace elements of polyarenes.[107] The authors recommend a more selective PID with an 8.3 eV lamp. An analogous result has been obtained in a study of synthetic fuel using a 10.2 eV lamp.[108] The employment of 9.5 and 8.3 eV lamps made it possible to ensure a higher selectivity in relation to polyalkylated arenes, napthalene, and *N*-heterocyclic compounds, but the absolute sensitivity was significantly lower than that obtained with a 10.2 eV lamp. The insufficient selectivity of the PID-10.2 to aromatic amines and their halogeno- and nitro-derivatives and the insufficient sensitivity of the PID-9.5 to nitro- and dinitro-amines precluded the determination of the admixture of these compounds in a complex mixture of subtances.[89] For this purpose, it was necessary to employ columns with a greater separating capacity or to fractionate more fully the sample before the gas-chromatographic analysis.

In order to increase the sensitivity of PID to steroids and alcohols, it has been suggested that they be converted with the aid of flophemesyl chloride (pentafluorophenyldimethylsilyl chloride) into the corresponding derivatives.[90,109] The DL of the initial substances and their derivatives, obtained on a capillary column (15 m × 0.33 mm) with SP 2100 at 275 °C and a PID at 300 °C, are compared in Table 7.

The possibilities for the quantitative determination of more than 40 chlorine-, sulphur-, phosphorus-, and nitrogen-containing pesticides and for the recognition of their structures using PID with two lamps (9.5 and 10.2 eV) have been investigated.[110,111] A highly sensitive method has been developed for the determination of methadone in blood plasma. When a PID and a capillary column (25 m × 0.2 mm) with VR-5 was used, the DL was 10 fg.[112] Significant advantages of PID with a 10.2 eV lamp compared with FID have been discovered in the analysis of the methyl esters of saturated and unsaturated $C_{16}-C_{18}$ essential acids. In terms of sensitivity, the PID was superior to the FID by a factor of five and in addition to experiments with the PID the molar response was found to vary linearly with the number of double bonds in the acid molecule.[91] It has been suggested that the PID be used for the continuous monitoring of the content of epoxyethane in air[113] and for the determination of PH_3,[114] amines,[115] light hydrocarbons, arsine, phosphine, hydrogen sulphide, carbon disulphide, dimethyl sulphoxide, and chlorofluorohydrocarbons.[116] A portable Photovac 10A10 chromatograph, fitted with (0.25–4) m × 2.5 mm Teflon columns with SE-30 or CSP-20M, deposited on Chromosorb GAWDMCS, was used in the last case. The separation was carried out at room temperature. The detection limit for chlorofluorohydrocarbons was 10^{-8}%. In PID, new chemically bound stationary phases were tested for DB-624 capillary columns[117] and for HNU-permabond packed columns.[118] The phases proved to be extremely effective for the determination of polyarenes and chlorophenols[118]—the principal contaminants of the environment.[117] The piezoelectric detector was tested with the aid of the PID.[119]

Table 7. Detection limits of steroids and their derivatives.

Compound	Detection limit, pg	
	initial compounds	derivatives
Androsterons	33.3	6.2
Testosterone	55.4	13.9
Cholesterol	ND*	21.2
Ergosterol	ND*	39.5
Oesterone	61.6	8.1
Oestradiol	69.0	10.1
Etisterone	ND*	29.9

*ND – not detected.

The PID has come to be widely used in specialised gas chromatographs and systems. A method has been described[120] for the identification of 40 solvents ranging from n-pentane to 1,1,2,2-tetrachloroethane, including aliphatic hydrocarbons, arenes, alcohols, ketones, etc., on a Nordion/HNU Micromat two-channel chromatograph. The sample was separated on two parallel quartz capillary columns 25 m long, with SE-54 and Yukon 50. A PID with a 10.2 eV lamp was used. The identification was based on a retention index data bank.

Two PID with a non-separated emission and detection compartments[19] were built into a 4-channel multidimensional chromatograph.[27] The PID detected permanent gases and C_1-C_2 hydrocarbons after their separation on a micropacked column (2 m × 0.53 mm) with Porapak N or on a capillary column of the PLOT type (10 m × 0.32 mm) with 5 Å molecular sieves. Heavier hydrocarbons were determined on capillary columns with chemically bound stationary phases connected to two FID. The combination of FID and PID in a multidimensional chromatograph has been used to determine volatile impurities (including oxygen-containing compounds) in air.[121,122] Through a three-way connector, 6% of the gas stream emerging from the first packed column with 1,2,3-tri(2-cyanoethoxy)propane was directed into the PID and benzene and toluene were determined quantitatively, the formation of the required fraction being monitored at the same time, i.e. the

instant of its being directed to the cryogenic trap was determined. The trapped fraction was analysed in detail on a quartz capillary column (50 m × 0.3 mm) with OV-101 connected to the FID.

Attempts were made to use the PID-10.2 in hypercritical fluid chromatography.[54] A design for a PID with a hermetic seal, withstanding high pressures of the carrier gas, has been described. Tests of the PID showed that the sensitivity of the detector, determined with respect to benzene, falls sharply with increase in the CO_2 pressure: it is 4×10^{-4} C g^{-1} at a 1 atm pressure and 5×10^{-8} C g^{-1} at 100 atm. There is a corresponding increase in the DL—from 2×10^{-9} to 1.8×10^{-5} g s^{-1}. The authors explained the reduced sensitivity of the PID by the quenching effect:

$$M + h\nu \rightarrow M^+ + \bar{e}, \quad CO_2 + \bar{e} \rightarrow CO_2^-,$$
$$CO_2^- + M^+ \rightarrow CO_2 + M.$$

It has been concluded that the PID cannot compete with the FID in liquid chromatography.

Investigators,[87] who tested the PID (model 52-02 from the HNU Systems Company) with a 10.2 eV lamp at atmospheric CO_2 pressure, arrived at the opposite view. A pneumoresistance, heated to 400 °C, was mounted at the outlet from a micropacked column, while the outlet from the PID freely communicated with the atmosphere. Comparison of the PID with the FID in the determination of polyarenes, up to coronene, showed that the DL with the PID (0.2—1 ng) is significantly lower than with the FID. Furthermore, owing to the instability of the flame, particularly at a high CO_2 flow rate (20—70 ml min^{-1}), sharp deviations and a shift of the zero line were observed when the FID was used. An experiment involving the use of a PID in high performance liquid chromatography (HPLC) for the analysis of traces of organic compounds has also been described.[123,124]

VII. Multidetector systems

Different variants of multidimensional chromatography with several selective detectors have undergone a new development recently.[125] The substances emerging from the column pass simultaneously to several detectors connected in series or in parallel. The simplified chromatograms thus recorded reflect mainly the presence of substances to which a particular selective detector is sensitive. The case where virtually all the substances are detected by the detectors but the signal from each detector for the same substance is different is also important. Since in the series connection of the detectors the amount of the substance entering into each detector is the same while in the parallel connection it is possible to measure and take into account the ratio of the separated fluxes, the ratio of the signals due to the same substance from two detectors A and B is the ratio of the sensitivity coefficients. For stable characteristics of the detectors and for linearity of their response, this ratio is independent of the concentration of the substances being determined and is a constant suitable for identification. In order to increase the stability of the constants, the responses are normalised with respect to a selected standard:

$$K_i^{A/B} = (R_i^A/R_{st}^A)/(R_i^B/R_{st}^B),$$

where $K_i^{A/B}$ is the ratio of the normalised responses of the detectors A and B with respect to the ith substance, R_i^A and R_{st}^A are the responses (the peak area or height) of the detector A with respect to the ith substance and the standard respectvely, and R_i^B and R_{st}^B are the responses of the detector B.

As will be shown below, the values of $K_i^{A/B}$ differ appreciably for substances of different classes of chemical compounds and significantly less so for substances within a single class. The quantities $K_i^{A/B}$ are therefore used mainly for group identification. A universal analytical system has been developed in which the sensitivity ratios for the two detectors are used together with universal retention indices.[126]

Table 8. The values of $K_i^{PID/FID}$ for organic compounds.[75]

Compound	$100\ K_i^{PID/FID}$	Compound	$100\ K_i^{PID/FID}$
n-Pentene	2	Hept-3-ene	51
n-Hexane	4	Hept-2-ene	57
n-Heptane	7	2-Ethylhex-1-ene	57
n-Octane	8	α-Pinene	75
n-Nonane	14	β-Pinene	65
n-Decane	16	Vinyl chloride	53
n-Undecane	15	1,1-Dichloroethylene	190
2,3-Dimethylbutane	7	Trichloroethylene	300
2,3-Dimethylpentane	10	Tetrachloroethylene	290
2,2,4-Trimethylpentane	18	*cis*-1,3-Dichloropropene	124
3-Methylheptane	7	Acetone	160
2,2,5-Trimethylhexane	21	Butanone	153
Cyclohexane	25	2-Pentanone	105
Methylcyclohexane	36	3-Pentanone	141
But-1-ene	65	Propionaldehyde	84
Pent-1-ene	64	Butyraldehyde	60
Hex-1-ene	59	Isobutyraldehyde	67
Hept-1-ene	49	Isovaleraldehyde	66
Oct-1-ene	44	Valeraldehyde	56
Non-1-ene	52	Methanethiol	650
Dec-1-ene	36	Ethanethiol	350
Undec-1-ene	35	Butanethiol	133
Tetrahydrothiophen	185	n-Butylbenzene	66
Benzene	112	p-Diethylkbenzene	75
Toluene	100	Indan	80
m-Xylene	95	Naphthalene	123
o-Xylene	77	Chlorobenzene	150
p-Xylene	105	*m*-Chlorotoluene	135
Ethylbenzene	87	*o*-Chlorotoluene	124
n-Propylbenzene	79	*p*-Chlorotoluene	130
p-Ethyltoluene	79	*m*-Dichlorobenzene	154
1,3,5-Trimethylbenzene	117	*o*-Dichlorobenzene	137
1,2,4-Trimethylbenzene	81	*p*-Dichlorobenzene	155

Note. A 10.0 eV lamp was used; the standard was toluene

1. The photoionisation detector/flame inisation detector combination

The flame-ionisation detector (FID) is a universal detector with a high sensitivity and a wide linear dynamic range. One of the first two-detector combinations developed abroad[127] and in our country[128] and designed for identification incorporated a FID. The properties of PID and FID have been compared.[129] Table 8 presents the values of $K_i^{PID/FID}$ for oganic compounds. The PID/FID combination was first tested for the group identification of hydrocarbons and pesticides.[69] The values of $K_i^{PID/FID}$, normalised for C_5—C_8 alkanes, alkenes, and arenes, differ appreciably: <2, 2—4, and 5—10 respectively. For the sulphur- and chlorine-containing pesticides having aromatic and aliphatic carbon skeletons, the values of $K_i^{PID/FID}$ differ by a factor of 12—16, while pesticides with alkene structures have intermediate values of $K_i^{PID/FID}$. The possibility of the group identification of hydrocarbons has been investigated in numerous studies. Polotnyuk et al.[130,131] successfully used the PID-10.2/FID combination to assign the components of petrol [gasoline] to alkenes and cycloalkanes (K_i = 0.02—0.45), alkenes and cycloalkenes (0.4—0.65), and dienes and arenes

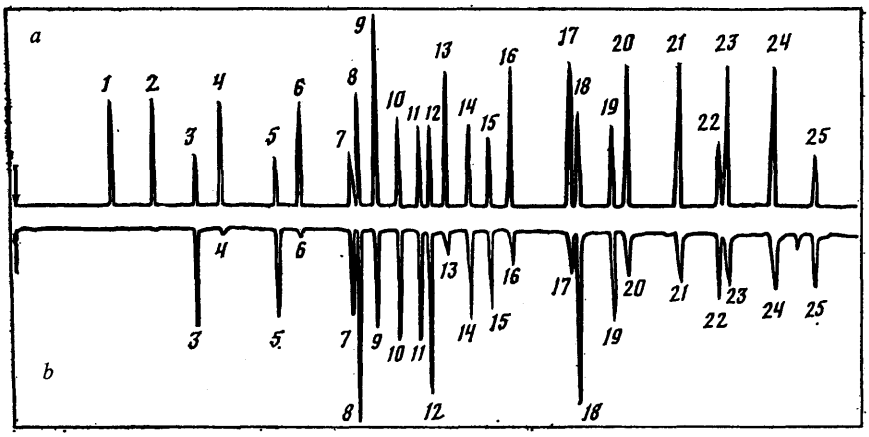


Figure 6. Chromatograms of a model mixture of hydrocarbons obtained with a FID (*a*) (8×10^{-9} A scale) and a PID-10.2 (*b*) (32×10^{-9} A scale).[57] 24 m × 0.5 mm × 1.1 μm glass capillary column with SE-54; carrier gas N_2; flow rate 1.6 ml min^{-1}; the stream of nitrogen from the column is divided between the detectors in proportions of 1 : 1; flow rate of the N_2 make-up gas for FID and PID 30 and 14 ml min^{-1} respectively; column temperature rise programmed between 40° and 270 °C at a rate of 6 K min^{-1}; temperature of detectors 270 °C; 0.12 μl sample injected directly into the column; *1*, n-C_5; *2*, n-C_6; *3*, benzene; *4*, n-C_7; *5*, toluene; *6*, n-C_8; *7*, ethylbenzene; *8*, *m*-xylene + *p*-xylene; *9*, n-C_9 + *o*-xylene; *10*, cumene; *11*, n-propylbenzene; *12*, mesitylene; *13*, n-C_{12}; *14*, *p*-cymene; *15*, n-butylbenzene; *16*, n-C_{11}; *17*, n-C_{12}; *18*, naphthalene; *19*, n-hexylbenzene; *20*, n-C_{13}; *21*, n-C_{14}; *22*, n-octylbenzene; *23* n-C_{15}; *24*, n-C_{16}; *25*, n-decylbenene.

(0.65 – 1.00) and demonstrated the effectiveness of this procedure for the refinement of the gas-chromatographic identification. According to the authors,[132,133,138] the ratios of the sensitivities of the PID and the FID combined with the retention indices ensure a reliable identification of the peaks. An experiment involving the group identification of alkanes (0 – 43), alkenes (44 – 48), and arenes (75 – 158) in $C_6 - C_9$ hydrocarbons present in air has been described.[55] Measurements have been made[57] of the quantities $K_i^{PID/FID}$ using PID-10.2 for methyl ethers and aldehydes (< 1) and alkanes, isoalkanes, naphthenes, and alcohols (1 – 6), alkenes (12 – 17), alkylbenzenes (6 – 17), and *N*-heterocyclic compounds (5 – 40). It was shown that, with increase in the molecular weight of the substances, the overlap of the $K_i^{PID/FID}$ ranges for different groups increases (Fig. 6). The photoionisation detector with a 9.5 eV lamp is more selective but its sensitivity is appreciably lower. The reliability of the group identification could be increased by employing two groups of tabulated values of $K_i^{PID/FID}$,[75] which assigned the test substances to halogenoalkanes, alkanes, cycloalkanes, trimethylalkanes, alkynes, alkenes, aldehydes, ketones, arenes, halogenoarenes, and sulphur-containing hydrocarbons. The substances emerging from the column during the first 17 min were identified in terms of one group of values, while those eluted after 17 min were identified in terms of the second group. The values of $K_i^{PID/FID}$ for these substances are listed in Table 8.

The same workers used a parallel PID/FID combination for the determination of $C_1 - C_{10}$ hydrocarbons in air.[134] The impurities were concentrated from air in a cryogenic trap and were separated on a capillary column 60 m long with SE-30. Alkanes, alkenes, and arenes were differentiated.

2. The photoionistion detector/electron capture detector combination

The high sensitivity of the ECD to organic halogeno-compounds makes it irreplaceable in the determination of halogenohydrocarbons in the environment. It has been acknowledged that the PID/ECD combination is promising for the determination of chlorine-containing compounds in atmospheric waste.[133]

In the study of Jaramillo et al.,[133] as in those of Polotnyuk et al.[131] and Towns et al.,[132] the values of $K_i^{PID/FID}$ served as an additional factor for the identification of the individual compounds. The combination of PID with ECD makes it possible to differentiate chlorobenzenes in terms of the number of chlorine atoms in the molecule.[135] The difference is based on weak dependence of the sensitivity of the PID-10.02 on the chlorine content (Table 4) and on the appreciable increase in the ECD signal on passing from chlorobenzene to dichlorobenzene and further to hexachlorobenzene. Accordingly, the PID/ECD signal ratio varies from 4.0 and 0.03. The values of $K_i^{PID/FID}$ are also used to identify hydrocarbons and their nitro-derivatives.[80,135] In this case, the sensitivities of the detectors change in the opposite direction. The values of $K_i^{PID/FID}$ are 25 – 78 for polyarenes, 0.3 – 0.6 for nitropolyarenes, 1 – 1.5 for nitrotoluenes, and 0.004 – 0.020 for dinitrotoluenes. Thus the identification of arenes and their nitro- and dinitro-derivatives is extremely reliable.

3. Combination of the photoionisation detector with electrical conductivity detector

Chlorine-containing compounds are detected selectively by the Hall or Coulson electrical conductivity detector (ECD). This feature of the ECD has been used to determine halogenohydrocarbons in

water, while light arenes were detected with a PID-10.2 connected in series with an ECD.[136] Three columns were used to separate halogenohydrocarbons and alkylbenzenes—the main column and the two special columns. The employment of selective detectors simplifies the chromatogram. Out of the 42 substances detected in the sample, the PID failed to detect 18 halogenohydrocarbons, while the ECD failed to detect nine alkylbenzenes. A similar problem was solved using the halogen variant of the ECD and a PID-9.5.[137] In a sample of soil water (volume 5 ml), it is possible to determine with the aid of the ECD chlorinated hydrocarbons at concentrations up to 0.6–4.0 μg litre^{-1}, while with the aid of the PID it is possible to determine C_6-C_8 arenes at concentrations up to 1.0–1.1 μg litre^{-1}.

Methods have been developed for the determination of volatile organic compounds in drinking water using gas extraction and concentration[138] and also in sewage on quartz capillary columns.[139] The influence of experimental parameters on the duration of analysis and the reproducibility of the determination of 36 chlorohydrocarbons and arenes in natural water using a series-connected combination of a PID and an ECD in capillary columns 0.32 and 0.53 mm in diameter has been investigated in detail.[140] It has been shown that the PID/ECD combination makes it possible to reduce the analytical time and the cost of analysis as a result of the high selective sensitivity of the PID to hydrocarbons and of the ECD to nitrogen-, sulphur-, and halogen-containing compounds.[141] The PID/ECD combination has been used successfully to determine DDT and DDE impurities (10 p.p.m.) in the presence of 1000 p.p.m. of toxaphene.[125] The use of a PID with a 9.5 eV lamp permitted the selective detection of *p,p'*-DDT and *p,p'*-DDE, which have aromatic rings in their structure, while the employment of the ECD permitted the detection of all the halogen-containing substances.

4. The combination of the photoionisation detector with other detectors

The series connection of PID with 10.2 and 8.3 eV lamps and of a thermionic detector tuned to determine nitrogen-containing compounds has been used for the structural identification of aromatic and aliphatic amines.[142] Fig. 7 shows that the combination of the PID-10.2 with a (N/P)-detector makes it possible to differentiate reliably hydrocarbons from amines, while the combination of the PID-8.3 with a (N/P)-detector makes it possible to differentiate primary amines from secondary and tertiary amines. The ratio of the PID signal to the signal of the (N/P)-detector is appreciably greater for tertiary amines compared with secondary amines (Table 9).

The development of an improved UV-detector based on the absorption of light in the far UV region and having a working chamber with a volume of 40 μl increased significantly the possibilities for its combination with PID fitted with 10.2 and 11.7 eV lamps.[143] The UV-detector detects certain Freons, methane, and water to which the PID-11.7 is almost insensitive. It is recommended that the PID/UV detector response ratio be used to identify low-molecular-weight hydrocarbons, aldehydes, alcohols, and sulphur-containing compounds.[86]

Combinations of PID fitted with lamps having different energies have been used to identify hydrocarbons. The PID-11.7/PID-10.2 response ratios proved suitable for the differentiation of alkanes, alkenes, cycloalkanes, and arenes.[72] The combination of PID fitted with 9.5 and 8.3 eV lamps is sensitive to the structure of polyarenes and can be used to differentiate isomers. For example, the PID-9.5/PID-8.3 response ratio is 13 for anthracene and 43 for phenanthrene.[144]

5. Combination of three detectors

The combination of PID with two detectors has been used to analyse organic impurities in air and different gases. The PID/FID/ECD combination has been used.[74,76,145,146] In this combination, the universal FID is designed to detect hydrocarbons, PID is designed to detect alkenes and arenes, and ECD is designed to detect halogenohydrocarbons, i.e. the entire set of the principal low-boiling compounds usually present in air.

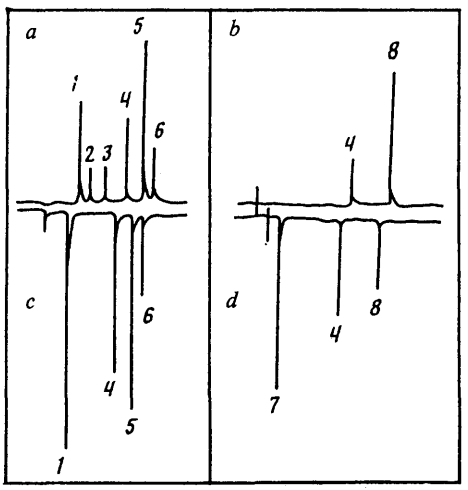


Figure 7. Chromatograms of amines obtained with a PID-10.2 (*a*), a PID-8.3 (*b*), and a (N/P)-detector (*c* and *d*); column 1.8 m long with Synerg C-AP at temperatures programmed from 80° to 190 °C at a rate of 15 K min^{-1} and with a helium carrier gas flow rate of 30 ml min^{-1}; *1*, n-heptylamine; *2*, n-dodecane; *3*, n-tridecane; *4*, di-n-hexylamine; *5*, dicyclohexylamine; *6*, dodecylamine; *7*, n-hexylamine; *8*, tri-n-hexylamine.[142]

Table 9. The ratio of the PID and (N/P)-detector signals for certain amines.

Compound	Signal ratio	
	PID-10.2 signal: (N/P)-detector signal	PID-8.3 signal: (N/P)-dector signal
Di-n-hexylamine	2.3	0.01
Tri-n-hexylamine	4.0	0.04
Dibenzylamine	6.4	0.004
Tribenzylamine	9.8	0.3

The stream of carrier gas emerging from the capillary column 60 m long and containing Al_2O_3/KCl was divided in proportions of 1 : 5 between ECD and PID + FID.[76] The impurities from one litre of air were concentrated in a cryogenic accumulator and C_1-C_2 halogenohydrocarbons were determined by the ECD with a DL in the range $1 \times 10^{-10}-9 \times 10^{-9}$%; benzene, C_3-C_8 alkenes and

alkanes, and C_1-C_3 chloroalkenes were determined by the PID-10.2 with a DL in the range $5 \times 10^{-12}-1 \times 10^{-8}$%, and C_2-C_8 aliphatic hydrocarbons and benzene were determined by the FID and a DL of $(1.2-5) \times 10^{-9}$%. A trap cooled to −173 °C was also used by Rudolph and Jepsen.[74] The detectors were connected in series. For an air sample volume of one litre, the DL for the detection of C_1-C_2 halogenohydrocarbons and CS_2 by the ECD was $2 \times 10^{-11}-3 \times 10^{-10}$%, the DL for C_3-C_6 hydrocarbons and certain chloroalkanes detected by the FID was $5 \times 10^{-10}-5 \times 10^{-11}$%, the DL for C_3-C_6 hydrocarbons and halogenohydrocarbons detected by the PID-11.7 was $2 \times 10^{-10}-2 \times 10^{-9}$%, and the DL for propene, butadiene, benzene, trichloroethylene, and CS_2 detected by the PID-10.2 was $2 \times 10^{-11}-3 \times 10^{-10}$%. The three detectors indicated made it possible to identify twenty organic compounds out of the 150 found in air.[146] The identification was based on the retention times and the detector response ratios. The advantages of the series connection of a UV-detector, a PID, and an FID have been examined.[147] The detector system has been recommended for the analysis of industrial gaseous waste and smoke and exhaust gases. It has been suggested that a combination of a PID, an ECD, and an ultrasonic detector be used for the determination of impurities comprising inert, corrosive, and combustible substances (at the level of p. p. m.) in different gases.[148] The characteristics of the detection of nitrogen, argon, hydrogen, oxygen, methane, ammonia, silanes, phosphine, arsine, etc. by the ultrasonic detector have been examined.

6. Devices for multidimensional detection

The combinations examined represent mechanical combinations of standard detecting devices. Multidimensional detectors, in which there are one or several detection zones combined in a single shell while the output signals reflect different properties of the detected molecules, have been developed vigorously recently. A design has been proposed for a detector with two chambers separated by a LiF or MgF_2 window in which the ionisation current and non-absorbed photons are recorded.[149] An example of a multidimensional detector, in which photoionisation is used and there is one detection zone, is provided by a device where the principal element is an evacuated chamber and a laser beam is used to ionise the compounds emerging from the column and entering the chamber and to excited their fluorescence.[150] The total electron current is measured with the aid of an electrode placed in the chamber. The fluorescence emitted is detected by a photomultiplier. Positive ions enter a time-of-flight mass spectrometer tuned to a specific mass. Thus the device ensures the detection of three different angles. Its operation was tested on a model mixture of 64 compounds. The sensor measuring the total electron current detected 24 compounds, predominantly of an aromatic character, with a detection limit of 6−500 pg. The mass detector had a significantly greater sensitivity: the detection limit varied from 1 to 63 pg. The fluorescence signal arose from 15 substances. The use of a controllable vacuum UV laser is in general extremely promising for photoionsation detection, because it increases the spectral selectivity and ionisation efficiency, reduces the detection volume, and creates the possibility of measuring the ionic mobilities. The PID constructed on the basis of these principles make it possible to detect polycyclic arenes with the detection limit of 0.3−50 pg.[151]

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Photoionisation sensors are some of the principal detectors in gas chromatographs together with FID, ECD, (N/P)-detectors, and the katharometer. The high sensitivity to many organic and inorganic compounds (the sensitivity is in fact highest to certain classes of compounds) together with a pronounced selectivity and a wide linear dynamic range constitute the advantages of the use of PID in gas-chromatographic analysis. Important features of PID are the possibility of the specific regulation of the selectivity by employing UV lamps with different emission energies and also an increased sensitivity to the structure of the carbon skeleton of the molecule. The use of new materials, the improvement of the design, and an increase in the operating life of the lamps are the principal ways of improving the operating characterisics of PID and of securing reproducible detector signals. The development of detectors based on laser multiphoton ionisation is also promising.

References

1. S E Lovelock *Nature*, 1960, **186** 401
2. *Series HNO 300 Chromatographs.* Publicity leaflet from the HNU Systems Company, 1988
3. *The Varian 3600 Chromatograph.* Publicity leaflet from the Varian Company, 1988
4. *The DI-200 Chromatograph.* Publicity leaflet from the Delsi Company, 1988
5. *The Model 421 Chromatograph.* Publicity leaflet from the AID Company, 1987
6. L Ya Gavrilova, V I Zheivot, O A Emel'yanova *Usp. Khim.*, 1984, **53**(12) 2078 [English translation in *Russ. Chem. Rev.*, 1984(12)]
7. P Verner *J. Chromatogr.*, 1984, **300** 249
8. J N Driscoll *J. Chromatogr. Sci.*, 1985, **23** 488
9. M E Akopyan *Fizika Vakuumnogo Ul'trafioletovogo Izucheniya* (The Physics of Vacuum Ultraviolet Radiation), Izd. Naukova Dumka, Kiev, 1974, p. 113
10. G V Marr *Photoionisation Process in Gases*, Acad. Press, New York, 1968, 268 pp
11. F I Vilesov *Usp. Fiz. Nauk*, 1963, **81** 669
12. M E Akopyan, Yu L Sergeev, F I Vilesov *Khim. Vys. Energii*, 1970, **4** 305
13. M Yamane *J. Chromatogr.*, 1963, **11** 158
14. M Yamane *J. Chromatogr.*, 1964, **14** 355
15. S Roesler *Anal. Chem.*, 1964, **36** 1900
16. D C Locke, Y E Meloan *Anal. Chem.*, 1965, **37** 389
17. Y C W Price, D C Fenimor, P G Simmonds, A Zlatkis *Anal. Chem.*, 1968, **40** 541
18. J Rosiek, W Gucowski, S Lasa *Chem. Anal.*, 1976, **21** 1251
19. K Kawazoe, T Kamo, Y Takata, N Shikama *Bunseki Kagaku*, 1985, **34** 309
20. N A Spivak *Zh. Anal. Khim.*, 1982, **37** 759
21. R R Freeman, W E Wentwork *Anal. Chem.*, 1971, **43** 1987
22. Europe. P. 0 184 912.
23. Q Jin, G Yang, Z Guo, J Lio *J. Microchem.*, 1987, **35** 281
24. R C Leveson, N Y Barker *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1982*, No. 238
25. J Meek, J Craggs *Electrical Breakdown in Gases* (Translated into Russian), Inostr. Lit., Moscow, 1960, 605 pp
26. US P. 4 266 196

27. H Tani, M Furumo *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1986, **9** 712
28. USSR P. 160 032; *Byull. Izobret.*, 1964, (2)
29. J Sevčic, S Krysl *Chromatographia*, 1973, **6** 375
30. N Ostojic, Z Sternberg *Chromatographia*, 1974, **7** 3
31. J N Driscoll, J B Clarici *Chromatographia*, 1976, **9** 567
32. J N Driscoll, S Ford, L Jaramillo, et al. *Am. Lab.*, 1978, **10** 137
33. J F Rabek *Experimental Methods in Photochemistry and Photophysics* (Translated into Russian), Izd. Mir, Moscow, 1986, 608 pp
34. P Marneck *J. Opt. Soc. Am.*, 1965, **55** 921
35. L P Shishatskaya, P A Tsiryul'nik, V M Reiterov, et al. *Optiko-Mekhanicheskaya Promyshlennost'*, 1972, No. 10, p. 69
36. A R Oyler, D L Bodenner, K J Welch, et al. *Anal. Chem.*, 1978, **50** 837
37. A N Freedman *J. Chromatogr.*, 1982, **236** 11
38. B I Khrushch, Yu A Ershov, A M Lyulichev, et al. *Khim. Vys. Energii*, 1977, **11** 332
39. I V Smushkov, L M Soifer, M I Shakhnovich *Kristallicheskie Opticheskie Materialy dlya Vakuumnoi Ul'trafioletovoi Oblasti* (Crystalline Optical Materials for the Vacuum Ultraviolet Region), Izd. Nauka, Leningrad, 1986, 59 pp
40. V S Letokhov *Lazernaya Fotoionizatsionnaya Spektroskopiya* (Laser Photoionisation Spectroscopy) Izd. Nauka, Moscow, 1987, 308 pp
41. A I Zaidel', E Ya Shpaider *Vakuumnaya Spektroskopiya i Ee Primenenie* (Vacuum Spectroscopy and Its Applications), Izd. Nauka, Leningrad, 1967, 431 pp
42. S A Yakovlev *Optiko-Mekhanicheskaya Promyshlennost'*, 1978, (4) 52
43. L P Shishatskaya *Optiko-Mekhanicheskaya Promyshlennost'*, 1984, (9) 54
44. S A Yakovlev, I A Nevyazhskaya *Fotometriya i Ee Metrologicheskoe Obespechenie. Trudy 5-i Vsesoyuznoi Nauchno-Tekhnicheskoi Konferentsii* (Photometry and Its Metrological Basis. Transactions of the 5th All-Union Science and Engineering Conference), Izd. Nauka, Moscow, 1984, p. 209
45. Y N Davenport, E R Adlard *J. Chromatogr.*, 1984, **290** 13
46. B D Towns, J N Driscoll, D Conron *Abstracts of the Pittsburgh Conference and Expositions on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1983*, No. 419
47. US P. 4 398 152
48. US P. 4 413 185
49. R C Leveson, N Y Barker *Anal. Instrument.*, 1981, **19** 7
50. *The Model PI 52-02A Photoionisation Detector.* Publicity leaflet from the HNU Systems Company, 1988
51. J N Driscoll *Am. Lab.*, 1986, **18** 95
52. R Yoder, R Sacks *J. Chromatogr. Sci.*, 1987, **25** 21
53. S Kapila, C R Vogt *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1981, **4** 233
54. W Gmür, J O Bosset, E Plattner *Chromatographia*, 1987, **23** 199
55. W Nutmagul, D R Cronn, H H Hill *Anal. Chem.*, 1983, **55** 2160
56. *The Photoionisation Detector for the MGC 4000 Laboratory Gas Chromatograph.* Publicity Leaflet from the Chromatron Factory, Academy of Sciences of the German Democratic Republic, 1988
57. J A Yancey *Adv. Instrument. Proc. USA Intern. Conf. and Exbit., Philadelphia, 1982*, No. 37. Pt. 2, p. 547
58. L F Jaramillo, J N Driscool *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1979, **2** 536
59. USSR P 968 751; *Byull. Izobret.*, 1982, (39)
60. K Okazaki *Technology of Ceramic Dielectrics* (Translated into Russian), Izd. Energiya, Moscow, 1976, 336 pp
61. S S Vashchun, L I Voitenko, A A Melik'yan, et al. *Zavod. Lab.*, 1986, (11) 5
62. DDR P. 232 992
63. USSR P. 1 430 862; *Byull. Izobret.*, 1988, (38)
64. USSR P. 1 444 659; *Byull. Izobret.*, 1988, (46)
65. J G Senum *J. Chromatogr.*, 1981, **205** 413
66. E W McDaniel *Collision Phenomena in Ionised Gases* (Translated into Russian), Izd. Mir, Moscow, 1967, 832 pp
67. P A Rodriguez, C L Eddy, C R Culberton *J. Chromatogr.*, 1985, **330** 365
68. *The PID-13 Photoionisation Detector.* Publicity leaflet from the Design Bureau of the Academy of Sciences of the Estonian SSR, 1986
69. J N Driscoll, J Ford, L F Jaramillo, et al. *J. Chromatogr.*, 1978, **158** 171
70. M E Casida, K C Casida *J. Chromatogr.*, 1980, **200** 35
71. M L Langhorst *J. Chromatogr. Sci.*, 1981, **19** 98
72. J N Driscoll *J. Chromatogr. Sci.*, 1982, **20** 91
73. J N Driscoll *J. Chromatogr.*, 1977, **134** 49
74. J Rudolph, C Jebsen *J. Environment. Anal. Chem.*, 1983, **13** 129
75. R D Cox, R F Earp *Anal. Chem.*, 1982, **54** 2265
76. F J Reineke, K Bächmann *J. Chromatogr.*, 1985, **323** 323
77. V B Stein, R S Narang *Bull. Environmen. Contam. Toxicol.*, 1981, **27** 583
78. V B Stein, R S Narang *Anal. Chem.*, 1982, **54** 991
79. J Meili, P Bronniman, B Brechbühler, et al. *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1979, **2** 475
80. I S Krull, M Swartz, R Hilliard, et al. *J. Chromatogr.*, 1983, **260** 347
81. A Korus, J Lasa *Rap. Inst. Fiz. Techn. Jadr. AGH*, 1986, **1**(199) 53
82. A Korus, J Lasa *EUROANALYSIS; 5: 5th European Conference on Analytical Chemistry, Cracow, 26–31 Aug., 1984*; Abstracts, Cracow, 1984, p. 69
83. A J Clark, A E McIntyre, J N Lester, et al. *Intern. J. Environment. Anal. Chem.*, 1984, **17** 315
84. J Yerpe, A Davis *J. Chromatogr. Sci.*, 1987, **25** 154
85. N E Hester, R A Meyer *Environment. Sci. Technol.*, 1979, **13** 107
86. J N Driscoll, B J Grimes, G F Hewitt *Kem. Kemi*, 1983, **10** 978
87. P G Sim, C M Elson, M A Quilliam *J. Chromatogr.*, 1988, **445** 239
88. P A Mulawa, S H Cadle *Anal. Lett.*, 1981, **14** 671
89. R M Riggin, T F Cole, S Billets *Anal. Chem.*, 1983, **55** 1862
90. I S Krull, M Swartz, J N Driscoll *Anal. Lett*, 1985, **18** 2619
91. *A Photoionisation Detector.* Publicity leaflet from the HNU Systems Company, 1978
92. W E Wentworth, A Tishbee, C F Batten, A Zlatkis *J. Chromatogr.*, 1975, **112** 229
93. S Kapila, D J Borhop, S E Manahan, G L Nichell *J. Chromatogr.*, 1983, **259** 205
94. I V Bondarenko, V L Budovich, M Ya Bykhovskii *Zavod. Lab.*, 1989, (1) 11

95. J H Becker, D Renaud, K Walsh, et al. *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J, 1986*, No. 194
96. S van Tassel, N Amalfitano, R S Narang *Anal. Chem.*, 1981, **53** 2130
97. R G Lewis, J D Mulio, R W Coutant, et al. *Anal. Chem.*, 1985, **57** 214
98. R W Coutant *Environ. Sci. Technol.*, 1982, **16** 410
99. N Langhorst, T Y Nestrick *Anal. Chem.*, 1979, **51** 2018
100. M Collins, N J Barker *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N.J., 1983*, No. 619
101. T Dumas, E J Bond *J. Agric. Food. Chem.*, 1985, **33** 276
102. T Dumas *J. Chromatogr.*, 1982, **247** 289
103. D B Smith, L A Krause *Amer. Ind. Hyg. Assoc. J.*, 1974, **29** 709
104. N S Narang, B Bush *Anal. Chem.*, 1980, **52** 2076
105. L F Jaramillo, J N Driscoll *J. Chromatogr.*, 1979, **186** 637
106. T A Amin, R S Narang *Anal. Chem.*, 1985, **57** 648
107. S L Kopczynski *Anal. Lett.*, 1984, **17** 97
108. J A Yancey *Instr. Technol.*, 1983, **30**(4) 65
109. I Krull, M Swartz, J N Driscoll *Anal. Lett.*, 1984, **17** 2369
110. J N Driscoll, J Ford *29th Pittsburgh Conference on the State of the Art in Analytical Chemistry and Applied Spectroscopy. Cleveland, Ohio; Abstracts, Monroeville, 1978*, No. 6.
111. J N Driscoll, L F Jaramillo, R G Hanisch, S D Soileaux *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1980*, No. 410
112. B Norlander, B Carlsson, A Bertler *J. Chromatogr. Biomed. Appl.*, 1986, **375** 313
113. J N Driscoll, E S Atwood, J Hayhurst *Int. Labmate*, 1988, **13** LG98
114. A Verstuyft *Rev. Am. Hyg. Assoc. J.*, 1978, **39** 431
115. G O Woods, J W Nicols *Los Angeles Alamos Sci. Lab. Project R-059, NJOSH-JA-77-12*, 1977
116. Y Kaneko *Nenryo Oyo bi Nensho; Fuel Combust.*, 1981, **48** 829
117. R R Freeman, R M A Lautano *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1986*, No. 1000
118. L F Jaramillo, J N Driscoll *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1980*, No. 413
119. M H Ho, G G Suilbault *Anal. Chem.*, 1983, **55** 1830
120. A Kiviranta, J N Driscoll *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1987*, No. 774
121. S Berg, A Jonsson *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1984, **7** 687
122. A Jonsson, S Berg *J. Chromatogr.*, 1983, **279** 307
123. D C Locke, B S Dhingra, A D Baker *Anal. Chem.*, 1982, **54** 447
124. J N Driscoll, D W Conron, P Ferioli, et al. *J. Chromatogr.*, 1984, **302** 43
125. I S Krull, M Swartz, J N Driscoll *Adv. Chromatogr.*, 1984, **24** 247
126. N F Belyaev, M S Vigdergauz *Zh. Anal. Khim.*, 1986, **41** 1882
127. A B Littlewood *J. Chromatogr.*, 1965, **3** 111
128. D N Sokolov, L K Golubova *Zavod. Lab.*, 1969, **35** (2)
129. H H Hill, M A Baim *Trends Anal. Chem.*, 1982, **1**(9) 206
130. V O Polotnyuk, I A Revel'skii, S A Leont'eva, A A Grinberg *Zh. Anal. Khim.*, 1984, **39** 529
131. V O Polotnyuk, I A Revel'skii, A A Grinberg, S A Leont'eva *Zh. Anal. Khim.*, 1985, **40** 511
132. B D Downs, J N Driscoll, E S Atwood, D Conron, R Hogan *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1982*, No. 477
133. L F Jaramillo, J N Driscoll, D Conron *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1981*, No. 864
134. R D Cox, K W Lee, R F Earp *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1982*, No. 782
135. M Swartz, Xie Kuang-Hua, R Hilliard, et al. *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1983*, No. 421
136. B Kingsley, C Inin, D Coulson, et al. *Ann. Arbor. Sci.*, 1981, **4** 132
137. T F Cole, R M Riggin, M P Miller *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1983*, No. 209
138. B B Bernard, R C Hall *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, New Orleans, La., 1988*, No. 767
139. J Butler, T Wilks *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, New Orleans, La., 1985*, No. 374
140. M Duffy, J N Driscoll, S Pappas, W Sanford *J. Chromatogr.*, 1988, **441** 73
141. W A McKinley, R Anderson, P W Thide *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1982*, No. 473
142. B D Towns, J N Driscoll *Am. Lab.*, 1982, **14** 59
143. J N Driscoll, M Duffy, S Pappas *J. Chromatogr.*, 1988, **441** 63
144. D W Conron, J N Driscoll, B D Towns *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1983*, No. 618
145. J N Driscoll, J K Marshall, L F Jaramillo, et al. *Am. Lab.*, 1980, **12** 84
146. J W Bonelli, B Kebbekus, J Kemp *179th ACS Nat. Meet. Houston, Texas, 1980. Abstr. Pap., Washington, 1980*, No. 58
147. P Ferioli, J N Driscoll *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, New Orleans, La., 1985*, No. 725
148. J Butler *Abstracts of the Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N. J., 1986*, No. 110
149. Czech. P. 162 220
150. R L Dobson, A P D'Silva, S J Weeks, et al. *Anal. Chem.*, 1986, **58** 2129
151. C M Klimčak, J E Wessel *Anal. Chem.*, 1980, **52** 1239

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Modification of polymers by polymeric additives

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ABSTRACT. The conditions for the thermodynamic compatibility of polymers and methods for its enhancement are examined. The study of the influence of various factors on the concentration-temperature limits of compatibility, dispersion stabilisation processes, and methods for the improvement of adhesion between phases in mixtures of thermodynamically incompatible polymers is described. Questions concerning the improvement of the physicomechanical characteristics of polymer dispersions are considered.

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I. Introduction

The acceleration of scientific and technical progress requires the creation of new materials with the needed set of properties. Composite materials incorporating polymers containing a wide variety of fillers, mixtures and blends of two or more polymers, etc. have been acquiring an increasing role in the solution of this problem at the present time.

Since the preparation of new polymeric materials with the required properties can no longer be wholly based on the synthesis of new high-molecular-weight compounds, the era of problems concerning the modification of polymers already produced by industry and the preparation of materials with the required properties on their basis has now dawned. One of the most readily available and economically favourable modification procedures involves the preparation of mixtures and blends of two or more polymers, interpenetrating networks, etc. The properties of such systems are determined by their structure, whose formation is associated with the thermodynamic compatibility or incompatibility of the components and mechanism of phase separation under the conditions of the preparation of the composition and its conversion into finished articles. The practical experience gained in the preparation and use of finished articles made from such materials has shown that, in order to obtain the desired properties, thermodynamic compatibility of the components is needed in some cases, whilst in others it is in fact undesirable. For example, the view has been expressed[1] that, in terms of their mechanical properties, two-phase mixtures are superior to single-phase mixtures and that the subdivision of systems into thermodynamically compatible or incompatible has no great practical value. On the other hand, analysis of literature data has led Paul and Barlow[2] to the conclusion that materials obtained from compatible systems have on the whole better properties. A truly homogeneous product can be obtained from thermodynamically compatible polymers. In the case of compatible systems, a synergism is observed in a series of important physicomechanical properties such as moduli and strength, the transparency of the materials is ensured, and there are other advantages.[3–8] The compatibility of polymers guarantees also the operational reliability of the articles made from them, especially under the conditions of variable loads and in different temperature regimes. Much attention has therefore been devoted in recent years, particularly abroad, to the search for thermodynamically compatible pairs and significant progress on these lines has been achieved: about 300 thermodynamically compatible polymer pairs have now been discovered.[8–12]

In those cases where for the attainment of the required properties mixtures of thermodynamically incompatible polymers are used (impact-resistant plastics, certain adhesives), it is essential to stabilise the dispersion because, owing to the weak adhesion between the phases in such cases, difficulties arise in the attainment of the required degree of dispersion of the mixture components during their processing and their stability is impaired both during preparation and during use.[3] In many instances the weak adhesion between the phases impairs the mechanical properties.[3,13–16] Much attention has therefore been devoted nowadays to problems of the stabilisation of mixtures of this kind, the improvement of adhesion between the phases, etc.

This review surveys the literature data on the compatibility of polymers and on its dependence on various factors. Questions concerning the stabilisation of dispersions and the regulation of the properties of materials made from mixtures of thermodynamically incompatible polymers are also considered.

II. The compatibility of polymers and methods for its regulation

A large number of both original publications and reviews and monographs have been devoted to problems of the compatibility of polymers and the search for thermodynamially compatible polymer systems.[2,8,12,17,18] The study of the thermodynamic compatibility of polymers has led to the conclusion that in the vast majority of cases it is determined by specific interactions, which ensure the exothermicity of the mixing process, i. e. lead to a negative enthalpy of mixing.[3,10,18–22] It has been demonstrated for the first time by Tager and co-workers[23,24] that the entropy of mixing of thermodynamically compatible polymers is also negative. On this basis, the requirement that $\Delta S < 0$ has been put forward as one of the conditions for the compatibility of polymers.[25] Since the enthalpy

and entropy of mixing of compatible systems are negative, these systems should separate into layers on heating, i.e. should be characterised by the presence of a lower consolute temperature (LCT). Indeed the majority of the thermodynamically compatible polymer pairs found hitherto do have a LCT.[9-11] Upper consolute temperatures (UCT) are characteristic mainly of oligomer–oligomer and oligomer–polymer mixtures, mixtures of polymers with plasticisers, and mixtures of certain homopolymers with copolymers.[11,26-30]

In order to account for the exothermicity of the mixing process, the concept of the "mutually complementary difference" was put forward,[17] whose essential feature is that the macromolecules of the mixed polymers should contain groups complementing one another and capable of forming hydrogen bonds with one another or electron donor–electron acceptor complexes. This concept actually constitutes the basis of the study of polymer solutions.[31] A somewhat different approach has been used[32] to describe processes involving the mixing of homopolymers with variable-composition copolymers (binary interactions model). We shall consider these approaches in relation to specific examples.

1. The formation of ion pairs

Polystyrene is known to be incompatible with polyacrylate and polyisobutylene.[33] Nevertheless, polystyrene modified by a sulphonic acid or 4-vinylpyridine is compatible with the above polymers provided that polyacrylate, for example, is modified by 4-vinylpyridine, while polyisobutylene is modified by a sulphonic acid.[34] Such mixtures are compatible over the entire range of compositions, provided that the number of modifying groups in each polymer exceeds 5%.[34] The compatibility is caused by the formation of ion pairs as a result of the protonation of the pyridine ring by the sulphonic acid group. The Coulombic interaction between the ions is sufficient to ensure compatibility. Similarly the formation of stable intermolecular pyridine–carboxylate bonds (ion pairs) ensures the compatibility of oppositely charged polyelectrolytes such as the butadiene–methacrylic acid copolymer and the butadiene–2-methyl-5-vinylpyridinium iodide copolymer.[35,36] The formation of ion pairs leads to the compatibility of the lithium salts of the styrene–methyl methacrylate copolymer with poly(ethylene oxide) and poly(propylene oxide) [37-39] and also of the lithium salts of the ethyl acrylate–acrylic acid copolymer with polyethyleneimine.[40] It has been shown[38] that an increase in the radius of the cation (the replacement of Li by K or Na) in the salts of the styrene–methyl methacrylate copolymer containing 10.4 mol% of acrylate reduces the phase separation temperature of its mixtures with poly(ethylene oxide) and poly(propylene oxide) (systems with a LCT).

2. Other specific interactions

Polyolefins with high molecular weights are as a rule incompatible with other polymers.[33] However, chlorination of polyethylene, for example, makes it compatible with poly(vinyl chloride),[41-43] poly(methyl methacrylate) (when polyethylene contains between 27 and 50% of chlorine),[44-46] polycaprolactone (when polyethylene contains more than 25% of chlorine),[47] and poly(neopentyl glycol adipate) (when polyethylene contains between 42 and 48% of chlorine).[48] The compatibility of chlorinated polyethylene for example, with poly(methyl methacrylate) has been explained by the negative enthalpy of mixing, which can be caused by the formation of hydrogen bonds between the α-hydrogen atoms of polyethylene and the C=O groups of poly(methyl methacrylate) or by dipole–dipole interactions of the type C=O...Cl–C.[44] In particular, the compatibility of chlorinated polypropylene with polyesters has been explained[49] by dipole–dipole interactions of the type C=O...Cl–C, because the chlorinated polypropylene used in the above study did not have sufficient α-hydrogen atoms for the formation of hydrogen bonds with the C=O groups of the polyesters.

The method involving the Fourier transformation of IR spectra has been widely used in recent years to detect the occurrence of specific interactions (for example, hydrogen bonding).[50-62] It has been shown for mixtures of poly-4-vinylphenol with ethylene–vinyl acetate copolymers[52] that this method makes it possible to estimate even quantitatively the strength and number of intermolecular bonds and their temperature dependence. Measurements of the absorption band intensities in the region of 1738 and 1708 cm^{-1} (the frequencies of the free and hydrogen-bonded C=O groups) have been used[52] to estimate the fraction of carbonyl groups participating in the formation of hydrogen bonds and the heats of formation of the complex. The calculations were performed for two specimens: one of them was obtained from solution and dried at room temperature, while the other was first heated to 463 K. The spectra of the first specimen were obtained on heating and those of the second on cooling. In the former case, the free carbonyls participated in the formation of hydrogen bonds. If the intensities (areas) of the absorption bands near 1738 and 1708 cm^{-1} of the dried film obtained from the solution are designated by I_1 and I_2 respectively and those of the bands of the heated film are designated by I_1' and I_2', then

$$a_2(I_1 - I_1') = a_1(I_2' - I_2),$$

whence

$$a_1/a_2 = (I_1 - I_1')/(I_2' - I_2),$$

where a_1 and a_2 are the absorption coefficients for 1738 and 1708 cm^{-1} bands respectively. Having determined the ratio a_1/a_2, it is possible to calculate the fraction of carbonyl groups involved in the formation of hydrogen bonds.

In order to calculate the intermolecular interaction forces, the 1 : 1 complex is represented as a mixture of poly-4-vinylphenol with the ethylene–vinyl acetate copolymer at molar concentrations designated by [–OH] and [–C=O] respectively. The concentration of carbonyl groups involved in the formation of hydrogen bonds is designated by x. We then have in a simplified form

$$\text{—OH} + \text{—C=O} \overset{K}{\rightleftarrows} \text{—OH...O=C—},$$
$$K = x/([\text{—OH}] - x)([\text{—C=O}] - x),$$
$$\ln K = (-\Delta H/RT) + C,$$

where K is the equilibrium constant and ΔH the enthalpy of formation of the complex.

The dependence of $\ln K$ on $1/T$ is illustrated in Fig. 1, which shows that, below the glass point of the system (T_g = 360 K), the dependence of $\ln K$ on $1/T$ becomes non-linear, which may be associated with the non-equilibrium nature of the system. The values of ΔH and C were determined from the initial section of the $\ln K = f(1/T)$ relation and were found to be 21.4 kJ mol^{-1} and −6.55 respectively. Using these values as a basis, Moskala et al.[52] calculated the fraction of carbonyl groups participating in the formation of hydrogen bonds and found that at temperatures below T_g it exceeds the experimental value (curves *2* and *5* in Fig. 2). This is evidence that below T_g the system is indeed in a state of non-equilibrium possibly because of the low mobility of the

macromolecules under these conditions. With increase in the vinyl acetate content in the system, the consolute temperature increases, i.e. hydrogen bonding becomes possible at a higher temperature (Fig. 2). It has also been suggested that the LCT be estimated approximately from the temperature variation of the shift of the stretching vibration frequency of the C=O groups.[53] For example, it has been shown by this method[53] that the LCT should be observed in the temperature range 363–383 K for mixtures of chlorinated poly(vinyl chloride) with the ethylene–vinyl acetate copolymer and in the range 383–403 K for mixtures of poly(vinyl chloride) with the ethylene–vinyl acetate copolymer.

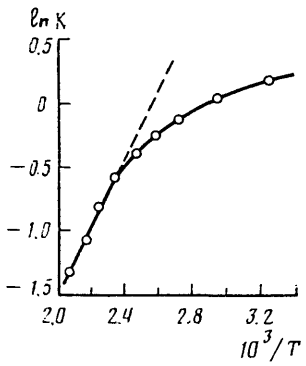


Figure 1. Dependence of $\ln K$ on $1/T$ for an 8 : 8 mixture of poly-4-vinylphenol with the ethylene–vinyl acetate copolymer (45% of vinyl acetate).[52]

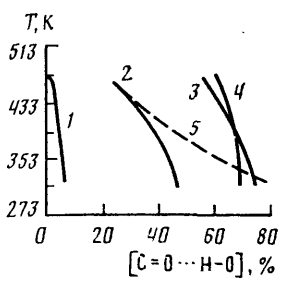


Figure 2. Temperature dependence of the fraction of C=O groups participating in the formation of hydrogen bonds for mixtures of poly-4-vinylphenol with 8 : 2 ethylene–vinyl acetate copolymers for different contents of vinyl acetate in the copolymer:[52] *1*–*4*, experimental data; *5*, calculation. Content of vinyl acetate in the copolymer (%): *1*, 25; *2* and *5*, 45; *3*, 70; *4*, 100.

A shift of the absorption bands of the hydroxy-group (3100–3700 cm^{-1}) has been observed in mixtures of poly(methyl vinyl ether) with polycaprolactone [57] and of poly(methyl vinyl ether) with the polyhydroxylated ether of bisphenol A with increase in the content of the second component.[58] The occurrence of specific interactions has been observed by this method also in mixtures of polycarbonate with poly(hexamethylene adipate),[59] of polycaprolactone with poly(vinylidene fluoride)–vinyl chloride and vinylidene chloride–acrylonitrile homopolymers and copolymers,[59,60] of poly(vinyl chloride) with poly-ε-caprolactone,[51] of poly(vinyl chloride) with poly-α-methyl-α-n-propyl-β-propiolactone and poly-β-valerolactone,[50] of poly(vinyl chloride) with ethylene–dimethacrylamide ethylene dimethacrylate–ethyl acetate–CO, ethylene dimethacrylate–vinyl acetate–CO, and ethylene dimethacrylate–ethylhexyl acrylate–CO copolymers,[62] of poly(vinyl chloride) with ethylene–vinyl acetate copolymers,[53] of poly(vinylidene fluoride) with poly(methyl methacrylate),[52] and also of the styrene–allyl alcohol copolymer with poly(vinyl acetate), polycarbonate, and poly(methyl methacrylate) with different degrees of stereoregularity.[61] In mixtures of the styrene–allyl alcohol copolymer with polycarbonate, the maximum degree of compatibility was attained when the content of OH groups in the copolymer was approximately 9%, while in its mixtures with polycaprolactone the dependence of the thermodynamic interaction parameter on the content of the OH groups passed through a minimum whose position corresponded to an approximately 3% content of these groups in the copolymer.[61,63] The formation of hydrogen bonds is the cause of the compatibility of polyhexafluoromethylvinylcarbinol and its copolymers with styrene (for styrene contents from 0.1 to 12%), poly(methyl methacrylate), poly(ethyl methacrylate), and poly(butyl methacrylate), polycaprolactone, and poly(methyl vinyl ether),[55] and also with poly-2,6-dimethyl-1,4-phenyleneoxybisphenol A carbonate.[56] In these systems, the hydrogen of the hexafluorocarbinol group forms a hydrogen bond with the carbonyl, ether, and carbonate groups of the polymeric admixtures. Under these conditions, an increase in the content of the OH groups in the copolymer raises the phase separation temperature (systems with a LCT).

Numerous studies have been devoted to the compatibility of poly(vinyl chloride) with other polymers.[64–84] A characteristic feature of these mixtures is that hydrogen and electron donor–electron acceptor bonds can be formed in them.[18,85,86] Poly(vinyl chloride) is compatible with poly(alkyl acrylates) when the number of carbon atoms in the alkyl group is less than 4 and with poly(alkyl methacrylates) if the number of carbon groups is less than 6. Thus it follows that poly(vinyl chloride) should mix with poly(methyl methacrylate). In practice, contradictory results have been obtained for this system. Thus the presence of a LCT has been observed,[67] while in other studies[83,84] a HCT has been noted! These contradictions have been explained[67] by the non-equilibrium nature of the system. The results of the study[87] in which the compatibility of poly(vinyl chloride) with poly(alkyl acrylates) and poly(alkyl methacrylates) was investigated are of interest from this point of view. It was observed that the curve relating the Flory–Huggins thermodynamic interaction parameter χ_{12} to the length of the alkyl group in poly(alkyl methacrylates) and poly(alkyl acrylates) passes through a minimum, i.e. there is a minimum concentration of ester groups at which these polymers mix with poly(vinyl chloride). An attempt was made to explain this finding by the relative contributions of the specific and dispersion interactions.[87] For this purpose, the heats of mixing were measured for the oligomers modelling the polymethacrylates and polyacrylates (M = 1000 to 3000) with chlorinated paraffin (M = 437, chlorine content 53.1%), modelling poly(vinyl chloride). The heats (enthalpies) of mixing, measured calorimetrically, proved to be negative in all cases, with the exception of the mixture with oligomethacrylate. The contributions to the heat of mixing by dispersion interactions, calculated on the

basis of the theory of solubility parameters, and by specific interactions (the difference between the overall and calculated heats of mixing) were estimated and it was noted that, in order to ensure compatibility, it is essential that the specific interactions should overlap the dispersion interactions. The heats of mixing of model compounds were clearly correlated with the compatibilities of the corresponding high-molecular-weight components. However, a reliable correlation was not observed between the heats of mixing and the thermodynamic interaction parameters χ_{12}, which can apparently be due to the contribution of the non-combinatorial entropy of mixing to the parameter χ_{12}.[18]

In connection with the use in a number of studies of model low-molecular-weight analogues, mention should be made of the method, proposed by Ebert et al.,[88] for the determination of the heats of mixing of compatible polymers by measuring the heats of the phase separation process. Differential scanning calorimetry (DSC) is used for such measurements. The sign of the DSC peak depends on the sign of the heat of mixing: an endothermic heat of phase separation corresponds to an exothermic heat of mixing and conversely. The size of the DSC peak, which is proportional to the integral heat of phase separation, corresponds approximately to the overall heat of mixing. The method has been tested in relation to a mixture of poly(ethyl acrylate) with poly(vinylidene fluoride). The heats of mixing found by this method agree with the corresponding values for oligomeric mixtures of the same type obtained calorimetrically.

The thermodynamic compatibility of chlorinated poly(vinyl chloride) (chloride content 67.2%) with polycaprolactone, poly(hexamethylene sebacate), poly-α-methyl-α-n-propyl-β-propiolactone, polyvalerolactone, poly(ethylene adipate), poly(ethylene succinate), and poly-β-propiolactone has been explained by specific interactions.[65,69] It has been shown in relation to a mixture of poly-ε-caprolactone with α-deuteriated poly(vinyl chloride) and solutions of polycaprolactone in carbon tetrachloride, tetrahydrofuran (THF), and chloroform and of methyl acetate (as a model analogue of ester groups) in pure water and in solution in carbon tetrachloride, that $-CH\ldots OOC-$ interactions between the $-CH(D)$ groups of poly(vinyl chloride) and the $-COO$ groups of polycaprolactone take place in systems of the poly(vinyl chloride)–polycaprolactone type.[54] The compatibility of the vinylidene chloride–acrylonitrile (20%), vinylidene chloride–vinyl acetate (20%), and vinylidene chloride–vinyl chloride (12%) copolymers with polycaprolactone, poly(hexamethylene sebacate), poly-α-methyl-α-n-propyl-β-propiolactone, and poly(ethylene adipate) is determined by the interaction of the C=O and C–Cl dipoles.[89] The altered thermodynamic interaction parameter is then a function of mixture composition. It is of interest that polylactones are incompatible with poly(vinyl fluoride) and poly(vinylidene fluoride).[79] It has been suggested[79] that this is associated with the significant difference between the electronegativities, atomic radii, and molar attractions of the chlorine and fluorine atoms (fluorine is more negative than chlorine, as a result of which it forms stronger chemical bonds with other atoms[90]). The compatibility of polylactones with poly(vinyl bromide) is greater than with poly(vinyl chlorides). On the other hand, poly(vinylidene fluoride) is compatible with many poly(alkyl methacrylates) and poly(alkyl acrylates) [98] containing short alkyl groups.

The compatibility of chlorinated polymers [poly(vinyl chloride), chlorinated poly(vinyl chloride), chlorinated polyethylene] with poly(ethylene terephthalate), poly(butylene terephthalate), and poly(hexamethylene terephthalate) and also of polyesters of the type of polycaprolactones, poly(2,2,-dimethyl-1,3-propylene adipate), poly(1,4-cyclohexanedimethylene succinate), and poly(2,2-dimethyl-1,3-propylene succinate) with chlorinated polymers has also been explained by the interaction of chlorine atoms with C=O groups.[93–96] Compatibility is achieved for a high chlorine content and for a definite concentration of C=O groups in the polymers.[97] The region corresponding to the compatibility of the hydroxyethyl ether of bisphenol A with aliphatic polyesters,[96] of chlorinated poly(vinyl chloride) with polyesters,[69] of poly(2,6-dimethyl-1,4-phenylene oxide) with aliphatic polyesters, etc.[98] is determined by the CH_3/COO ratio. Consequently it might have been expected that the introduction of C=O groups into the corresponding polymer or copolymer should have ensured its compatibility, for example, with chlorinated polymers, which has in fact been confirmed experimentally.[62,99,100] It has been suggested that in all the examples quoted the compatibility is determined by the formation of hydrogen bonds between the α-hydrogen atoms of poly(vinyl chloride) and the C=O groups of the added polymers or copolymers.

Interesting results have been obtained in the study of the influence of the position of the substituent on the compatibility of poly(2,6-dimethyl-1,4-phenylene oxide) with halogen-substituted styrene copolymers.[101–103] The above polymer is known to be compatible with polystyrene,[33] but is not compatible with poly-*o*-chlorostyrene, poly-*p*-chlorostyrene, or poly-*o*-fluorostyrene.[101,102] Poly(phenylene oxide) is compatible with styrene–halogenostyrene copolymers only for certain contents of halogenostyrene.[105] Thus poly(phenylene oxide) is compatible with *o*-chlorostyrene–*p*-chlorostyrene copolymers for a *p*-chlorostyrene content in the copolymer from 23 to 65%. It is also compatible with *o*-fluorostyrene–*o*-chlorostyrene copolymers for a *o*-chlorostyrene content between 15 and 36% and with *o*-fluorostyrene–*p*-chlorostyrene copolymers for a *p*-chlorostyrene content from 5 to 80%.[102] However, poly(phenylene oxide) is incompatible with the *p*-chlorostyrene–*p*-fluorostyrene copolymer of any composition.[102,103] The authors believe that in the examples quoted the compatibility is determined by repulsion effects, while incompatibility is determined by the specific interaction between different covalently linked comonomers.[103] The halogen content in the styrene–halogenostyrene copolymer for which poly(phenylene oxide) is compatible with the copolymer depends under these conditions on the type of halogen and increases in the following sequence: *o*-Br < *p*-F < *p*-Br < *o*-Cl < *o*-F.

It is noteworthy that in mixtures of homopolymers with copolymers the transition from compatibility to incompatibility occurs much more abruptly after a slight change in the composition of the copolymer.[96,104–106] A general characteristic feature of such mixtures is the presence of the so called "compatibility windows" which are observed also when the corresponding homopolymers are incompatible. For example, neither polystyrene nor polyacrylonitrile are compatible with poly(methyl methacrylate) and poly(ethyl methacrylate). However, the styrene–acrylonitrile copolymer is compatible with them.[107,108] The ethylene–vinyl acetate and butadiene–acrolynitrile copolymers are compatible with poly(vinyl chloride), but the corresponding homopolymers are incompatible with the latter.[73]

Clearly, such behaviour of systems of this kind cannot be accounted for by purely specific intermolecular interactions. In order to describe the thermodynamic behaviour of such systems, a binary interaction model has been proposed,[32] which includes intramolecular and intermolecular interactions. In this model, a mixture of a copolymer with a homopolymer is regarded as a ternary system incorporating as components the comonomers 1 and 2 of the

copolymer with volume fractions φ'_1 and φ'_2 respectively and the homopolymer 3, whose composition differs from those of the comonomers. Account is taken of three types of interactions: 1 with 2, 1 with 3, and 2 with 3. The parameter B_{ij} is used as the characteristic of the interactions. It is related to the usually employed Flory–Huggins thermodynamic interaction parameter χ_{ij} by the expression

$$\frac{B_{ij}}{RT} = \frac{\chi_{ij}}{V_i} = \frac{\chi_{ji}}{V_j} = \bar{\chi}_{ij},$$

where V_i and V_j are the molar volumes of the units of components i and j. For the effective interaction parameter, one can write

$$B = B_{13}\varphi'_1 + B_{23}\varphi'_2 - B_{12}\varphi'_1\varphi'_2, \qquad (1)$$

where B_{12} is the parameter of the interaction between the copolymer components 1 and 2 and B_{13} and B_{23} are the parameters of the interaction of the comonomers (1 and 2) of the copolymer with the monomeric units of the homopolymer (component 3). The first two terms of Eqn. (1) characterise the additional interaction of the polymer 3 with the comonomers 1 and 2, while the third term characterises the interaction between the comonomers 1 and 2 in the copolymer. It is seen from Eqn. (1) that, if $B_{12} > 0$, then the comonomers 1 and 2 are "unlike"[18] and the repulsion forces between them lead to values of B smaller than the additive values. On the other hand, if $B_{12} < 0$, then the values of B are greater than the additive values. Fig. 3 illustrates schematically the possible situation arising for different values of the parameters B_{ij}. The case presented in Fig. 3*b*, where all the B_{ij} are positive, is of interest. In this case the polymer 3 is not miscible with either comonomer 1 or 2. However, if the parameter B_{12} is fairly large, namely

$$B_{12} > (\sqrt{B_{13}} + \sqrt{B_{23}})^2,$$

a range of copolymer compositions φ'_1 arises in which $B < 0$ and this copolymer is compatible with the polymer 3. This apparently in fact accounts for the existence of the "compatibility windows" in many systems: the addition of the polymer 3 to the copolymer "dilutes" the unfavourable interactions between the comonomers 1 and 2 of the copolymer, creating "pure" exothermic conditions even when the binary interactions of the monomer 1 with the monomer 2 are endothermic, i. e. there are no specific interactions between the components.

Fig. 3 also illustrates other possible variants, which may lead to either the compatibility or the incompatibility of the components. For example, Fig. 3*c* illustrates the case where all the binary parameters are negative, i. e. any pair of the three mixture components is compatible. However, the model predicts that, for certain copolymer compositions, the latter will be incompatible with the homopolymer 3. Fig. 3*a* presents the standard situation in which the comonomer 2 of the copolymer mixed exothermically with the homopolymer 3, while the comonomer 1 is immiscible with the homopolymer 3. With increase in the fraction of the comonomer 1 in the copolymer, conditions for endothermic mixing are attained, the point corresponding to the transition from the exothermic to endothermic mixing then depending on the sign and magnitude of the parameter B_{12}.

The proposed model has been used[32] to describe the thermodynamic behaviour of mixtures of copolymers of different composition with other copolymers and homopolymers. For example, mixtures of the hydroxyethyl ether of bisphenol A with a series of polycarbonates, including also their low-molecular-analogues (the CH_x and CO groups), which were regarded as "comonomers", have been investigated.[32] Fig. 4 presents the dependence of the effective interaction parameter B, determined by various methods (calorimetry, melting point depression, sorption), for these mixtures on the volume fraction of the CH_x groups. By combining the parameters B_{ij}, it is possible to obtain with the aid of Eqn. (1) a curve which describes most effectively the experimental data. The continuous curve in Fig. 4 was obtained for $B_{12} = 1050$, $B_{13} = 350$, and $B_{23} = 700$ J cm^{-3}. It is striking that all three interaction parameters proved to be positive, i. e. in this case there are no specific interactions. When a number of other systems were considered, a satisfactory correlation was also found between the predictions of the model and experimental data.[109,110] For example, the model describes satisfactorily the results of the study of the compatibility of chlorinated poly(vinyl chloride) with ethylene–vinyl acetate copolymers[109] and of poly(tetramethylbisphenol A carbonate) with styrene–methyl methacrylate copolymers.[110] Apparently this model can be used to describe the thermodynamic behaviour of mixtures of three polymers and the interaction parameters can be determined using model oligomers.[111]

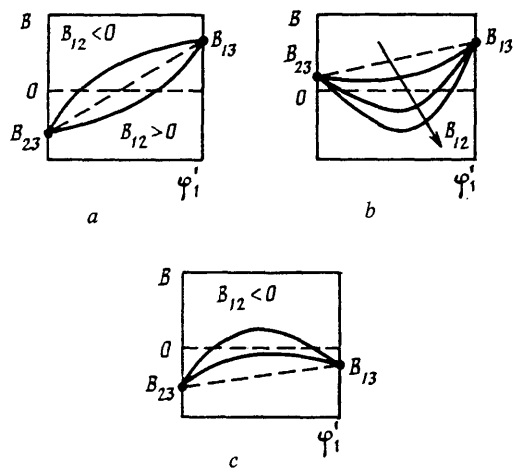


Figure 3. Schemes illustrating the concentration dependence of the effective interaction parameter B in mixtures of a homopolymer with variable-composition copolymers for different ratios of the binary interaction parameters:[32] *a*, B_{12} and $B_{23} < 0$ while $B_{13} > 0$ (upper curve) or B_{12} and $B_{13} > 0$ while $B_{23} < 0$ (lower curve); *b*, all three binary parameters (B_{12}, B_{13}, and B_{23}) are positive; *c*, all three binary parameters (B_{12}, B_{13}, and B_{23}) are negative. The curves in Fig. 3*b* are displaced downwards with increase in the parameter B_{12} and those in Fig. 3*c* are displaced upwards with increase in the parameter B_{12} in absolute magnitude [see Eqn. (1)].

3. The influence of other factors on the compatibility of polymers

(a) The introduction of a third component into a mixture of two polymers. If a third component (a polymer or copolymer), compatible with each of the polymers being mixed, is introduced into a mixture of two incompatible polymers, then such a ternary mixture becomes compatible.[112–116] Thus, when poly(vinylidene fluoride),

which is compatible with poly(methyl methacrylate) and poly(ethyl methacrylate) but the latter are incompatible with one another, is introduced into their mixture, the resulting ternary mixture proves to be compatible.[112] The mixture of poly(vinyl chloride) with the SKN-40 copolymer is compatible, while its mixture with the vinylidene chloride–vinyl chloride copolymer is incompatible.[115] On the other hand, the ternary mixture is compatible. However, the replacement of SNK-40 by SKN-30 makes all three pairs incompatible. Nevertheless, the ternary system is compatible.

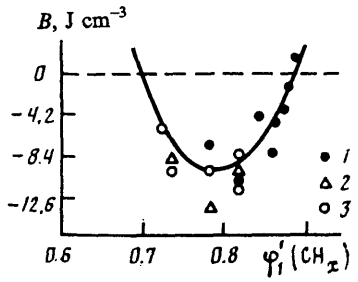


Figure 4. Interaction parameters for mixtures of aliphatic polyesters and their low-molecular-weight analogues with the polyhydroxylated ester of bisphenol A obtained by the calorimetric (*1*), melting point depression (*2*), and sorption (*3*) methods.[32]

Mixtures of polycarbonate with styrene–acrylonitrile copolymers containing 13 or 25% of acrylonitrile in the copolymer are incompatible.[116] However, the addition of even 1% of a polyester of the type of poly(1,4-butylene adipate), poly(1,4-cyclohexane-dimethylene succinate) or poly-ε-caprolactone is sufficient to obtain a single-phase mixture with polycarbonate : copolymer ratios of 1 : 1 or 1 : 3. The region of compatibility in the ternary mixture then increases with increase in the acrylonitrile content in the copolymer from 13 to 25%. The introduction of butadiene and styrene copolymers respectively into a mixture of polybutadiene and polystyrene oligomers lowers the phase separation temperature (system with a UCT).[114]

(b) Deuteriation of one of the mixture components. The temperature and concentration ranges corresponding to the miscibility of two copolymers can be altered by deuteriating one of the components. For example, non-ideal mixing is observed in mixtures of deuteriated and non-deuteriated polystyrenes.[117] Deuteriation of polystyrene increases the phase separation temperature of its mixtures with poly(vinyl methyl ether) (a system with a LCT).[118,119] The replacement of hydrogen by iodine in polystyrene makes the polystyrene–iodine-containing polystyrene system incompatible.[120] The UCT is increased similarly in the polystyrene–polybutadiene system on deuteriation of polybutadiene.[118] The change in compatibility in such systems has been explained by the change in the chain conformation on deuteriation.[118,119]

(c) The influence of the stereoregularity of one of the components. The stereoregularity of one of the mixture components has a significant influence on compatibility.[61,121,122] Thus, according to the results of Fourier transform IR spectroscopic analysis, maximum intermolecular interaction is observed in a mixture of the styrene–allyl alcohol copolymer with syndiotactic poly(methyl methacrylate), while in the mixture with the isotactic homopolymer the interaction is a minimum.[61] Isotactic poly(methyl methacrylate) is incompatible with poly(vinyl chloride) over the entire range of compositions, whereas with the syndiotactic homopolymer it forms a compatible system when the latter contains up to 60% of the syndiotactic polymer. For higher contents of syndiotactic poly(methyl methacrylate) (>60%), the system separates into two phases, one of which contains the pure syndiotactic poly(methyl methacrylate) while the other is a 60 : 40 mixture of syndiotactic poly(methyl methacrylate) and poly(vinyl chloride).[78] The influence of the stereoregularity of poly(methyl methacrylate) and its compatibility with poly(vinylidene fluoride) can be inferred from the Flory–Huggins thermodynamic interaction parameter χ_{12}, which is −0.13, −0.10, and −0.06 for mixtures with isotactic, atactic, and syndiotactic poly(methyl methacrylates) respectively.[122]

(d) The influence of the solvent. In many cases mixtures of polymers are obtained from their solutions in a common solvent.[33] It has been demonstrated experimentally and theoretically[17,123,124] that the compatibility of polymers in a common solvent depends on the difference between the parameters of the thermodynamic interaction of the solvent with each polymeric component (the so called "$\Delta\chi$ effect"[123]). Hence errors may arise in the assessment of the compatibility of two polymers isolated from a common solvent. For example, polystyrene is compatible with poly(vinyl methyl ether),[11] but in solvents with different affinities for the two polymers "closed regions" of incompatibility may be observed.[124] The films obtained from such solutions may contain microheterogeneous regions because during the evaporation of the solvent the system passes through a region of incompatibility and the structure formed in this composition range is retained, since the viscosity of the mixture increases significantly under these conditions.[125]

Thus the compatibility or incompatibility of polymers in solution does not alone guarantee their compatibility or incompatibility after the removal of the solvent. A mixture of poly(bisphenol A carbonate) with poly(methyl methacrylate), which many workers have regarded as incompatible,[11,126] may serve as a typical example. It has been shown[127] that in a number of instances the mixture separates into two phases: for example, if it has been obtained from solution in methylene chloride and THF by evaporating the solvent or by precipitating the polymers from the solution with methanol and also if it has been prepared from the melt. On the other hand, the system obtained by precipitating the same polymers from the same solvents with heptane is compatible over the entire range of compositions and it has a LCT. This must be borne in mind in considering systems in which both a LCT and a UCT are observed.

The influence of the difference between the affinities of the solvent for each polymer can exceed the influence of the interaction between the polymers on their compatibility in solution. For example, in a study of mixtures of poly(ethylene oxide) with the styrene–methacrylic acid copolymer,[128] it was observed that the compatibility of these polymers in benzene increases with increasing content of methacrylic acid in the copolymer (up to 8 mol%) as a consequence of weak specific interactions beween the polymers. The same effect is observed in THF but it is weaker, while in chloroform the polymers are incompatible.

The study of the influence of the affinity of plasticising agents on the compatibility of polychloroprene and butadiene-styrene rubbers[129] showed that the compatibility of the rubbers is impaired

in the presence of plasticisers which are good solvents for both rubbers (dibutyl sebacate and MP-604 oil), while after the introduction of a poor solvent (stabiloil-18) it hardly changes. The reduction of the compatibility of rubbers after the introduction of a good solvent has been explained[129] by the shielding of the functional groups of the rubbers as a result of the solvation of their macromolecules by the plasticisers. On the other hand, it has been shown[111] that, after the introduction into a mixture of two thermodynamically compatible polymers of a third polymer, which forms mixtures with each of the remaining polymers having similar consolute temperatures, the compatibility of the latter polymers increases. A significant decrease in compatibility occurs when the consolute temperatures for mixtures of the added third polymer with each of the blended polymers differ significantly. We may note that this system can be described satisfactorily within the framework of the binary interactions model.[32]

Apart from the factors enumerated, the consolute temperature is influenced significantly also by applied pressure.[130-135] Thus it has been observed for mixtures of poly(ethyl acrylate) with poly(vinylidene fluoride)[130] that, when the content of the latter in the mixture is up to 30%, the turbidity point for the system initially decreases with increase in pressure, then passes through a minimum, and finally increases. With increase in the content of poly(vinylidene fluoride) in the mixture (in excess of 40%), the turbidity point monotonically increases with increasing pressure (system with a LCT). In mixtures of poly(2,6-dimethyl-1,4-phenylene oxide) with styrene–*p*-fluorostyrene copolymers, the LCT increased with increasing pressure over the entire range of the latter.[131] In mixtures having a UCT (mixtures of oligostyrenes with oligobutenes and oligopropylenes),[132] an increase in pressure results in an increase in the UCT.

Whereas the parabolic dependence of the consolute temperature on pressure predicted by the theory for polymer solutions[17] has been confirmed experimentally,[133] for mixtures of polymers the available experimental data are insufficient to reach general conclusions. It is only known that the application of an electric field increases the LCT.[136]

III. The stabilisation of dispersions and regulation of the properties of materials based on mixtures of thermodynamically incompatible polymers

Typical examples of the modification of one polymer by the addition of another are provided by the preparation of rubber-reinforced glass plastics,[137,138] epoxide resins,[139] rubbers reinforced by thermoplastics and thermoreactive resins, etc.[140] All these systems are multiphase. Important factors determining the properties of such systems are the degree of dispersion of the additive in the matrix of the other polymer, adhesion at the interface, and the structure and properties of the interfacial layer.[3,141] The adhesion between the phases is especially important, because, for example, under the conditions of poor adhesion, the mechanical stresses in one phase are not transmitted effectively to the second phase, as a result of which the mechanical properties of the system may be impaired.[3] Consequently, with the exception of certain special cases,[142] a good adhesion between the phases is essential in multiphase mixtures. For this purpose, one introduces the so called "compatibility inducers", which may be block or graft copolymers having blocks with the same chemical composition as the blended polymers,[3,143] as well as other polymers improving the compatibility of the initial components.[144] The mutual binding of the phases can also be improved by creating interphase cross-links[145-148] and by generating interpenetrating networks.[149]

In this review we shall consider mainly the results of the latest studies on dispersion stabilisation processes and methods for the regulation of properties of systems obtained from thermodynamically incompatible polymers.

1. Introduction of compatibility inducing additives

One of the ways of solving the problem of the stability of mixtures of incompatible polymers involves the wide scale employment of block and graft copolymers,[3,143] constituting compatibility inducing additives, especially in the preparation of impact-resistant compositions.[3] It has been shown in a number of studies[150-153] that the introduction of a graft copolymer such as hydrogenated butadiene–styrene into a mixture consisting of low density polyethylene and polystyrene increases the tensile strength but the elongation at rupture remains small. On the other hand, when 9% of a diblock copolymer with an equivalent composition is introduced into the mixture, then the tensile strength, elongation at rupture, and Young's modulus all increase and other system characteristics are also improved. With increase in the molecular weight of the copolymer, these characteristics are improved and even synergism of the properties is observed. A similar effect has been noted also after the introduction of such a copolymer into a mixture of high density polyethylene with polystyrene.

Comparative studies of the morphology and mechanical properties of polyethylene–polystyrene mixtures have shown that the introduction into them of a styrene–butadiene block copolymer whose blocks are separated by a styrene–butadiene statistical copolymer [for example of the type PS–$(PS/PBD)_{stat}$–PBD] induces a greater effect than introduction of the simple diblock copolymer.[153] The authors believe[153] that the unique effect of this copolymer is caused by its partial compatibility with polystyrene and polyethylene at the interface, i.e. it behaves as a stabilising agent for the homopolymers and promotes the creation of a "stepwise" modulus responsible for the improvement of the mechanical properties. Furthermore, after the introduction of such a block copolymer there is a significant increase in the dispersion of this system and synergism of the properties is manifested in the range of compositions where the mixture is enriched in the polymer matrix. When the mixture contains up to 80% of polystyrene, a system with a structure of the "network in network" type is produced. The introduction of the α-methylstyrene–methyl methacrylate block copolymer into a mixture of poly(vinylidene fluoride with poly-α-methylstyrene also leads to a decrease in the size of the dispersed particles and to an increase in tensile stress and Young's modulus.[151] The ethylene–propene copolymer, introduced into a mixture of polyethylene with polypropylene, also has an emulsifying effect.[154-157] The introduction of a copolymer increases the affinity between the components, which is manifested by a more effective homogenisation of the mixtures.[154] As a result, the mixtures are deformed more uniformly and are characterised by greater elongations with rupture. In the given instance, the macromolecules of the copolymer, dispersed in amorphous regions of polyethylene and polypropylene, ensure high degrees of interpenetration of the components.[154] Polyethylene and polypropylene are partially compatible in the melt,[155,156] but the introduction of the copolymer stabilises the two-phase structure of the melt.

An emulsifying effect has been observed also after the introduction of the α-methylstyrene–graft methyl methacrylate copolymer into a mixture of poly(vinylidene fluoride) with poly-α-methylstyrene.[157] In particular, the size of the particles diminished significantly in this system, a maximum appeared on the relation between the tensile strength and composition for a 70% content of poly(vinyl fluoride), and additivity of Young's moduli was observed. On the other hand, in the absence of the copolymer, the tensile strength and Young's moduli were described by curves with a minimum.

Other examples of the use of block or graft copolymers as compatibility inducing additives may be found in a review.[3] The choice of the appropriate copolymer should be based, according to Paul and Newman,[3] on the following requirements: (1) it must reduce the interfacial energy, (2) it must promote a finer dispersion of the components during the mixing process, (3) it must stabilise the mixture and prevent the separation of the components, and (4) it must improve the adhesion between the phases. The desired effects can be attained when the appropriate copolymer is located on the interface between two phases.[3]

The compatibility inducing agent may be also a third polymeric component introduced into a mixture of two thermodynamically incompatible polymers.[158–161] For example, in order to improve the properties of mixtures of low density polyethylene with other polymers [polystyrene poly(vinyl chloride), polypropylene], additives such as the ethylene–propene copolymer, natural rubber, polybutadiene, the acrylonitrile–butadiene–styrene ternary copolymer (ABS resin), copolymers of the butadiene–styrene type with a 72% content of butadiene, chlorinated polyethylene containing 42 and 20% of chlorine, and polyurethane containing ethylene adipate blocks.[161] It has been shown that the introduction of a third component into 1 : 1 mixtures improves the mechanical properties and that the increase in impact resistance is accompanied by an increase in elongation at rupture. Particularly high impact resistances and elongations at rupture have been observed after the introduction of the butadiene–styrene rubber into a mixture of polystyrene with polyethylene. The improvement of the properties of such systems can be accounted for by the formation of an elastomeric layer at the interface and by the dispersing capacity of the modifying additives. The improvement of the interfacial interaction and hence the improvement of the physicomechanical properties of mixtures of various rubbers (strength, ozone and weather resistance, resistance to thermal ageing, reduction of the embrittlement temperature, and reduction of the density of vulcanising agents) is promoted by the introduction of chlorinated polymers into such rubbers.[143] The modifying effect of additives of this kind is mainly determined by their polarity. Thus the modification of a mixture of thermoplastic polyurethane with poly(vinyl chloride) by a more polar rubber leads to the formation of compositions with high strength parameters.[162] The interaction between the components of a heterogeneous mixture of two polymers intensifies also after the introduction of surfactants of different classes,[163] for example, after the introduction of ionogenic surfactants into mixtures of poly(vinyl chloride) with natural rubbers. The introduction of a surfactant into a mixture of an epoxide resin and silicone rubber ensures the appearance of a region of compatibility in oligomer–natural rubber systems.[164] The factor determining the properties of mixtures of poly(vinyl chloride) with chlorinated polyethylene is the compatibility of the added oligomer (high-molecular-weight oligobutadienes and oligobutadienes with OH and CN groups) with each mixture component.[159] In certain cases, the additives introduced increased the rate of "dissolution" of, for example, rubbers in one another at the same temperature of the treatment of the mixture, which is important for the preparation of layered (doubled) compositions (the introduction of peroxides into a mixture of polybutadiene with butadiene–styrene rubber[165]).

2. The role of interphase cross-links

One of the effective ways of stabilising mixtures of incompatible polymers is interphase cross-linking.[145–148] Thus cross-linking has been used to increase the stability of mixtures of polyethylene with poly(vinyl chloride).[145] The cross-linking of poly(vinyl chloride) was achieved by introducing 6-diallylamino-1,3,5-triazine-2,4-dithiol (DAATD) and polyethylene was cross-linked by introducing a mixture of DAATD with peroxides of different types. It has been shown that the more intense the adhesion interaction between the components, the better the mechanical properties of the system (strength and elongation at rupture). Nakamura et al.[145] attribute this effect to the formation of chemical bonds between poly(vinyl chloride) and polyethylene phases during the mixing process and after pressing. The introduction of the same cross-linking agent (DAATD) into a mixture of fluororubbers based on vinylidene fluoride or hexafluoropropene with epichlorohydrine and polyisoprene led to the formation of vulcanised rubbers with a high degree of cross-linking and good adhesion and mechanism properties. In a pure form, these rubbers are incompatible, but the introduction of the additive leads to a high degree of covulcanisation of individual rubbers at the interface.[146] Heating of the system or the addition of tetraalkylammonium bromide together with DAATD facilitates significantly the formation of cross-linked at the interface.

The modification of polystyrene by peroxide, dithiocarbamate, or perthiocarbamate groups ensures its mixing with natural rubber, the ethylene–propylene copolymer, butadienenitrile rubber, polypropylene, and polybutadiene.[147] The vulcanised mixtures of modified polystyrene with, for example, polybutadiene behave under dynamic conditions similarly to three-block copolymers. Polystyrene modified by groups which react with the double bonds of the elastomer reinforces the elastomer matrix.[147,148]

3. Specific interfacial interactions

Specific interactions at the interface also promote the stability of two-phase polymer mixtures.[166–170] For example, mixtures of poly(urethane-urea) with poly(vinyl chloride) are incompatible, but the formation of hydrogen bonds between the α-hydrogen atoms of poly(urethane-urea) and the chlorine atoms of poly(vinyl chloride) ensures effective interfacial adhesion.[166] The impact strength of the system passes through a maximum for a 7.5–15% content of poly(urethane-urea).

The adhesion between phases increases when electron donor–electron acceptor bonds are formed at the interface.[167,168] Such bonds are formed in mixtures of electron-donating and electro-accepting polycarbonates, polyterephthalates, or polyisophthalates obtained from 2-(*p*-dimethylaminobenzyl)propane-1,3-diol (donor) and 2-(3,5-dinitrobenzyl)propane-1,3-diol (acceptor)[168] and also from poly[*N*-(2-hydroxyethyl)carbazolyl methacrylate] (donor) and poly(methacryloyloxy-β-hydroxyethyl-3,5-dinitrobenzoate) (acceptor).[169] In the latter case the intermolecular complex formation increases the modulus of the mixture in the region of low-frequency dynamic loads and high temperatures by three orders of magnitude compared with the pure components. It is believed[169] that intermolecular complex formation leads to the formation of thermoreversible networks with an unusual topology which results in

the expansion of the frequency range of the elastic response of the mixtures. The presence of a maximum in the dependence of the decomposition energy on the composition of mixture of the sodium and zinc salts of an ethylene ionomer with rubbers (acrylonitrile or carboxylated acrylonitrile rubbers) has also been explained by the ionic interaction of polar phases.[170] A tenfold increase in the impact resistance of powdered mixtures of poly(phenylene oxide) (50 parts), the zinc salt of sulphonated (1.4 mol% of sulphur), polystyrene (9 parts), sulphonated (0.6 or 1.4 mol% of sulphur) polystyrene (9 parts), the ethylene–propylene copolymer (9 parts), and zinc stearate (9 parts) in the presence of triphenyl phosphate (14 parts) is also caused by the interaction at the interface.[167] (The mixtures were obtained by dry blending with subsequent extrusion at 453–523 K.)

4. The addition of small amounts of one polymer to another

Numerous studies devoted to the influence of the addition of small amounts of one polymer to another on the physicomechanical and physicochemical properties of the systems, especially on their viscosity, have been published in recent years.[171–181] Viscosity is an important technological parameter and the characteristic features of its variation with composition have been examined in particularly great detail. Attention has been concentrated on the elucidation of the mechanism of the influence of additives on the viscosity.[172,181] A series of anomalies in the concentration dependence of the viscosities of melts of mixtures of polymers (over a narrow range of concentrations, predominantly for a low content of one of the components) have been discovered.[181] As a rule, at low concentrations of the additives a sharp decrease in viscosity is observed. For example, the viscosity of the incomptible thermoplastic polyamide–liquid crystal copolyester system based on 6-hydroxy-2-naphthoic and *p*-hydroxybenzoic acids diminishes sharply in the presence of small amounts of a copolymer in the mixture.[174] The addition of vinyl chloride–vinyl acetate or vinyl chloride–propylene copolymers reduces the viscosity of poly(vinyl chloride) and facilitates its treatment.[175] The greatest effect is then exhibited by copolymers with a low molecular weight. The addition of 10% of butadiene-styrene rubber to the butadiene–styrene–butadiene copolymer diminishes the viscosity of the latter almost by a factor of 2,[176] which has been explained by the localisation of the added rubber with short chains at the interface and the consequent facilitation of the flow of the copolymer. The similar introduction of small amounts of the styrene–maleic anhydride (14% of the anhydride) copolymer reduces significantly the fluidity of poly(bisphenol A polycarbonate).[177]

It is possible to quote very many similar examples.[182–186] In our view, among the existing explanations of the observed anomalies, that according to which their appearance is associated with the transition of the system from the single-phase state to the two-phase state and conversely can be regarded as the most acceptable.[180,181] This was first demonstrated in a study where the concentration dependence of the viscosity was compared with the Flory–Huggins prameter χ_{12} of the thermodynamic interaction between the mixture components in melts at identical temperatures. Satisfactorily parallel concentration variations of the viscosity and the parameter χ_{12} were observed. In particular, for positive values of χ_{12} (thermodynamically incompatible system), the viscosity proved to be less than the additive value, while for negative values (compatible system) it proved to be higher than the additive value. It was concluded that a sharp fall of the viscosity of melts of polymer mixtures at low concentrations of the added polymer occurs when the system passes from the single-phase to the two-phase state.[179] The form of the phase diagram apparently make it possible to predict the concentration and temperature dependences of the viscosities of melts of polymer mixtures. Hitherto, such comparison of the concentration variation of the viscosity with the phase diagram has been achieved in only one study.[179]

Extremum changes have been observed also in a number of other physicochemical and physicomechanical characteristics of systems at low concentrations of the added polymer.[187–200] Thus the improvement of high density polyethylene after the introduction into the latter of small amounts of thermoelastoplastics has been explained by the latter being distributed in the non-ordered regions of the polyethylene with retention of the primary crystalline state.[191]

It has been suggested that the increase in strength on extension of polypropylene containing small amounts of a thermoelastoplastic (up to 1%) occurs as a result of the surface interaction of the polystyrene units with the structural formations in polypropylene, which leads to the joint orientation of polypropylene and the thermoelastoplastic.[193] The authors[191] concluded that the micro-additives play the role of a filler of the structural defects, facilitating the plastic deformation and ensuring the formation of a finer and uniform structure. The reason why the strength properties of the systems are impaired on further increase in the amount of the additives are still not understood.

The high tensile strength (above the additive value) of low density polyethylene with added ethylene–propylene copolymer has been explained[195] by the partial compatibility of the copolymer with polyethylene in the melt: on cooling the mixture of polyethylene with the crystalline copolymer (with a degree of crystallinity from 1 to 20%), a cross-linked matrix is formed as a result of the joint crystallisation. The synergism of the properties of mixtures of high density polyethylene with the ethylene–propylene copolymer and also of isotactic polypropylene with the same copolymer has been explained by partial compatibility.[196] The strength properties are improved with increase in the compatibility of the modifying additive and the polymers. This is achieved, for example, by increasing the content of the component A in a copolymer of the A–B type when it is mixed with the corresponding type A homopolymer. The necessity for the partial compatibility of the components in order to achieve a high impact strength was also noted in a study of mixtures of poly(bisphenol A carbonate) with the styrene–acrylonitrile copolymer and the same copolymer grafted on polybutadiene.[197] The change in the position of the mechanical losses peak and of the complex shear modulus for a styrene block copolymer modified by resins has also been explained by the compatibility of the modifying additive with the polymer matrix.[198]

It is known that an excess volume of mixing obtained for compatible systems, i.e. $\Delta V = V_{mix} - \Sigma\varphi_i V_i < 0$. This reduces the number of external degrees of freedom[18] and hence lowers the mobility of the chains and increases the packing density. Partial compatibility ensures the mutual binding of the phases, i.e. interfacial adhesion as a result of which the physicomechanical characteristics of systems of this kind are improved.[3]

IV. Conclusion

The examples examined in the review indicate convincingly that polymers differing in chemical structrure and involving opposite principles, which complement one another, are most effectively miscible[10] (the concept of "the mutually complementing difference"

already mentioned[17]). Since in such cases the enthalpy of mixing is negative, systems of this kind should be characterised by a LCT. Indeed, according to Krause,[9] among the known thermodynamically compatible polymer pairs, 75% have a LCT. Consequently, in order to ensure thermodynamic compatibility it is essential to select components such that their functional groups are capable of strong interaction or one or both components must be modified in such a way that the "mutually complementing differences" are ensured.

In devising compositions which need not satisfy the requirement of thermodynamic compatibility, it is necessary to solve the problem of the stabilisation of the dispersion by introducing "compatibility inducing additives", by organising interphase cross-links, or by ensuring partial compatibility of the components both in the preparation of the composition and in its conversion into finished articles. In other words, it is essential to ensure a satisfactory interfacial adhesion at least in those cases where the system must have a high strength.

References

1. V E Gul', M S Akutin *Osnovy Pererabotki Plastmass* (Principles of the Processing Plastics), Izd. Khimiya, Moscow, 1985, 400 pp
2. D R Paul, J W Barlow *IV Symp. Plast. 81: Polymer Blends, Warwick 1981*, London, 1981, p. 71/1
3. D R Paul, S Newman (Editors) *Polymer Blends* (Translated into Russian), Izd. Mir, Moscow, 1981, Vol. 1, 550 pp; Vol. 2, 454 pp
4. A F Yee *Polym. Eng. Sci.*, 1977, **17** 213
5. J R Fried, W J MacKnight, F E Karasz *J. Appl. Phys.*, 1979, **50** 605
6. N N Mel'nikova, T P Chistyakova, A Yu Shveikina, et al., Manuscript deposited at the TsNIITEILegprom., 29. 04. 86, No. 1621-ln
7. A F Yee, M A Maxwell *J. Macromol. Sci.*, 1980, **17B** 513
8. L M Robeson *Polymer Compatibility and Incompatibility. Principles and Practice* (Edited by K Sole), Symp. Series, Harwood Acad. Publ., Midland, Michigan, 1981, Vol. 2, p. 177
9. S Krause *Pure Appl. Chem.*, 1986, **58** 1553
10. A A Tager, V S Blinov *Usp. Khim.*, 1987, **56**(6) 1004 [English translation in *Russ. Chem. Rev.*, 1987(6)]
11. A E Nesterov, Yu S Lipatovk *Fazovoe Sostoyanie Rastvorov i Smesei Polimerov* (The Phase State of Solutions and Mixtures of Polymers), Izd. Naukova Dumka, Kiev, 1987, 166 pp
12. V N Kuleznev, L S Krokhina *Usp. Khim.*, 1973, **42**(7) 1278 [English translation in *Russ. Chem. Rev.*, 1973(7)]
13. D R Paul, C E Vinson, C E Locke *Polym. Eng. Sci.*, 1972, **12** 156
14. C E Locke, D R Paul *J. Appl. Polym. Sci.*, 1973, **17** 2597
15. D R Paul, J W Barlow *J. Macromol. Sci., Rev. Macromol. Chem.*, 1980a, **18** C 109
16. W M Barenstein, D Heikens, P Piet *Polymer*, 1974, **15** 119
17. O Olabisi, L M Robeson, M T Shaw *Polymer-Polymer Miscibility*, Head Press, New York etc., 1979, 370 pp
18. A E Nesterov, Yu S Lipatov *Termodinamika Rastvorov i Smesei Polimerov* (Thermodynamics of Polymer Solutions and Blends), Izd. Naukova Dumka, Kiev, 1984, 294 pp
19. A A Tager *Kompozitsionnye Polimernye Materialy* (Composite Polymeric Materials), Izd Naukova Dumka, Kiev, 1987, No. 33, p. 3
20. R Koningsveld, L A Kleinjens *J. Polym. Sci., Polym. Symp.*, 1977, (61) 221
21. A A Tager *Fizikokhimiya Polimerov* (Physical Chemistry of Polymers), Izd. Khimiya, Moscow, 1978, 544 pp
22. T Nishi *J. Macromol. Sci., Phys.*, 1980, **B17** 517
23. A A Tager, T I Scholohovich, Yu S Bessonov *Eur. Polym. J.*, 1975, **11** 231
24. A A Tager, T I Sholokhovich, I M Sharova, et al. *Vysokomol. Soedin., Ser A*, 1975, **17** 2766
25. A A Tager *Vysokomol. Soedin., Ser A*, 1977, **19** 1659
26. G F Roginskaya, V N Volkov, A I Kusaev, et al. *Vysokomol. Soedin., Ser A*, 1984, **26** 1020
27. A E Chaelykh, I N Sapozhnikova *Usp. Khim.*, 1984, **53**(11) 1827 [English translation in *Russ. Chem. Rev.*, 1984(11)]
28. A V Kotova, A E Chalykh, N N Avdeev, S M Mezhikovskii *Vysokomol. Soedin., Ser A*, 1982, **24** 460
29. A E Chalykh, I N Sapozhnikova *Vysokomol. Soedin., Ser A*, 1981, **23** 169
30. A E Chalykh, N N Avdeev, S M Mezhikovskii *Dokl. Akad. Nauk SSSR*, 1978, **22** 464
31. A A Tager *Vysokomol. Soedin., Ser A*, 1984, **26** 659
32. D R Paul, J W Barlow *Polymer*, 1984, **25** 487
33. A E Nesterov *Spravochnik po Fizicheskoi Khimii Polimerov* (Handbook of the Physical Chemistry of Polymers), Vol. 1, *Svoistva Rastvoro i Smesei Polimerov* (The Properties of Polymer Solutions and Blends), Izd. Naukova Dumka, Kiev, 1984, 375 pp
34. A Eisenberg, P Smith, Z-L Zhou *Polym. Eng. Sci.*, 1982, **22** 1117
35. E P Otocka, F P Eirich *J. Polym. Sci. A-2*, 1968, **6** 921
36. E P Otocka, F P Eirich *J. Polym. Sci. A-2*, 1968, **6** 1857
37. M Hara, D Wollmann, A Eisenberg *Am. Chem. Soc., Polym. Prepr.*, 1984, **25** 280
38. M Hara, A Eisenberg *Macromolecules*, 1987, **20** 2160
39. M Hara, A Eisenberg *Macromolecules*, 1984, **17** 1335
40. A Simmons, A Eisenberg *Am. Chem. Soc., Polym. Prepr.*, 1986, **27** 341
41. C P Doubé, D J Walsh *Eur. Polym. J.*, 1981, **17** 63
42. C P Doubé, D J Walsh *Polymer*, 1979, **20** 1115
43. C Zhikuan, D J Walsh *Makromol. Chem.*, 1983, **184** 1459
44. D J Walsh, S Laingle, C Zhikuan *Polymer*, 1981, **22** 100
45. D J Wash, J S Higgins, C Zhikuan *Polymer*, 1982, **23** 336
46. C Zhikuan, S Ruona, D J Walsh, J S Higgins *Polymer*, 1983, **24** 263
47. G Belogrey, R E Prud'homme *J. Polym. Sci., Polym. Phys. Ed.*, 1982, **20** 191
48. S H Goh, K S Siow, T T Nguyen, A Nam *Eur. Polym. J.*, 1984, **20** 65
49. D Allard, R E Prud'homme *J. Appl. Polym. Sci.*, 1982, **27** 559
50. D F Varnell, D F Coleman *Polymer*, 1981, **22** 1324
51. D F Coleman, J Zarian *J. Polym. Sci., Polym. Phys. Ed.*, 1979, **17** 837
52. E J Moskala, S E Howe, P C Painter, M M Colemann *Macromolecules*, 1984, **17** 1671
53. D F Coleman, E J Moskala, P C Painter, et al. *Polymer*, 1983, **24** 1410
54. D F Varnell, E J Moskala, P C Painter, M M Colemann *Polym. Eng. Sci.*, 1983, **23** 658
55. E M Pearse, T K Kwei, B Y Min *J. Macromol. Sci.*, 1984, **A21** 1181

56. S P Ting, E M Pearse, T K Kwei *J. Polym. Sci., Polym. Lett. Ed.*, 1980, **18** 201
57. E J Moskala, M M Colemann *Polym. Commun.*, 1983, **24** 206
58. M M Colemann, E J Moskala *Polymer*, 1983, **24** 251
59. D F Varnell, J P Runt, M M Colemann *Polymer*, 1983, **24** 37
60. A Carton, M Aubin, R E Prud'homme *J. Polym. Sci., Polym. Lett. Ed.*, 1983, **21** 45
61. F Cangelosi, M T Shaw *Am. Chem. Soc., Polym. Prepr.*, 1983, **24** 258
62. M Iskander, C Tran, L M Robeson, L M McGrath *Polym. Eng. Sci.*, 1983, **23** 682
63. R S Barnum, S H Goh, D R Paul, J W Barlow *J. Appl. Polym. Sci.*, 1981, **26** 3917
64. K Marčinčin, A Ramonov, B Pollak *J. Appl. Polym. Sci.*, 1972, **16** 2239
65. G Belogrey, M Aubin, R E Prud'homme *Polymer*, 1982, **23** 1051
66. Y P Singh, R P Singh *Eur. Polym. J.*, 1984, **20** 201
67. H Jager, E J Vorenkamp, G Challa *Polym. Commun.*, 1983, **24** 290
68. M H Lehr *Polym. Eng. Sci.*, 1985, **25** 1056
69. J S Ziska, J W Barlow, D R Paul *Polymer*, 1981, **22** 918
70. M Aubin, R E Prud'homme *Polymer*, 1981, **22** 1223
71. J F Kennedy *J. Polym. Sci., Polym. Chem. Ed.*, 1976, **14** 123
72. G A Zakrzewski *Polymer*, 1973, **14** 347
73. C F Hammer *Macromolecules*, 1971, **4** 69
74. L M Robeson *J. Polym. Sci., Polym. Lett. Ed.*, 1978, **16** 261
75. G Belogrey, M Aubin, R E Prud'homme *Polymer*, 1982, **23** 1051
76. D J Hourston, I D Hughes *Polymer*, 1979, **20** 823
77. D J Walsh, J G McKeown *Polymer*, 1980, **21** 1130
78. J W Schurer, A De Boer, G Challa *Polymer*, 1975, **16** 201
79. M Aubin, R E Prud'homme *J. Polym. Sci., Polym. Phys. Ed.*, 1981, **19** 1245
80. D J Walsh, J G McKeown *Polymer*, 1980, **21** 1335
81. D J Walsh, G L Cheng *Polymer*, 1982, **23** 1965
82. D J Walsh, G L Cheng *Polymer*, 1984, **25** 19
83. A E Chalykh, I N Sapozhnikova *Vysokomol. Soedin., Ser. A*, 1979, **21** 1664
84. I N Razinskaya, B N Shtarkman, L I Batueva, et al. *Vysokomol. Soedin.*, 1979, **21** 1860
85. O Olabisi *Macromolecules*, 1975, **8** 316
86. B N Shtarkman *Plastifikatsiya Polivinilkhlorida* [The Plasticisation of Poly(vinyl chloride)], Izd. Khimiya, Moscow, 1975, 248 pp
87. D J Walsh, G L Cheng *Polymer*, 1984, **25** 499
88. M Ebert, R W Garbella, J H Wendorff *Macromol. Chem. Rapid. Commun.*, 1986, **7** 65
89. M Aubin, Y Bedard, M-F Morrisette, R E Prud'homme *J. Polym. Sci., Polym. Phys. Ed.*, 1983, **21** 233
90. W A Sheppard, C M Sharts *Organic Fluorine Chemistry* (Translated into Russian), Izd. Mir, Moscow, 1972, 480 pp
91. T Nishi, T T Wang *Macromolecules*, 1975, **8** 909
92. R E Bernstein, C A Cruz, D R Paul, J W Barlow *Macromolecules*, 1977, **10** 681
93. E M Woo, J W Barlow, D R Paul *J. Appl. Polym. Sci.*, 1983, **28** 1347
94. M Aubin, R E Prud'homme *Am. Chem. Soc., Polym. Prepr.*, 1983, **24** 182
95. **M Aubin, R E Prud'homme *Polym. Eng. Sci.*, 1984, 24** 350
96. J E Harris, S H Goh, D R Paul, J W Barlow *J. Appl. Polym. Sci.*, 1982, **27** 839
97. C Trembley, R E Prud'homme *J. Polym. Sci., Polym. Phys. Ed.*, 1984, **22** 1857
98. P Alexandrovich, F E Karasz, W J MacKnight *Polymer*, 1977, **18** 1022
99. L M Robeson, J E McGreath *AIChE Symp. Ser.*, 1977, **73** 151
100. L M Robeson, J E McGreath *Polym. Eng. Sci.*, 1977, **17** 300
101. R Vuković, V Kuresević, F E Karasz, et al. *Int. Union Pure Appl. Chem., 28th Macromol. Symp. Amherst., 1982*, p. 707
102. R Vuković, V Kuresević, N Segudović, et al. *J. Appl. Polym. Sci.*, 1983, **28** 1379
103. G Brinke, F E Karasz, W J MacKnight *Macromolecules*, 1983, **16** 1827
104. F Kollinsky, G Market *Adv. Chem. Ser.*, 1971, (99) 175
105. V R Landi *Rubber Chem. Technol.*, 1975, **45** 222
106. N F Bakeev, Z F Zharikova, Yu M Malinskii, A L Izyumnikov *Vysokomol. Soedin., Ser. B*, 1977, **19** 823
107. J S Chiou, D R Paul, J W Barlow *Polymer*, 1982, **23** 1543
108. D J Stein, R H Yung, K H Illers, H Hendus *Angew. Makromol. Chem.*, 1974, **36** 83
109. T Shiomi, F E Karash, J W MacKnight *Macromolecules*, 1986, **19** 2644
110. K E Min, D R Paul *Macromolecules*, 1987, **20** 2828
111. K E Min, J S Chiou, J W Barlow, D R Paul *Polymer*, 1987, **28** 1721
112. T K Kwei, H L Frish, W Radigan, S Vogel *Macromolecules*, 1977, **10** 787
113. S H Goh, K S Slow *Thermochim. Acta*, 1985, **105** 191
114. D Rigby, J L Lin, R-J Roe *Macromolcules*, 1985, **18** 2269
115. Y Y Wang, S A Chen *Polym. Eng. Sci.*, 1981, **21** 47
116. V S Shah, J S Keitz, D R Paul, J W Barlow *J. Appl. Polym. Sci.*, 1986, **32** 3863
117. F S Bates, G D Wignall *Macromolecules*, 1986, **19** 932
118. E L Atkin, L A Kleintjens, R Koningsveld, L J Fetters *Makromol. Chem.*, 1984, **185** 377
119. H Wang, G Hadziioannou, R S Stein *J. Polym. Sci., Polym. Phys. Ed.*, 1983, **21** 159
120. T P Russel, R S Stein *Am. Chem. Soc., Polym. Prepr.*, 1979, **20** 24
121. J Wanderschueren, A Janssen, M Ladang, J Niezette *Polymer*, 1982, **23** 395
122. E Roerdink, G Challa *Polymer*, 1978, **19** 173
123. L Zeman, D Patterson *Macromolecules*, 1972, **5** 513
124. A Robard, D Patterson, G Delmas *Macromolecules*, 1977, **10** 706
125. M Bank, J Leffingwell, C Thies *Macromolecules*, 1971, **4** 43
126. V A Izvozchikova, I N Razinskaya, L V Adamova, et al. *I Vsesoyuznaya Konferentsiya "Smesi Polimerov": Tezisy Dokadov* (The I All-Union Conference on "Polymer Blends"; Abstracts of Reports), Ivanovo, 1986, p. 26
127. J S Chiou, J W Barlow, D R Paul *J. Polym. Sci., Polym. Phys. Ed.*, 1987, **25** 1459
128. J Lecourtier, F Lafuma, C Quivoron *Makromol. Chem.*, 1982, **183** 2021
129. L V Adamova, N E Klimova, T V Litvinova, et al. *I Vsesoyuznaya Konferentsiya "Smesi Polimerov": Tezisy Dokadov* (The I All-Union Conference on "Polymer Blends"; Abstracts of Reports), Ivanovo, 1986, p. 36
130. Y Suzuki, Y Miyamoto, H Miyaji, K Asai *J. Polym. Sci., Lett. Ed.*, 1982, **20** 563

131. Y Maeda, F E Karash, W J MacKnight, R Vuković *J. Polym. Sci., Polym. Phys. Ed.*, 1986, **24** 2345
132. B A Wolf, G Blaum *J. Polym. Sci., Polym. Symp.*, 1977, (21) 251
133. S Saeki, N Kuwahara, K Hamako, et al. *Macromolecules*, 1986, **19** 2553
134. V P Privalko, K N Petrenko, Yu S Lipatov *Dokl. Akad. Nauk Ukrain. SSR, Ser. B*, 1986, (8) 50
135. D J Walsh, J S Higgins, S Rostami, K Weeraperuma *Macromolecules*, 1983, **16** 391
136. S Reich, J M Gordon *J. Polym. Sci., Polym. Phys. Ed.*, 1979, **17** 371
137. C B Bucknall *Toughened Plastics* (Translated into Russian), Izd. Khimiya, Leningrad, 1981, 328 pp
138. H Keskkula *Polymer Compatibility and Incompatibility. Principles and Practice* (Edited by K Solc), Symp. Series, Harwood Acad. Publ., Midland, Michigan, 1981, Vol. 2, p. 235
139. C B Bucknall, T Yoshii *Brit. Polym. J.*, 1978, **10** 53
140. A G Shvarts, B I Dinzburg *Sovmeshchenie Kauchukov s Plastikami i Sineticheskimi Smolami* (The Blending of Rubbers with Plastics and Synthetic Resins), Izd. Khimiya, Moscow, 1972, 224 pp
141. Yu S Lipatov *Mezhaznye Yavleniya v Polimerakh* (Interfacial Phenomena in Polymers), Izd. Naukova Dumka, Kiev, 1980, 260 pp
142. A F Yee *J. Mater. Sci.*, 1977, **12** 757
143. G Maglio, R Palumbo *Proceedings of 2nd Polish–Italian Joint Seminar on Multicomponent Polymer Systems, Lodz, 1982*, Plenum Press, New York–London, 1984, p. 41
144. A O Grigorov, Yu A Zeichenko, A I Andreeva *I Vsesoyuznaya Konferentsiya "Smesi Polimerov": Tezisy Dokladov* (The I All-Union Conference on "Polymer Blends"; Abstracts of Reports), Ivanovo, 1986, p. 149
145. Y Nakamura, K Mori, Y Yochida, K Tamura *Kobunshi Ronbunshu* (Chemistry of High Polymers), 1984, **41** 531
146. Y Nakamura, K Mori, K Vada *Kobunshi Ronbunshu* (Chemistry of High Polymers), 1984, **41** 539
147. L Slusarski, Y Kuszynski *Proceedings of 2nd Polish–Italian Joint Seminar on Multicomponent Polymer Systems, Lodz, 1982*, Plenum Press, New York–London, 1984, p. 179
148. A J Coran, R Patel *Rubber Chem. Technol.*, 1983, **56** 1045
149. Yu S Lipatov, L M Sergeeva *Vzaimopronikayushchie Polimernye Setki* (Interpenetrating Polymer Networks), Izd. Naukova Dumka, Kiev, 1978, 160 pp
150. R Fayt, R Jerome, P Teyssie *J. Polym. Sci., Polym. Lett. Ed.*, 1981, **19** 79
151. T Ouhadi, R Fayt, R Jerome, P Teyssie *Polym. Commun.*, 1986, **27** 212
152. R Fayt, R Jerome, P Teyssie *J. Polym. Sci., Polym. Phys. Ed.*, 1981, **19** 1269
153. R Fayt, R Jerome, P Teyssie *J. Polym. Sci., Polym. Phys. Ed.*, 1982, **20** 2209
154. L D'Orazio, R Greco, F Martuscelli, G Ragosta *Proceedings of 2nd Polish–Italian Joint Seminar on Multicomponent Polymer Systems, Lodz, 1982*, Plenum Press, New York–London, 1984, p. 127
155. L D'Orazio, R Greco, G Makarells, et al. *Polym. Eng. Sci.*, 1982, **22** 536
156. L D'Orazio, R Greco, F Martuscelli, G Ragosta *Polym. Eng. Sci.*, 1983, **23** 489
157. M M Dumoulin, C Farha, L A Utracki *Polym. Eng. Sci.*, 1984, **24** 1319
158. M R Shishesaz, A Donatelli *Polym. Eng. Sci.*, 1981, **21** 869
159. F Deak, M Akutin, J Szerge, et al. *Müanyag Gumi*, 1984, **21** 122
160. K Dimov, M Savov, J Georgiev *Acta Polym.*, 1980, **31** 394
161. A Ghaffar, C Sadrmohaghegh, G Scott *Eur. Polym. J.*, 1981, **17** 941
162. E Yu Borisova, T A Erykalova, S V Vladychina, et al. *I Vsesoyuznaya Konferentsiya "Smesi Polimerov"; Tezisy Dokladov* (The I All-Union Conference on "Polymer Blends"; Abstracts of Reports), Ivanovo, 1986, p. 166
163. L G Epshtein, E I Nagumanova, V A Voskresenskii *I Vsesoyuznaya Konferentsiya "Smesi Polimerov"; Tezisy Dokladov* (The I All-Union Conference on "Polymer Blends"; Abstracts of Reports), Ivanovo, 1986, p. 166
164. V G Khozin, A V Murafa, Yu M Budnik, et al. *I Vsesoyuznaya Konferentsiya "Smesi Polimerov"; Tezisy Dokladov* (The I All-Union Conference on "Polymer Blends"; Abstracts of Reports), Ivanovo, 1986, p. 69
165. T Ougizawa, T Inoue, H W Kammer *Macromolecules*, 1985, **18** 1059
166. J Mokry, J Stresinska, Z Peltzbauer, K Macrinein *Chem. Zvesti*, 1983, **37** 783
167. J R Campbell, P M Conroy, R A Florence *Am. Chem. Soc., Polym. Prepr.*, 1986, **27** 331
168. M Ohno, J Kumanotani *Polymer*, 1979, **11** 947
169. H A Schneider, H J Cantow, V Pearce *Am. Chem. Soc., Polym. Prepr.*, 1982, **23** 203
170. A Murakami, H Kanatani, T Yoshiki *Kobunshi Ronbunshu* (Chemistry of High Polymers), 1981, **38** 507
171. D N Emel'yanov, V A Myachev, V E Dreval' *I Vsesoyuznaya Konferentsiya "Smesi Polimerov"; Tezisy Dokladov* (The Ist All-Union Conference on "Polymer Blends"; Abstracts of Reports), Ivanovo, 1986, p. 149
172. V N Kuleznev *Smesi Polimerov* (Polymer Blends), Izd. Khimiya, Moscow, 1980, 304 pp
173. A S Levashova, V N Kuleznev, L V Vershinina *I Vsesoyuznaya Konferentsiya "Smesi Polimerov"; Tezisy Dokladov* (The Ist All-Union Conference on "Polymer Blends"; Abstracts of Reports), Ivanovo, 1986, p. 155
174. A Siegmann, A Dajan, S Kenig *Polymer*, 1985, **26** 1325
175. M Kozlowski, W Laskawski *Angew. Makromol. Chem.*, 1980, **91** 1
176. N Sivashinski, D S Soog *J. Polym. Sci., Polym. Lett. Ed.*, 1983, **21** 459
177. M G Hansen, D G Bland *Polym. Eng. Sci.*, 1985, **25** 896
178. D J Bye, I S Miles *Eur. Polym. J.*, 1986, **22** 185
179. Yu S Lipatov, A E Nesterov, V F Shumsky, et al. *Eur. Polym. J.*, 1982, **18** 981
180. Yu S Lipatov, V F Shumskii, E V Lebedev, A E Nesterov *Dokl. Akad. Nauk SSSR*, 1987, **244** 148
181. V F Shumskii *Fizikokhimiya Mnogokomponentnykh Polimernykh Sistem* (Physical Chemistry of Multicomponent Polymer Systems), Izd. Naukova Dumka, Kiev, 1986, Vol. 2, p. 279
182. C D Chan, T C Yu *J. Appl. Polym. Sci.*, 1971, **15** 1163
183. A Plochocki, J Jedlinska *Polymer*, 1971, **17** 323
184. A Plochocki *J. Appl. Polym. Sci.*, 1972, **16** 987
185. A Plochocki *Trans. Soc. Rheol.*, 1976, **20** 287

186. C D Han, Y W Kim, S J Chen *J. Appl. Polym. Sci.*, 1975, **19** 831
187. Yu S Lipatov, A E Fainerman, O V Anokhin *Dokl. Akad. Nauk SSSR*, 1976, **231** 381
188. Yu S Lipatov, V F Rosovitskii, E V Lebedev, et al. *Dokl. Akad. Nauk Ukrain. SSR, Ser. B*, 1976, (8) 713
189. Yu S Lipatov, E P Mamunya, E V Lebedev, et al. *Vysokomol. Soedin, Ser. B*, 1981, **23** 284
190. E P Mamunya, E V Lebedev, Yu S Lipatov *Vysokomol. Soedin, Ser. A*, 1979, **21** 1008
191. T I Sogolova, M A Akutin, D Ya Tsvankin, et al. *Vysokomol. Soedin, Ser. A*, 1975, **17** 2505
192. M S Akutin, B N Artemenko *Vysokomol. Soedin, Ser. A*, 1968, **10** 561
193. M S Akutin, A N Shabardin, Z I Salina *Vysokomol. Soedin, Ser. B*, 1972, **14** 769
194. A V Konovalov, M S Akutin, M L Kerber, et al. *Vysokomol. Soedin, Ser. B*, 1976, **18** 247
195. G A Lindsay, C J Singleton, C J Carman, R W Smitt *Am. Chem. Soc., Polym. Prepr.*, 1978, **19** 206
196. R Greco, C Mancarella, E Martuscelli, et al. *Polymer*, 1987, **28** 1923
197. G Weber, J Schoeps *Angew. Makromol. Chem.*, 1985, **136** 45
198. J B Glass *Rubber Chem. Technol.*, 1985, **58** 973
199. M May, T Ganceva, C Walther, A Marinova *Plast. Kautsch.*, 1985, **32** 449
200. L Malderkern, S Go *J. Polym. Sci., Polym. Phys. Ed.*, 1977, **15** 1189

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The gas-chromatographic and gas-chromatographic–mass-spectrometric identification of halogen-containing organic compounds

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ABSTRACT. The problem of identifying halogen-containing organic compounds in their gas-chromatographic and gas-chromatographic–mass-spectrometric (GC-MS) determination in different materials has been examined. Particular attention has been paid not to the complete characterisation of methods for carrying out this analysis but to the most important problem of increasing the selectivity at the stages of sampling, separation, and interpretation of the gas-chromatographic and GC-MS information.

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I. Introduction

The examination of the gas-chromatographic and mass-spectrometric analysis of halogen-containing organic compounds (HOC) is important, since these compounds are widely used in industry, agriculture, medicine, and everyday life. Since only a few compounds of this class are found in natural materials, and most are manufactured by man, the analysis of materials of this kind often requires their selective determination in much larger quantities of a large number of compounds of other classes. Thus the problems of selective sampling, separation, detection, and the reliable interpretation of the data are extremely important for halogen derivatives.

Published data on methods for analysing halogen-containing compounds in various materials, developed up to the early nineteen-eighties, have been summarised in various reviews[1–3] and monographs.[4–6] Special sections in handbooks[7,8] have been devoted to the determination of traces of HOC in the air of industrial plants and in the atmosphere.

Several hundred studies of different aspects of the analysis of HOC are now published every year, and these data require systematisation. In addition to an increase in the range of substances determined, there is a tendency towards a more rigorous characterisation of procedures in order to increase the accuracy and selectivity of analysis and to simplify methods of sampling. A number of topics, in particular the selection of sorbents for concentrating traces of substances to be analysed and the conditions for their gas-chromatographic separation, to which particular attention was paid in earlier reviews,[1–7] do not now require examination, since the corresponding procedures have been systematised and standardised.[9] Thus in the present review particular attention is paid not to a detailed description of specific procedures for analysing HOC in different materials but to the presentation of the general principles of their gas-chromatographic and mass-spectrometric identification, quantitative analysis, and methods for increasing the selectivity of the determination by using special methods of detection.

In recent years, more accurate data have been obtained on the high toxicity of various halogen-containing compounds.[10–12] Mutagenic activity has been noted for 40 substances of this type used in industry.[13] Thus it is necessary to develop reliable highly sensitive procedures for determining HOC in the atmosphere, water and effluents, soils, biological materials, foodstuffs, and other substances.

The large number of HOC produced on the industrial scale can be classified in two groups, according to their physicochemical properties. The first group consists of volatile polyhalogenocarbons, Freons, halogen-containing monomers, and solvents. The second group consists of high-boiling polychlorinated hydrocarbons, pesticides, the starting materials for their synthesis, and metabolism products. The particular danger of the contamination of the environment by materials of the first group (in particular the simplest polychlorofluorocarbons) is now considered to be the possible destruction of the ozone layer in the atmosphere as a result of photochemical reactions involving Hal' radicals, first noted in 1974 [14,15] (these questions have been discussed in detail[8]). Until recently it was considered that these compounds are produced exclusively by man, but in 1985, chloro- and chlorofluoromethanes were detected in volcanic gases.[16,17] Previously, only the natural production of CH_3Cl,[16] CH_3Br, and, possibly, CF_4,[18] had been noted. The existence of natural sources of HOC may lead to a re-examination of estimates of the potential danger of these substances for the ozone layer of the atmosphere.

Polychlorinated aromatic hydrocarbons, chlorine-containing pesticides, and other compounds of this kind are not highly volatile, so that they are concentrated in condensed media.[19–21] Nevertheless, they are detected at considerable distances from their sites of use (as far as the Arctic regions).[22–26] The global contamination of the biosphere by chlorine-containing compounds makes it important to control their concentration in compounds of food chains[27] and biological materials.[28]

The most toxic representatives of this group of HOC are polychlorinated dibenzo-*p*-dioxins, dibenzofurans, diphenyl ethers, and similar substances having a teratogenic action. The intensive study of methods for detecting and identifying these compounds began after the chemical plant disaster in Seveso (Italy) in 1976, which led to the sudden release of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, long-term contamination of the environment, and cases of acute poisoning.[29] Polychlorodibenzodioxins and -furans may be formed by the oxidation of polychlorobiphenyls (added to pesticides)[30] or by the oxidative chlorination of aromatic compounds by HCl in air,[31] but most of these compounds released into the atmosphere are produced by the thermal treatment of chlorine-containing polymers, including the combustion of household refuse.[32–35] The chlorination of drinking water leads to the appearance in it of traces of polychloro-aromatic hydrocarbons and phenols,[36,37] whose concentration also requires effective control.

II. Basic principles of the separation, selective detection, and gas-chromatographic identification of halogen-containing substances

One of the most important tasks in the gas-chromatographic analysis of HOC is to achieve the maximum selectivity with respect to compounds of this type, in order to eliminate the influence of interfering components and to increase the reliability of identification and quantitative analysis. The possibilities for achieving this are different at the stages of sampling and preparing specimens for analysis, chromatographic separation, and detection of the substances being determined.

1. Sampling and preparation of specimens for analysis

The reactivity and specific chemical properties of halogen-containing compounds generally do not differ significantly from those of their analogues not containing halogens. For this reason, the selective extraction of HOC from specimens being analysed at the stages of sampling and specimen preparation is usually impossible. Only isolated examples of this selectivity are known, based on specific reactions of the substances being analysed. Thus a method for determining hexachloroacetone in air[38] is based on its absorption by anhydrous methanol, which is accompanied by the quantitative reaction:

$$(CCl_3)_2CO + CH_3OH \rightarrow CCl_3CO_2CH_3 + CHCl_3.$$

Both reaction products are determined in the subsequent gas-chromatographic analysis of the solution obtained. The detection limit using an electron capture detector is 3 μg m^{-3}.

The same principle (trapping in liquid absorbers which react with specific substances) is used successfully in the analysis of free halogens and hydrogen halides in air.[1,39–42]

The anlaysis of traces of organic halogen-containing compounds in gases at the level of several p. p. t. (parts per trillion by volume) is carried out by the direct introduction of large gas specimens using highly sensitive selective detectors,[43,44] or cryogenic concentration in special traps or preliminary columns not selective with respect to substances of other classes,[18,45,46] or trapping on solid sorbents. The subsequent desorption of the substances being determined is carried out thermally, directly in the analytical column, or by treating the sorbent with organic solvents and analysis of the eluate.[47] The desorption of halogen-containing compounds from active carbon by water vapour is possible in principle.[48] To trap the most volatile compounds, including perfluoroalkanes, Freons, etc., active carbons with a specific surface of up to 1000 m^2 g^{-1} [47,49-52] or graphitised carbon black (Carbopack B type) with a specific surface of about 100 m^2 g^{-1} [53] are used. The thermally stable polymeric sorbent Tenax (poly-*p*-2,6-diphenylphenylene oxide) is effective not only for concentrating low-boiling halogenoalkanes and chlorinated aromatic hydrocarbons[54–57] but also chlorine-containing pesticides.[58] The carbon sorbent Ambersorb XE-340 is used for the same purposes.[59]

In thermal desorption from carbon sorbents and even the chemically most inert Tenax, however, it is necessary to take account of the possible thermal decomposition of primarily high-boiling halogen-containing compounds as a result of their dehydrohalogenation. Thus the recovery of various pesticides in desorption from 0.11 g of Tenax at temperatures of 250–325 °C and a carrier-gas (helium) velocity of 11.2 ml min^{-1} has the following values (% of the original quantity)[58]:

α-$C_6H_6Cl_6$	97±8	*pp'*-DDT	60±2
Heptachlor	26±5	*pp'*-DDT	20±1
Dieldrin	120±3	perylene (for comparison)	82±2 .

Another factor responsible for the loss of compounds being analysed and distortion of the results of a quantitative analysis may be incomplete trapping in the cryogenic trap, particularly for low-boiling compounds.[60]

When working with polymeric sorbents, it is necessary to take account of the presence of traces of halogen-containing substances in the background emanation of the polymer itself.[61,62] To prevent the incomplete trapping of low-boiling compounds, polymeric sorbents with a specific surface of up to several hundred m^2 g^{-1} are used (Chromosorbs 101, 103, 107, Porapaks M, Q, T, Cekachrom 2, 3, CE-1, CE-2, etc.).[63–65] The basic characteristics of all solid sorbents are the specific retention volumes of each of the substances being determined at the sampling temperature (V_g, litre g^{-1}) and the maximum sample gas volumes, related to V_g by the simple expression $V_g^{max} \simeq V_g(1 - 2/\sqrt{N})$,[7] where N is the efficiency of the sorption tube in theoretical plates. These data have been published for the simplest HOC.[63,64]

In the study of the concentration of volatile halogen-containing compounds in liquid specimens (including aqueous solutions), the best method is apparently vapour-phase analysis (VPA),[66] which is based on information on the composition of the condensed phases obtained by analysing the gaseous media present in contact with them. The possibilities provided by the method are determined by the distribution coefficients of the substances being analysed between the liquid and gas phases. In some cases the differences in these coefficients for different substances make it possible to increase the selectivity. In general, the term vapour-phase analysis includes both the analysis of the equilibrium or non-equilibrium gas phase above the specimen[66] and the complete sweeping of the components being determined from solutions by a stream of carrier gas followed by their sorption.[55,67] The detection limit of the method can be varied by changing the temperature of the analysis and by adding salting-out agents. For example, the addition of sodium sulphate (20 g) to an aqueous solution (50 ml) when capillary columns and an electron capture detector are used lowers the detectable concentrations of CH_3Cl from 1.6 p. p. m. to 1.3 p. p. m., $CHCl_3$ from 2.4 p. p. m. to 0.9 p. p. m., and C_6H_5Cl from 1.5 p. p. m. to 0.4 p. p. m.[68]

Vapour-phase analysis is effective in the determination of a wide range of chlorine and bromine derivatives of methane and ethane in drinking water,[69–73] traces of chloroform in blood plasma,[74]

monomer residues in polymeric materials (for example vinyl chloride in polyvinyl chloride[75,76]), solvents in foodstuffs,[77] traces of volatile halogen-containing substances in organic electrolytes,[78,79] etc. Of particular interest is the vapour-phase analysis of specimens which cannot be introduced into a chromatographic column because of their thermal instability, reaction with a phase, etc. This method has been used to determine traces of polychlorinated C_1-C_3 hydrocarbons in $SiCl_4$, $POCl_3$, $GeCl_4$, BBr_3, and BCl_3.[80]

The extraction of solid or liquid specimens by organic solvents (usually with boiling points not higher than 100 °C) is most frequently used in the analysis of less volatile halogen-containing organic compounds: herbicides,[81] chlorobenzenes, chlorotoluenes, hexachlorobutadiene, and polychlorobiphenyls,[82,83] chlorostyrenes,[84] and polychlorodibenzo-*p*-dioxins.[85,86] After concentration of the extract, it is possible to achieve a degree of enrichment of up to $(1-3) \times 10^3$ with a degree of extraction of 50–98%. Light halogenomethanes can be analysed in this way only by electron capture detectors and solvents with respect to which their sensitivity is low.[81,87] Concentration in this case becomes impossible, and direct VPA of the original specimens is preferable.

The large number of preliminary stages in the analysis of traces of HOC in dilute solution (gas or liquid extraction, concentration on solid sorbents) leads to a slight regular decrease in the accuracy of quantitative determinations as a result of the accumulation of both random and systematic errors. Thus in a number of cases the direct introduction of the specimens being analysed into packed or capillary columns with grafted stationary phases is more appropriate. For example, when this method is used to analyse aqueous solutions, it is possible to achieve detection limits of 2 p. p. b. for CH_2Cl_2, 0.1 p. p. b. for CH_3CCl_3, 0.15 p. p. b. for $CCl_2=CHCl$, and 0.1 p. p. b. for C_2Cl_4.[88] A similar method has been used not only for aqueous solutions but also for dilute solutions in organic solvents.[89,90]

A particular case of the special treatment of specimens of non-volatile or thermally unstable compounds for analysis involves the preparation of derivatives suitable for gas-chromatographic analysis.[91] If these derivatives contain halogen atoms, the problem of increasing the selectivity of detection is solved simultaneously (see above). For compounds containing active hydrogen atoms (NH, OH, SH groups), the derivatives are most frequently heptafluorobenzoates, trifluoroacetates, pentafluoropropionates, and heptafluorobutanoates. This method is used to analyse amino-acids,[92–94] dipeptides,[95] mono-, di-, and oligosaccharides,[96–99] aromatic amines,[100,101] β-arylamines, their metabolites, and aliphatic diamines,[102–104] ethylene glycol in blood serum,[105] the oxidation products of coal[106] (in the last case, use is made of peroxotrifluoroacetic acid, which acts simultaneously as oxidant and as reagent for derivative formation), etc. The analysis of organic acids as their hexafluoroisopropyl esters after treatment with $(CF_3)_2CHOH$ has been recommended.[107]

Various halogen-containing compounds (the halides of silicon, boron, etc.) are highly reactive and unstable under the conditions of gas-chromatographic analysis. Special methods for dealing with compounds of this kind have been described.[108]

2. The gas-chromatographic separation of halogen-containing compounds

The conditions for the optimum gas-chromatographic separation are different for volatile halogen derivatives and high-boiling polychlorinated aromatic compounds. The analysis of substances of the first group is usually carried out on packed columns with a high concentration of the stationary phases[69,81] or on polymeric or inorganic sorbents modified by various additives. Thus a column containing Carbopack B treated with 0.5% SP-1000 (3 m) is effective for separating halogen derivatives with boiling points from –24 °C (CH_3Cl) to 121 °C (C_2Cl_4).[109] A packing with similar characteristics consisting of 0.2% of polar Carbowax 1500 on Carbopack C (specific surface about 10 $m^2\ g^{-1}$) is effective for the temperature-programmed separation of a mixture of substances with boiling points from 40 °C (CH_2Cl_2) to 132 °C (chlorobenzene), that is practically all aliphatic C_1 and C_2 chlorine derivatives.[110] Combined colums with polar and non-polar stationary phases,[69] molecular sieves,[109] or silica gels[52] are sometimes used.

Gas-adsorption capillary columns with a coating of aluminium oxide or silica gel are effective for separating low-boiling halogen-containing compounds.[18,111]

Compounds of the second group are usually analysed on glass or quartz capillary columns containing high-temperature silicone stationary phases with low or medium polarity,[30,43,46,83,85,112–120] or on packed columns with a low concentration (not more than 5%) of similar phases.[81,110,121] Since polychlorinated biphenyls, dibenzo-*p*-dioxins, dibenzofurans, and other representatives of this group of compounds are specific materials distinguished by the simultaneous presence of a large number of similar substances, including isomers (polychlorobiphenyls, for example, form a "group" of 209 theoretically possible compounds), in a number of cases special optimisation of the temperature conditions of the analysis is appropriate, to increase the efficiency of their separation.[122] This analysis requires high temperatures (150–300 °C), at which it is necessary to take account of the possible decomposition of various substances in the chromatographic column. Thus dehydrochlorination of chlorine-containing pesticides has been observed on glass columns with surfaces modified by $BaCO_3$.[123]

An increase in the selectivity of the determination of halogen-containing compounds at the separation stage is possible by using reaction gas chromatography,[1] including the removal of interfering components in preliminary or subsequent columns. This method is effective for determining traces of CH_3Cl, CH_3Br, and C_2H_5Cl in CH_3OH using a capillary column. The solvent is trapped selectively at the column outlet in a trap containing activated Al_2O_3 at 30 °C, which is heated to 200 °C when the analysis is complete.[124] For chlorine-containing pesticides, polychloroaromatic compounds, etc., a useful version of reaction chromatography involves their catalytic hydrogenation to hydrocarbons with preservation of the carbon framework of the molecules (the so-called "carbon skeleton chromatography"),[1,125] carried out in a preliminary column reactor by means of the hydrogen used as carrier gas. This method makes it possible to lower the temperature and time of the analysis, and does not require the use of selective detectors.

Other effective methods for separating mixtures of polychloroaromatic compounds are liquid[126,127] and "fluid"[128,129] chromatography (in a stream of non-ideal eluants at pressures and temperatures in the column exceeding the critical parameters of the eluant).

3. Methods for detecting halogen derivatives

The maximum selectivity in the analysis of halogen-containing compounds is achieved at the stage of their detection using selective gas-chromatographic detectors or mass spectrometers. The widely used electron capture detectors (ECD) solve this problem effectively, but increasing use is being made of mass spectrometers, which provide much greater possibilities and a controllable selectivity of detection.

Chromatographic detectors based on the general principle of the change in the electronic conductivity of the gaseous medium in the presence of halogen-containing substances (electron capture and constant recombination) are fairly simple to use, and have been employed in a large number of studies of the analysis of varied halogen-containing compounds, for example free iodine,[130] volatile halogenocarbons in water and in air,[38,47,57,81,88,131,132] 1-bromo-1-chloro-2,2,2-trifluoroethane (Halothane) in air,[133] chlorobenzenes,[82] polychlorophenols,[134] halogen-containing pesticides,[81,89,135] etc. Signals from three detectors have been recorded simultaneously to increase the selectivity of the determination of halogen-containing substances in air.[136]

Important features of electron capture detectors are the comparatively short linear range (about two orders of magnitude),[137] which makes it difficult to carry out quantitative analysis, and the marked dependence of the relative response of the detector on the nature, number, and even the position of the halogen atoms in the molecule. The use of these detectors therefore requires the constant application of specially prepared calibration mixtures of the compounds being analysed.[138–140] The dependence of the relative response of ECD on the number of chlorine atoms in a series of chlorobenzenes is illustrated by the results of a study[141] given in Table 1. Since the relative sensitivity coefficients depend on the operating conditions of the detector and differ considerably even for isomers, in quantitative analysis it is necessary to have standard specimens of all the substances being determined. A practical consequence of this is a difference in the detection limits for chlorobenzenes using ECD. For example, when aqueous solutions are extracted with pentane, about 0.01 ng litre^{-1} penta- and hexachlorobenzenes can be determined, whereas the corresponding value for the mono-substituted compound is only 500 ng litre^{-1}.[82] It is not yet possible to calculate the relative sensitivity coefficients for ECD. These parameters of halogen derivatives can be calculated by an additive scheme only for thermal conductivity detectors.[142]

Table 1. Relative response of the electron capture detector for chlorobenzenes.[141]

Degree of substitution	Relative response	Degree of substitution	Relative response
Monochlorobenzene	1	Tetrachlorobenzenes	
Dichlorobenzenes		1,2,3,4-	$12\cdot10^3$
1,2-	550	1,2,3,5-	$10\cdot10^3$
1,3-	610	1,2,4,5-	$5.8\cdot10^3$
1,4-	280	Pentachlorobenzene	$23\cdot10^3$
Trichlorobenzenes		Hexachlorobenzene	$30\cdot10^3$
1,2,3-	$7.2\cdot10^3$		
1,2,4-	$4.0\cdot10^3$		
1,3,5-	$4.5\cdot10^3$		

The low sensitivity of ECD to compounds containing one fluorine or chlorine atom explains the observed[1] difficulty of determining vinyl chloride. Thus for substances of this kind, it is preferable to use flame ionisation[76] or photo-ionisation[143,144] detectors. It has been reported,[145] however, that the sensitivity of ECD to vinyl chloride increases by a factor of about 10^3 (from 1 ng to 1.4 pg) when N_2O (10–50 p.p.m.) is added to the gas (nitrogen) passing into it. The observed effect is due to the appearance in the gas phase of O^- ions, formed by the reaction of N_2O with thermal electrons. A chromatograph with a detector modified in this way, when 1 cm^3 of air is introduced directly, can determine vinyl chloride at a concentration of about 0.5 p.p.m. (1.4 mg m^{-3}), which, however, is higher than the level officially established in the USSR for the limiting permissible concentrations of this substance (0.1 mg m^{-3} for a working area, and 0.005 mg m^{-3} for atmospheric air).

The mass spectrometer, used as a chromatographic detector under total ion current recording conditions or under the conditions of mass fragmentography (detection of the signals of ions with previously specified mass numbers), has a longer linear range than ECD.[146] An additional advantage of the mass spectrometer is that it is possible to carry out a quantitative analysis not only by absolute calibration but also by isotopic dilution. Thus in the determination of the isomers of hexachlorocyclohexane, known quantities of its completely deuteriated analogue $C_6D_6Cl_6$ were added to the specimens.[146] Analysis by absolute calibration or mass-spectrometric detection is complicated by the difficulty of determining the ionisation cross-sections of different substances, but according to recent data, they can be calculated by additive schemes to within about 5%.[147]

Gas chromatographic–mass-spectrometric (GC-MS) analysis is widely used in the selective determination of poly-chlorinated aromatic hydrocarbons and their derivatives in complex mixtures with ionisation by electron impact[148–151] and with chemical ionisation.[152,153] The method involving the detection of the negative ions formed in chemical ionisation is particularly important for determining traces of the most toxic chlorinated dibenzo-*p*-dioxins, dibenzofurans, etc., since it has the lowest detection limit (down to 10^{-18} g according to some estimates).[154–161] The method involving ionisation at atmospheric pressure has similar advantages.[162,163]

Because of the importance of the selective detection of HOC, detectors of other types are used for their determination. It has been shown possible to identify halogens in organic compounds and to determine their mass fractions to within 3–6 rel. % with a detection limit down to 1 pg s^{-1} using detection in a corona discharge [a helium plasma with an electronic temperature of $(5-7)\times10^3$ K] from the wavelengths and intensities of the lines of the atomic emission of free halogen atoms in both the microwave[164,165] and near infrared[166] ranges. These plasma detectors are fitted with monochromators (usually diffraction gratings) and a set of recording assemblies, making it possible to determine several elements simultaneously (C, H, N, O, F, Cl, Br, I, S) [165,166] and to establish the empirical formulae of the compounds being analysed. The construction of detectors of this kind designed for capillary columns has been described.[167,168]

The possibilities provided by molecular emission spectroscopy have made it possible to produce another type of selective gas-chromatographic detector having a long linear range and a low noise level. The halogen-containing compounds leaving the packed column react with metallic indium in a hydrogen flame, after which the molecular emission signals of the indium halides are recorded at 360 nm (chloride), 376 m, (bromide), or 410 nm (indium iodide).[169] An infrared detector with Fourier transformation has been used for the chromatographic determination of polychlorodibenzo-*p*-dioxins. New electrical conductivity detectors can be used even with capillary columns.[170,171] The construction of selective detectors based on the Hall effect has been proposed.[172,173]

In the analysis of traces of polychlorinated aromatic compounds, extensive use is made of mass spectrometers with several mass analysers, effective for the analysis of complex mixtures (MS-MS). In this case, the chromatographic separation need not be so efficient,[173–175] and this stage may even be eliminated completely.[175] The direct analysis of mixtures for individual components by MS-MS using comparatively simple instruments makes it possible to develop the most rapid methods for their determination.[176–178]

The possibilities provided by the use of resonance two-photon ionisation for the detection of halogen-containing compounds have been studied.[179]

When ionisation is carried out by electron impact, the most widely used method of selective detection is mass fragmentography, which is effective both for volatile halogen-containing compounds[180–182] and for polychlorinated aromatic hydrocarbons[183,184] and pesticides.[115] The mass numbers of the principal peaks in the spectra of each component (m/z), some of which are given in Table 2, are usually chosen for diagnostic purposes.

Table 2. Mass numbers of the principal peaks of the mass spectra for the detection of various halogen-containing compounds under mass-fragmentographic conditions.[180–182]

Compound	m/z	Compound	m/z
Methyl chloride	50	1,2-Dichloroethylene	61
Dichloromethane	49, 84	1,2-Dichloropropane	63
Trichloromethane	83	2,3-Dichloroprop-1-ene	75
Tetrachloromethane	117	1,3-Dichloroprop-1-ene	75
Freon 13	69	Dichlorobromomethane	83
Freon 12	85	Chlorodibromomethane	129
Freon 11	101	Tribromomethane	171
Freon 22	67	1,2-Dibromoethane	107, 108
Freon 114	85	Chlorobenzene	112
Freon 113	101	Chlorotoluenes	91
1,1,1-Trichloroethane	97	Dichlorobenzenes	146
Trichloroethylene	95	Dichlorotoluenes	125
Tetrachloroethylene	129, 166	Trichlorobenzenes	180
1,1-Dichloroethane	63	Fluorobenzene	96
1,2-Dichloroethane	62	Difluorobenzenes	95
1,1,2-Trichloroethane	97	Pentafluorobenzenes	168
1,1,2,2-Tetrachloroethane	129	Fluorobromobenzenes	95
1,1-Dichloroethylene	61	Lindane	181

If this method of detection is used with chemical ionisation, the signals of the protonated molecular ions $[M + H]^+$ are usually recorded.

In mass fragmentography, instruments with a low resolution $[(1-1.5) \times 10^3]$, calibrated from integral mass numbers, are most frequently used. Comparatively recently (1981), an improvement of this method, namely high-resolution mass fragmentography, was proposed for instruments with a resolving power of not less than 2.5–3 thousand.[185] The extremely high selectivity of this method of detection has proved useful in the analysis of halogen-containing substances.[109,186] This selectivity is based on the specific values of the mass "defects" (ΔM) for the halogens [the differences between the exact masses of the atoms and their integral (by definition) mass numbers], which distinguish them from other elements found in organic compounds:

Element	ΔM	Element	ΔM	Element	ΔM
^{19}F	−0.0015	^{12}C	0	^{28}Si	−0.0231
^{35}Cl	−0.0311	^{1}H	0.0067	^{32}S	−0.0279
^{79}Br	−0.0183	^{14}N	0.0031	^{31}P	−0.0262
^{127}I	−0.0553	^{16}O	−0.0051		

In this case the mass fragmentograms are recorded from the exact values of the masses of the characteristic ion detected, given in Table 3.

Table 3. Exact masses of halogen-containing ions for the detection of various compounds under the conditions of high-resolution mass fragmentography.[109]

Compound	Ions detected	Masses of the ions (a.m.u.)	Compound	Ions detected	Masses of the ions (a.m.u.)
CHF_2Cl	$CHF^{35}Cl$	66.975	$CFCl_3$	$CF^{35}Cl_2$	100.936
	$CHF^{37}Cl$	68.972		$CF^{37}Cl^{35}Cl$	102.933
CF_2Cl_2	$CF_2{}^{35}Cl$	84.967	$C_2F_3Cl_3$	$CF^{35}Cl_2$	100.936
	$CF_2{}^{37}Cl$	86.964		$CF^{35}Cl^{37}Cl$	102.933
$CHFCl_2$	$CHF^{35}Cl$	66.975	CH_3CCl_3	$C_2H_3{}^{35}Cl_2$	96.961
	$CHF^{37}Cl$	68.972		$C^{35}Cl_3$	116 906
CH_2Cl_2	$CH_2{}^{35}Cl_2$	83.953	CCl_4	$C^{35}Cl_3$	116.907
	$CH_2{}^{37}Cl^{35}Cl$	85.950	C_2HCl_3	$C_2H^{35}Cl_2$	94.945
$C_2F_4Cl_2$	$CF_2{}^{35}Cl$	84.967			
	$CF_2{}^{37}Cl$	86.964			

4. The gas-chromatographic identification of halogen-containing substances

The gas-chromatographic identification of organic compounds is based on the accurate measurement of the retention parameters, of which the most reproducible forms are interpolation relative quantities, called retention indices.[187] Under isothermal analysis conditions, Kovac's retention indices are generally used:

$$I = 100n + 100\,(\lg t'_x - \lg t'_n)/(\lg t'_{n+1} - \lg t'_n),$$

where t'_x, t'_n, and t'_{n+1} are the corrected retention times of the substance being determined and the nearest reference components (n-alkanes) containing n and $n + 1$ carbon atoms, and $t' = t - t_0$, where t_0 is the retention time of the non-sorbed gas.

There is as yet no single generally accepted system of retention indices for temperature-programmed conditions. Among different methods for calculating them, mention may be made of a recently proposed system of linear–logarithmic indices,[188] in which the uncertainties in their calculation are smaller than those for other methods.

When non-selective chromatographic detectors are used, the reliability of identification only from the indices is low. Any additional information increased considerably the reliability of the assignment. Detailed catalogues of retention indices[189,190] have now been produced, but successful identification from these data requires the maximum possible additional characterisation of compounds of different classes. This explains the appearance of a large number of special publications giving the results of the determination of the retention indices of series of compounds with similar structures, including homologues, on different stationary phases. Among halogen derivatives, data of this kind have been obtained for alkyl chlorides,[191] the alkyl esters of chloroacetic acids,[192] chloromethyl esters,[193,194] chloroethanols,[195] the corresponding carboxylates,[196] chloroalkyl acetates,[197] chloropropanoates and chlorobutanoates,[198,199] chloroalkyl chloroacetates,[200] methyl chloro-

propanoates,[226] and the products of the halogenation and hydrohalogenation of alkyl acrylates.[201] The following aromatic compounds have been characterised: alkyl chlorobenzoates,[202] chloroalkyl benzoates and nitrobenzoates,[203,204] halogen-substituted benzenes, toluenes, and anisoles,[205,206] chlorinated 4-hydroxybenzaldehydes,[207] isomeric chlorophenols,[208] and pentafluorobenzoates.[209] The relationship between the structure of chlorophenoxyalkanecarboxylic acids and their retention indices has been discussed.[210] The relative retention times of 39 polychlorodibenzo-*p*-dioxins on weakly polar polydimethylsiloxane stationary phases have been determined.[30,211] Among the isomeric tetrachlorodibenzo-*p*-dioxins, the shortest relative retention time is shown by the isomer with the chlorine atoms in positions 1, 3, 6, and 8 (0.55), and the maximum by the 1,2,8,9-isomer.[1,21] The retention time of the most toxic 2,3,7,8-tetrachloro-derivative is usually taken as unity.[30] The retention indices of these dioxins can be calculated using additive schemes.[212–214] The difficulty of the gas-chromatographic identification of the compounds of these groups, however, makes it necessary to develop more complex methods based on pattern recognition techniques.[215,216]

Data on the retention indices of a number of toxic substances, including halogen derivatives, were published only in 1985.[217] More than 600 compounds, including chlorine-containing pesticides, have been characterised by their so-called effective retention temperature.[218]

The low sensitivity of selective gas-chromatographic detectors towards reference n-alkanes makes it necessary to use other reference homologues. As compounds of this kind for use with ECD, the esters of trichloroacetic acid CCl_3CO_2R, where R = n-C_nH_{2n+1}, have been recommended; the esters are given standard values of $100n$.[219] The method of identification based on this system for calculating the indices has been used in the determination of chlorine-containing pesticides and polychlorobiphenyls.[219,220] This set of reference components cannot be used to analyse low-boiling polyhalogenomethanes and -ethanes, however, since the first member of the series of trichloroacetates in the n-alkane system has an index of about 900 on non-polar silicone phases, so that lower values of the indices cannot be determined. For this reason, n-alkyl bromides[222] and n-alkyl iodides[223] have also been recommended as reference halogen-containing compounds.

Thermospray detectors are suitable for the analysis of both halogen-containing compounds and N- and P-containing substances, so that the homologous series of tri-n-alkylamines can be used as reference components.[223] The proposed[224,225] "universal" reference homologous series of bis(trifluoromethyl)thiophosphonates $(CF_3)_2P(S)OC_nH_{2n+1}$ can be used with practically all types of chromatographic detector, since the molecules contain halogen, sulphur, and phosphorus atoms simultaneously.

III. The mass-spectrometric characterisation and identification of halogen derivatives

According to present-day ideas, the fragmentation of halogen-containing organic compounds on electron impact shows no specific patterns. The most general direction of the decomposition of the molecular ions of all compounds of this type is the formation of $[M - Hal]^+$ ions and, less frequently, $[M - HHal]^{\cdot +}$. The probability that Hal$^{\cdot}$ radicals are removed increases in the order F < Cl < Br < I (with decrease in the electronegativity of the halogen).[226] The presence of other functional groups in the molecule may suppress considerably the fragmentation with rupture of C–Hal bonds, particularly for fluorides and chlorides. This is related to the relatively high ionisation energies (IE) of the non-bonding molecular orbitals localised on the halogen atoms, and the high probability of removal of an electron from other orbitals. This can be illustrated by the ranges of the IE of aliphatic halides, 10.7 ± 0.2 eV. (chloroalkanes), 10.1 ± 0.2 eV (bromoalkanes), and 9.2 ± 0.2 eV (iodoalkanes), compared with –9.2 ± 0.4 eV for alkanes, –9.3 ± 0.2 eV for ethers, –8.4 ± 0.1 eV for sulphides, etc.[227] The ionisation potentials of fluorine-containing compounds with different structures are generally greater than 10 eV. The fragmentation shows specific regularities only for polyhalogeno-derivatives, in particular perfluorinated derivatives.

The mass-spectrometric study of halogen-containing compounds is complicated by the low intensities of the peaks of the molecular ions, which correlate with the electronegativities of the halogen atoms and decrease in the order I > Br > Cl > F. The greatest difficulties are encountered in the detection of the mono-isotopic iodine and fluorine in organic compounds. Iodo-derivatives with sufficiently intense molecular ion peaks (not less than 1% of the total ion current) can be recognised from the large negative values of the homologous increments in the intensities of the [M + 1] isotopic peaks,[227] whereas the analysis of the spectra of fluoro-derivatives, which rarely give signals of this kind, is one of the most complex problems in mass-spectrometric identification. A general structural requirement for the production of the signals of the molecular ions of all halogen derivatives is the presence in the molecule of a p-π conjugated system for example $\rangle C=C-Hal$.[227]

The most important characteristic of polychloro- and polybromo-compounds is the presence of specific multiplets of the isotopic peaks in the mass spectra.[226,227] Their appearance makes it possible to achieve selectivity in the detection of halogen deriatives during GC-MS analysis by another period. A specially developed computer program makes it possible to detect these multiplets and to obtain information on the number of chlorine atoms in an unknown compound.[228,229] In this case the selective detector is a "mass spectrometer + computer" combination.

The difficulty of interpreting the mass spectra of fluorine-containing compounds makes it important to develop algorithms based on new principles. These include a method which requires a two-stage analysis of the data.[227] In the first stage (group identification or classification), an unknown compound can be assigned to a definite homologous series or group of homologues according to the numbers of homologous groups of principal peaks in the mass spectrum or (and) the statistically treated spectra of ion series. The subsequent refinement of the structure of the substance in the second stage is carried out with allowance for the known regularities of the fragmentation of the given series, together with the gas-chromatographic retention parameters.

Algorithms for group identification based on the statistically treated spectra of ion series have been characterised in detail, and the data for 20 series of halogen-containing substances have been given.[227] The further extension of the data base is extremely important, primarily to decrease the number of errors in second-order identification (the assignment of unknown substances to one of the series already characterised).[227] Table 4 gives the spectra of the ion series for several groups of fluorine-containing compounds. This method makes it possible to describe series in which the compositions of the members differ not by a CH_2 group but by another homologous difference, for example CF_2 (mass number 50).

In this case, compounds belonging to different homologous groups are obtained in a single series $y_M \equiv M \pmod{14}$, and the spectra of the ion series have a slightly lower reproducibility, which does not prevent the practical utilisation of these data.

Table 4. Mass spectra of the ion series of various groups of organofluorine compounds.[227]

Class of compound	Homologous group y_M	I_y in order of increasing y from 0 to 13*
n-Alkyl fluorides	6	$25_4\ 30_8\ 1_1\ 3_1\ 2_1\ 6_3\ 0\ 0\ 0\ 0\ 0\ 4_2\ 2_1\ 27_7$
s- and t-Alkyl fluorides	6	$4_4\ 4_3\ 1_1\ 4_1\ 8_5\ 57_8\ 3_2\ 0\ 0\ 0\ 0\ 2_2\ 1_1\ 12_4$
gem-Difluoroalkanes	10	$0\ 2_2\ 1_1\ 8_2\ 2_2\ 16_9\ 1_1\ 0\ 3_2\ 62_{10}\ 2_2\ 0\ 1_1\ 2_2$
Aryl fluorides	12	$1_1\ 3_2\ 0\ 1_1\ 1_1\ 4_1\ 2_1\ 3_1\ 3_1\ 4_1\ 2_1\ 46_9\ 23_9\ 7_2$
Perfluoroalkanes	**	$0\text{-}4_4\ 4_3\ 4_1\ 0\ 4_4\ 0\ 13_8\ 3_2\ 1_1\ 0\ 1_1\ 0\ 66_7$
Perfluoroalkenes	**	$2_2\ 5_4\ 5_4\ 6_4\ 3_3\ 9_7\ 2_2\ 6_4\ 2_1\ 4_2\ 2_2\ 2_2\ 1_1\ 51_{13}$
Perfluorocarboxylic acids and their esters	**	$1_1\ 9_4\ 5_2\ 40_4\ 1_1\ 3_3\ 0\ 4_4\ 3_2\ 5_5\ 1_1\ 4_3\ 0\ 24_6$

* I_y represents the total intensities of the signals of the homologous group y as a percentage of the total ion current ($\Sigma I_y = 100\%$); the subscripts give the standard deviations characterising the scatter in these quantities for different compounds of the given group.
** The mass numbers of the homologues are compared with respect to the modulus 50 (homologous difference CF_2) and not 14 (CH_2 group), so that they relate to different homologous groups $y_M = M \pmod{14}$.

An increase in the reliability of mass-spectrometric identification requires the elimination of the principal sources of inter-laboratory uncertainties in the mass spectra and the observation of various critria proposed for estimating the "quality" of mass spectra.[230] The simplest method of verifying the operating conditions of an instrument involves recording the spectra of standard compounds and comparing the peaks with tabulated values. Recommended reference substances are phenylbis(pentafluorophenyl)phosphine and *p*-bromofluorobenzene,[182,231,232] the data for which are given in Table 5.

The mass-spectrometric characterisation of halogen-containing compounds which have not been studied before covers an extremely wide range of materials. Because of the objective characteristics of the dissociative ionisation of substances of this class, however, the specific characteristics of their fragmentation often are not related to the presence of the halogen atoms in the molecule, but are determined completely by other functional groups. The fundamental facts include a new skeletal rearrangement in the molecular ions of dichloro- and difluorosilanes, associated with the elimination of dichloro- and difluorosilenes respectively:

$$[RR'SiHal_2]^{+\cdot} \rightarrow [RR']^{+\cdot} + SiHal_2.$$

The structural requirement for this process is the presence of multiple bonds or heteroatoms in the groups R and R'.[233] General rearrangements take place in the molecular ions of the trimethylsilyl and t-butyldimethylsilyl ethers of chlorine-containing alcohols, accompanied by the migration of a Cl atom to silicon and leading to the appearance in the spectra of peaks due to the ions $[(CH_3)_2SiCl]^+$ with *m/z* of 93 and 95.[234,235]

Polychlorinated compounds have been studied in detail not only in the solution of special analytical problems[236–239] but also frequently in the development of methods of detection and the interpretation of the mass spectra of these substances in the determination of pesticides and insecticides,[240–242] toxic polychloro-aromatic compounds,[148–151,243–245] etc. An independent direction of mass-spectrometric studies involves the investigation of potential metabolites of halogen-containing drugs.[246] A large number of papers have been devoted to the analysis of the regularities of the fragmentation of halogen-containing cyclo- and polyphosphazenes $(-PR_2=N-)_{3-n}$, a new promising class of monomers for the preparation of polymeric materials.[247–255] The mass spectra of the adducts of unsaturated compounds with 5,5-dimethoxytetrachloro-cyclopentadiene, which is a specific reagent for GC-MS analysis, have been characterised to establish not only the positions of the double bonds in unknown compounds but also, in the opinion of the authors cited,[256] their configuration.

Table 5. Standard mass spectra of phenylbis(pentafluorophenyl)-phosphine and *p*-bromofluorobenzene for standardising mass spectrometers.[182,231,232]

$C_6H_5P(C_6F_5)_2$		BrC_6H_4F	
m/z	I_{rel}, %	*m/z*	I_{rel}, %
51	30—60	50	15—40
68	$<0.02\ I^*_{69}$	75	30—70
69	not estimated (impurity)	95	100
		96	5—9
70	$<0.02\ I^*_{69}$	173	<1
127	40—60	174 M	>50
197	<1	175	2.5—4.5
198	100	176 M	$>50;\ 1.01\ I^*_{174}$
199	5—9		
275	10—30	177	2.5—4.5
365	~1		
441	<8		
442 M	>40		
443	>8		
444	[7—9		

*Relative to the intensities of the signals with the mass numbers indicated.

Chemical ionisation is most frequently used in mass fragmentography for detecting polyhalogeno-aromatic compounds.[152,153] Halogen-containing compounds are promising reagent gases for the selective detection of compounds of different chemical character. For example, the use of chlorobenzene (IE 9.04 eV) for this purpose in the analysis of mixtures of petroleum hydrocarbons makes it possible to record only the aromatic hydrocarbons (IE range 8.5 ± 0.3 eV), whereas alkanes (10.4 ± 0.5 eV) and cycloalkanes (10.1 ± 0.3 eV) are not detected.[257] The use of CH_3I leads to the formation in the gas phase of dimethyliodonium cations $[(CH_3)_2I]^+$, capable of effectively methylating the compound being analysed.[258] The characteristics of the production and reactivity of $[CCl_3]^+$ and $[CCl_3]^-$ ions under chemical-ionisation conditions have been discussed.[259,260]

The high electron affinity of halogen-containing compounds, compared with other organic compounds, is responsible for the large negative ion formation cross-section,[261] and makes negative ion mass spectrometry a promising method for detecting and identifying compounds of this type. In practice, anions are most frequently generated under chemical-ionisation conditions, when thermal electrons are present in the ion source. Under these conditions, aromatic compounds give intense signals due to the molecular radical-anions $M^{\cdot-}$ at a low fragmentation depth, and signals of the ions $[M - H]^-$ are typical of compounds not containing conjugated systems. Chemical ionisation with detection of negatively charged ions does not impose fundamental restrictions on the nature of the reagent gases (methane is usually employed), but in some cases, mixtures with halogen-containing substances, for example CH_3OH and $CHCl_3$ [262] or CH_4 and CH_2Cl_2,[263] are used. This method leads to the preferential formation of $[M + Cl]^-$ anions.

The mass spectra and optimum detection conditions for these ionisation conditions have been studied for a series of pentafluorophenyl compounds C_6F_5R (R = F, CH_3, NH_2, OH, SH, OCH_3, $OCOCH_3$, CHO, NO_2, and CN),[264] pentafluorobenzoyl derivatives of aminoacids,[92] chloro- and fluorochloroethylenes,[265,266] the pentafluoropropionates of hydroxylamine derivatives,[267] chloroglucuronides,[268] trifluoroacetyl derivatives of polyols (in particular myoinositol[269]), derivatives of α,β-difluorocinammic acids,[270] halogen-containing derivatives of dipeptides and their metabolites,[271] etc. The method is highly sensitive, since the efficiency of ionisation is high (close to 100%), and the spectra of the negative ions of the halogen-containing compounds in a number of cases have a high structural specificity, making it possible to distinguish isomers, which have similar positive-ion spectra. Only this method makes it possible to differentiate perfluorobuta-1,3-diene and the isomeric perfluorobut-2-yne and perfluorocyclobutene.[272] The high sensitivity of the method has led to its extensive application in the analysis of toxic polychlorinated aromatic compounds by GC-MS analysis.[154–161,273–277]

The detection of negative ions is also possible in so-called thermospray ionisation in liquid chromatograph–mass spectrometers used in the analysis of non-volatile or thermally unstable compounds, including pesticides.[278–280] The process of anion formation can be controlled by adding special halogen-containing additives to the eluant. For example, the addition of only 0.1–1% chloroacetonitrile increases considerably the sensitivity of the detection of phenols, as a result of the formation of $[M + Cl]^-$ ions.

Mass-spectrometric studies of one of the most important types of non-volatile compound, namely organic salts, including the large group of salts of hydrogen halides, have been reviewed.[281] The special methods of ionisation used to record the mass spectra of substances of this kind and high-boiling halogen derivatives include the field desorption of pesticides,[282] which may be combined with separation of the mixtures on a liquid chromatograph.[283] The mass spectra have been obtained under photo-ionisation conditions and analysed for halogenomethanes,[284] 1,1-difluoroethane,[285] 1,1-dichlorodifluoroethylene,[286] fluoroethylenes,[287] and 5-fluorouracil derivatives.[288] One of the promising methods of secondary ion emission with ionisation on solid supports, so-called fast atom bombardment (FAB), has been used to study fluoroalkyl sulphonates,[289] metabolites of 2-chloro-N-isopropylacetanilide,[290] iodoxamic acid and its dimethyl ester,[291] and the halides of various elements of Group IV of the periodic system.[292]

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The variety of existing methods and the constant development of new methods for the chromatographic and mass-spectrometric identification and quantitative determination of halogen-containing organic compounds is related to the need to solve a number of fundamental urgent problems. One of these is the contamination of the environment by substances which are produced almost exclusively by man. There are no effective natural decomposition mechanisms for these substances, which accumulate in different materials and have a cumulative effect. The influence of the emission of volatile fluorochlorohydrocarbons into the atmosphere on the stability of the ozone layer is now a controversial topic. The reliable control of the concentration of aromatic polychlorinated organic compounds in foodstuffs, soils, natural waters, effluents, etc. is undoubtedly important.

The effective solution of these problems makes special demands on analytical methods for determining halogen derivatives. These requirements include ensuring the minimum detection limit, decreasing the systematic and random errors of the analysis, and achieving the maximum selectivity, discussed in the present review, of the determination of HOC against a background of predominant quantities of interfering components of different chemical character. In addition a completely unique type of problem involves increasing the efficiency of methods for interpreting the results of gas-chromatographic and GC-MS analyses to establish the composition and structure of unknown components in complex mixtures. The greatest difficulties are encountered in the structural analysis and identification of fluorine-containing compounds, and the improvement of the appropriate algorithms is an extremely urgent task.

The variety of methods and techniques for carrying out all stages of the gas-chromatographic and GC-MS analysis and identification of HOC in different materials, reflected in the present review, provides an objective prerequisite for the selection of the best methods for solving specific problems. This characterisation of the determination of HOC by means of the single most important criterion, namely the maximum selectivity, should not however be considered in isolation from other parameters of analytical procedures, in particular the reliability of the identification of these compounds.

References

1. Yu S Drugov, N S Goryachev *Zh. Anal. Khim.*, 1981, **36** 371
2. A B Belikov, Yu S Drugov *Zh. Anal. Khim.*, 1981, **36** 1624
3. Yu S Drugov *Zavod. Lab.*, 1983, **49**(11) 16
4. Yu S Drugov, V G Berezkin *Gazokhromatograficheskii Analiz Zagryaznennogo Vozdukha* (The Gas-Chromatographic Analysis of Polluted Air), Izd. Khimiya, Moscow, 1981, 256 pp
5. *Applications of Mass Spectrometry to Trace Analysis* (Edited by S Facchetti), Elsevier, Amsterdam, 1982, 321 pp
6. Yu S Drugov, A B Belikov, G A D'yakova, V M Tul'chinskii *Metody Analiza Zagryaznenii Vozdukha* (Methods for the Analysis of Air Pollutants), Izd. Khimiya, Moscow, 1984, 384 pp
7. V A Isidorov, I G Zenkevich *Kromato-mass-spektrometricheskoe Opredelenie Sledov Organicheskikh Veshchestv v Atmosfere* (The Chromatographic–Mass-Spectrometric Determination of Traces of Organic Substances in the Atmosphere), Izd. Khimiya, Leningrad, 1982, 136 pp

8. V A Isidorov *Organicheskaya Khimiya Atmosfery* (The Organic Chemistry of the Atmosphere), Izd. Khimiya, Leningrad, 1985, 265 pp
9. W G Jennings, A Rapp *Sample Preparation for Gas-Chromatographic Analysis* (Translated into Russian), Izd. Mir, Moscow, 1986, 118 pp
10. K Ulm *J. Fluorine Chem.*, 1982, **21** 69
11. J A Seckar, H J Trochimowicz, G K Hogan *Food Chem. Toxicol.*, 1986, **24** 237
12. M J Mercier, M Lans, J De Gerlache *Mutagenicity, Carcinog. and Teratogenicity Ind. Pollutants*, New York, 1984, p. 281
13. Yu V Pashin, V I Kozachenko, T A Zatsepilova, L M Bakhitova *Khimicheskie Mutageny Okruzhayushchei Sredy* (Chemical Mutagens of the Environment), Izd. Nauka, Moscow, 1983, 140 pp
14. M J Molina, F S Rowland *Nature*, 1974, **249** 810
15. M J Molina, F S Rowland *Rev. Aerophys., Space Phys.*, 1974, 1
16. V A Isidorov, I G Zenkevich *Dokl. Akad. Nauk SSSR*, 1985, **280** 223
17. V A Isidorov, B V Ioffe *Dokl. Akad. Nauk SSSR*, 1986, **287** 86
18. T Noy, P Fabian, R Borchers, et al. *J. Chromatogr.*, 1987, **393** 343
19. R Macholz *Nahrung*, 1982, **26** 747
20. K Gumsch, H Haentzschel *Luft Ketetechn.*, 1982, **18** 196
21. H C Thompson, D C Kendall, W A Korfmacher, et al. *Environ. Sci. Technol.*, 1986, **20** 597
22. W W Berg, L E Heidt, W H Pollock, et al. *Geophys. Res. Lett.*, 1984, **11** 429
23. M Ochme, S Mane *Fresenius' Z. Anal. Chem.*, 1984, **319** 141
24. T J Murata *J. Environ.*, 1984, **20** 145
25. J Paasivirta, M Knuutila, R Paukku *Chemosphere*, 1985, **14** 1741
26. M I Afanas'ev, N K Vulykh, A N Zagruzina, et al. *Monitoring Fonovogo Zagryazneniya Prirodnoi Sredy* (Monitoring the Background Contamination of the Natural Environment), No. 3, 1985, p. 27
27. T Kashimoto *Environ. Conserv. Eng.*, 1984, **13** 389
28. D G Patterson, J S Holler, C R Lapeza, et al. *Anal. Chem.*, 1986, **58** 705
29. R L Rawls, D A O'Sullivan *Chem. Eng. News*, 1976, **54** 27
30. T Mazer, F D Hileman, R W Noble, J J Brooks *Anal. Chem.*, 1983, **55** 104
31. H O Rghei, G A Eiceman *Chemosphere*, 1985, **14** 167
32. E Benfenati, F Gizzi, R Reginato, et al. *Chemosphere*, 1983, **12**(9–10) 1151
33. K Ballschmiter, W Kraemer, H Magg, et al. *Chemosphere*, 1984, **13** 1139
34. J M Czuczwa, R A Hites *Environ. Sci. Technol.*, 1986, **20** 195
35. W Schaefer, K Ballschmiter *Chemosphere*, 1986, **15** 755
36. A R Oyler, R J Liukkonen, R J Lukasewycz, et al. *Environ.* 1982, **46** 73
37. S Onodera, N Iino, M Matsuda, S Ishikura *J. Chromatogr.*, 1983, **265** 201
38. E Kissa *Anal. Chem.*, 1983, **55** 1222
39. B Vierkorn-Rudolph, M Savelsberg, K Baechmann *J. Chromatogr.*, 1979, **186** 216
40. L J Anthony, B E Prescott *J. Chromatogr.*, 1983, **264** 405
41. M Noshiro, T Yarita, S Yonemori *Repts. Res. Lab., Asahi Glass Co.*, 1984, **34** 197
42. J M Cheplen, C S Barrow, E L White *Anal. Chem.*, 1984, **56** 1194
43. R G Melcher, V J Caldecourt *Anal. Chem.*, 1980, **52** 875
44. W C Kuster, P D Goldan, F C Fehsenfeld *J. Chromatogr.*, 1981, **205** 271
45. K Fushimi, Y Sugimura *Pap. Meteorol. Geophys.*, 1981, **32** 313
46. K Ballschmiter, P Mayer, T Class *Fresenius' Z. Anal. Chem.*, 1986, **323** 334
47. A L Sykes, D E Wagoner, C E Decker *Fresenius' Z. Anal. Chem.*, 1980, **52** 1630
48. G M Zubashvili, V P Musakina, G A Musakin, et al. *Zh. Prikl. Khim.*, 1981, **54** 1159
49. T Paryjczak, H Balczewska, W Ignaczak, et al. *Bromatol. Chem. Toksykol.*, 1985, **18** 69–73
50. M DeBortoli, E Pecchio *J. High Resol. Chromatogr., Chromatogr. Commun.*, 1985, **8** 422
51. T W D'Ottavio, R W Goodrich, R N Dietz *Environ. Sci. Technol.*, 1986, **20** 100
52. I A Tsubil'skaya, I G Zenkevich, A A Rodin *Tezisy Dokladov IX Vsesoyuznoi Konferentsii po Fazovoi Khromatografii* (Summaries of Papers Presented at the Ninth All-Union Conference on Gas Chromatography), Kuibyshev, 1987, p. 275
53. G Crescentini, F Bruner *J. Fluorine Chem.*, 1980, **16** 621
54. S Seshadri, J W Bozzelli *Chemosphere*, 1983, **12** 809
55. M D Erickson, M K Alsup, P A Hyldburg *Anal. Chem.*, 1981, **53** 1265
56. A I Clark, A E McIntyre, J N Lester, et al. *J. Chromatogr.*, 1982, **252** 147
57. M A Leiber, H C Berk *Anal. Chem.*, 1984, **56** 2134
58. J F Pankow, T J Kristensen *Anal. Chem.*, 1983, **55** 2187
59. P O Yeboah, W W Kolgore *Bull. Environ. Contam. Toxicol.*, 1984, **33** 13
60. J W Graydon, K Grob *J. Chromatogr.*, 1983, **254** 265
61. G MacLeod, J M Ames *J. Chromatogr.*, 1986, **355** 393
62. J F Walling, J E Bumgarner, D J Driscoll, et al. *Atmos. Environ.*, 1986, **20** 51
63. J Namiesnik, L Torres, E Kozlowski, et al. *J. Chromatogr.*, 1981, **208** 239
64. L Wennrich, W Engewald, T Welsch *Chem. Technol.*, 1981, **33** 203
65. W N Billings, T F Bidleman *Atmos. Environ.*, 1983, **17** 383
66. A G Vitenberg, B V Ioffe *Gazovaya Ekstraktsiya v Khromatograficheskom Analize. Parofaznyi Analiz i Rodstvennye Metody* (Gas Extraction in Chromatographic Analysis. Vapour-Phase Analysis and Related Methods), Izd. Khimiya, Leningrad, 1981, 280 pp
67. M Mehran *J. Chromatogr. Sci.*, 1985, **23** 546
68. M House *Anal. Chem.*, 1983, **20** 423
69. G Castello, T C Gerbino, S Kanitz *J. Chromatogr.*, 1982, **247** 263
70. B Kolb, M Auer, P Pospisil *J. Chromatogr.*, 1983, **279** 341
71. D Rinne, C J Bieber *Fresenius' Z. Anal. Chem.*, 1986, **325** 153
72. T Wang, R Lenahan *Bull. Environ. Contam. Toxicol.*, 1984, **32** 429
73. J Mueller, F Riedel *Communs. Eur. Communities, Rep. EUR 9436*, 1984, 373
74. G Aggazzotti, G Predieri, G Fantuzzi *J. Chromatogr.*, 1987, **416** 125
75. V V Zadimov, M P Potapova, A V Uvarov *Lakokras. Mater. Ikh Primenenie*, 1986, (6) 40
76. T A Kalmykova, A Ya Lazaris *Zh. Anal. Khim.*, 1986, **41** 2080

77. D L Heikes *J. Off. Anal. Chem.*, 1987, **70** 176
78. G I Bystrova, I G Zenkevich, B V Ioffe *Vestn. Leningr. Univ., Fiz., Khim.*, 1984, (22) 60
79. B V Ioffe, G I Bystrova, I G Zenkevich *Zh. Anal. Khim.*, 1985, **40** 306
80. Z Weidenhoffer, Z Pizak, J Dolansky *J. Chromatogr.*, 1985, **350** 324
81. P Burchill, A A Herod, K M Marsh, E Pritchard *Water Res.*, 1983, **17** 1905
82. B G Oliver, K D Bothen *Anal. Chem.*, 1980, **52** 2066
83. B G Oliver, K D Nicol *Chromatographia*, 1982, **16** 336
84. H Steinwandter, L Zimmer *Fresenius' Z. Anal. Chem.*, 1983, **316** 705
85. A C Viau, F W Karasek *J. Chromatogr.*, 1983, **270** 235
86. M L Gross *J. Chem. Ed.*, 1982, **59** 921
87. S D Boyce, J F Hornig *Water Res.*, 1983, **17** 685
88. K Grob, A Habich *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1983, **6** 11
89. A Zlatkis, F Wang, H Shanfield *Anal. Chem.*, 1983, **55** 1848
90. E Fogelqvist, M Larsson *J. Chromatogr.*, 1983, **279** 297
91. J Drozd *Chemical Derivatization in Gas Chromatography*, Elsevier, Amsterdam, 1981, 156 pp
92. A G Netting, A M Duffield *Biomed. Mass Spectrom.*, 1985, **12** 668
93. Y Okano, T Kadota, J Nagata, et al. *J. Chromatogr. Biomed. Appl.*, 1984, **310** 251
94. A I Krylov, V L Borodina, V A Rogozkin *Zh. Anal. Khim.*, 1986, **41** 2235
95. W Büser, H F Erbersdobler *J. Chromatogr.*, 1984, **303** 234
96. B Nilsson, D A Zopf *Glycoconjugates. Proceedings of the VIth International Symposium, Tokyo, 1981*, p. 248
97. B Nilsson, D A Zopf *Meth. Enzym.*, 1982, **83** 46
98. B Nilsson, D A Zopf *Arch. Biochem. Biophys.*, 1983, **222** 628
99. K Robards, M Whitelaw *J. Chromatogr.*, 1986, **373** 81
100. G Carlucci, L Airoldi, R Fanelli, et al. *J. Chromatogr. Biomed. Appl.*, 1984, **311** 141
101. V E Kirichenko, I A Piterskikh, A I Speshilova, et al. *Zh. Anal. Khim.*, 1987, **42** 1294
102. S A Barker, L C Tolbert, C B Brown *Org. Mass Spectrom.*, 1986, **21** 267
103. S D Roy, G McKay, E M Hawes, et al. *J. Chromatogr. Biomed. Appl.*, 1984, **310** 307
104. G B Baker, J T F Wong, R T Coutts, et al. *J. Chromatogr.*, 1987, **392** 317
105. J B Brooks, M T Basta, C C Alley, et al. *J. Chromatogr. Biomed. Appl.*, 1984, **309** 269
106. T V Verheyen, R B Johns *Anal. Chem.*, 1983, **55** 1564
107. L F Lindberg, S A Popov *Zh. Anal. Khim.*, 1987, **42** 139
108. N T Ivanova, L A Frangulyan *Gazokhromatograficheskii Analiz Nestabil'nykh i Reaktsionnosposobnykh Soedinenii* (The Gas-Chromatographic Analysis of Unstable and Reactive Compounds), Izd. Khimiya, Moscow, 1979, 232 pp
109. F Bruner, G Crescentini, F Mangani, et al. *Anal. Chem.*, 1981, **53** 798
110. *Supelco Chromatogr. Suppl. Internat. Cat.*, 1982, No. 20, 240 pp
111. L H Ghaoui, E Dessai, W E Wentworth, et al. *Chromatographia*, 1985, **20** 75
112. D T Williams, G L Lebel, T Furmanczyk *Chemosphere*, 1980, **9** 45
113. W Vogt, K Jacob, A B Ohnesorge, G Schwertfeger *J. Chromatogr.*, 1981, **217** 91
114. K E McLeod *Environ. Sci. Technol.*, 1981, **15** 926
115. A Garcia-Gutierrez, A E McIntyre, J N Lester, R Perry *Sci. Technol. Lett.*, 1983, **4** 129
116. K Ballschmiter, W Schäfer, H Buchert *Fresenius' Z. Anal. Chem.*, 1987, **326** 253
117. F I Onuska, K A Terry *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1986, **9** 671
118. A L Bergman, L Reutergaardh, M Aahlman *J Chromatogr.*, 1984, **291** 392
119. L G M Tuinstra, A H Roos, B Griepink, D E Wells *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1985, **8** 475
120. R M Smith, P W O'Keefe, D R Hilker, K M Aldous *Anal. Chem.*, 1986, **58** 2414
121. G J Hollod, S J Eisenreich *Anal. Chim. Acta*, 1981, **124** 31
122. H J Stan, B Steinbach *J. Chromatogr.*, 1984, **290** 311
123. T Gorski, W Buda *Rock Paust. hig.*, 1981, **32** 271
124. F R Guenther, S N Chesler *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1983, **6** 684
125. V D Chmil' *Zh. Anal. Khim.*, 1983, **38** 2224
126. L M Shalaby *Biomed. Mass Spectrom.*, 1985, **12** 261
127. J Nair, K M Munir, S V Bhide *J. Liq. Chromatogr.*, 1983, **6** 2829
128. S B Hawthorne, D J Miller *J. Chromatogr.*, 1987, **403** 63
129. E D Lee, J D Henion *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1986, **9** 172
130. S J Fernandez, L P Murphy, R A Rankin *Anal. Chem.*, 1984, **56** 1285
131. Y Makide, Y Kanai, T Tominaga *J. Chem. Soc. Jpn.*, 1981, 133
132. E Stottmeister, P Hendel, W Engewald *Acta Hydrochim. Hydrobiol.*, 1986, **14** 573
133. O L De Guevara, A A Godov, C C De Nava *J. Chromatogr.*, 1987, **403** 350
134. M J Bertrand, S Stefanidis, A Donais, B Sarrasin *J. Chromatogr.*, 1986, **354** 331
135. V E Kirichenko, G S Kulikova, K P Pashkevich *Okhrana Prirody i Primenenie Khimicheskikh Sredstv v Lesnom i Sel'skom Khozyaistve* (Environmental Protection and the Use of Chemicals in Forestry and Agriculture), Izd. Akad. Nauk SSSR, Leningrad, 1981, p. 139
136. F J Reineke, K Baechmann *J. Chromatogr.*, 1985, **323** 323
137. G Wells *J. Chromatogr.*, 1985, **436** 1
138. C Vidal-Madjar, F Parey, J L Excoffier, S Bekassy *J. Chromatogr.*, 1981, **203** 247
139. W P Schmidt, H L Rook *Anal. Chem.*, 1983, **55** 290
140. M Maeda, M Munemono *Kagaku*, 1984, **39** 282
141. A Bacaloni, G Goretti, A Lagana, et al. *Anal. Chem.*, 1980, **52** 2033
142. M S Kleshcheva, N E Shadrina, I T Korchnova, N B Shuvalova *Zh. Anal. Khim.*, 1980, **35** 128
143. R S Narang, B Bush *Anal. Chem.*, 1980, **52** 2076
144. T Dumas, E J Bond *J. Agric. Food Chem.*, 1985, **33** 276
145. P D Goldan, F C Fehsenfeld, W C Kuster, et al. *Anal. Chem.*, 1980, **52** 1751
146. M Suzuki *J. Chromatogr.*, 1984, **312** 403
147. W L Fitch, A D Sauter *Anal. Chem.*, 1983, **55** 832
148. J E Gebhart, T L Hayes, A L Alford-Stevens, W L Budde *Anal. Chem.*, 1985, **57** 2458
149. L E Slivon, J E Gebhart, T L Hayes, et al. *Anal. Chem.*, 1985, **57** 2464

150. D M L Fung, R K Boyd, S H Safe, B G Chittim *Biomed. Mass Spectrom.*, 1985, **12** 247
151. C M Meyer, P W O'Keefe, R G Briggs, D R Hilker *Biomed. Environ. Mass Spectrom.*, 1986, **13** 47
152. Y Iida, S Daishima, T Kashiwagi *Bunseki Kagaku*, 1983, **32** 80
153. R D Voyksner, J T Bursey, T W Pack, R L Porch *Anal. Chem.*, 1986, **58** 621
154. E Lewis, W D Jamieson *Int. J. Mass Spectrom. Ion Phys.*, 1983, **48** 303
155. M Oehme, S Manoe, H Stray *J. Chromatogr.*, 1983, **279** 649
156. R K Mitchum, W A Korfmacher, J R Althaus *Org. Mass Spectrom.*, 1984, **19** 63
157. M Oehme, P Kirschmer *Anal. Chem.*, 1984, **56** 2754
158. S Z Sha, A M Duffield *J. Chromatogr.*, 1984, **284** 157
159. N S Zarr, J L Lindgren, J M Jenks *Abstr. Pap. Pittsburg Conf., New Orleans, 1985*, p. 719
160. W F Miles, N P Gurprasad, G P Malis *Anal. Chem.*, 1985, **57** 1133
161. T Ramdahl, G E Carlberg, P Kolsaker *Sci. Total Environ.*, 1986, **48** 147
162. W A Korfmacher, R K Mitchum, F D Hileman, T Mazer *Chemosphere*, 1983, **12** 1243
163. W A Korfmacher, R K Mitchum *Org. Mass Spectrom.*, 1984, **19** 299
164. M A Eckhoff, T H Ridgway, J A Caruso *Anal. Chem.*, 1983, **55** 1004
165. K J Slatkavitz, P C Uden, L D Hoey, R M Barnes *J. Chromatogr.*, 1984, **302** 277
166. J M Keane, R C Fry, *Abstr. Pap. Pittsburg Conf., Atlantic City, 1986*, p. 483
167. G W Jansen, F A Huf, H J De Jong *Spectrochim. Acta, Part B*, 1985, **40** 307
168. S R Coode, B Chambers, N P Buddin *Spectrochim. Acta, Part B*, 1985, **40** 329
169. M Burguera, J L Burguera *Anal. Chim. Acta*, 1983, **153** 53
170. O Piringer, E Wolff *J. Chromatogr.*, 1984, **284** 373
171. J N Driscoll, D W Conron, P Ferioli *J. Chromatogr.*, 1984, **302** 269
172. C P Nulton, C L Haile, D P Redford *Anal. Chem.*, 1984, **56** 598
173. B I Shushan, S D Tanner *Chemosphere*, 1985, **14** 843
174. W V Ligon, R J May *Anal. Chem.*, 1986, **58** 558
175. R D Voyksner, J R Hass, G W Sovocool, M M Bursey *Anal. Chem.*, 1983, (4) 744
176. T Sakuma, B I Shushan, W R Davidson, S Nascon *Abstr. Pap. Pittsburg Conf., Atlantic City, 1982*, p. 665
177. B I Shushan, B A Thomson, L M Danylewych, J E Fulford *Abstr. Pap. Pittsburg Conf., Atlantic City, 1982*, p. 201
178. D F Hunt, J Shabanowitz, T M Harvey *Anal. Org. Micropollutants Water. Proceedings of the IIIrd European Symposium, Oslo, 1983*, p. 53
179. R Tembreull, C H Sin, H M Pang, D M Lubman *Anal. Chem.*, 1985, **57** 1186
180. D R Cronn, D E Harsch *Anal. Lett.*, 1979, **12** 1489
181. K Alben *Anal. Chem.*, 1980, **52** 1821
182. P Olynyk, W L Budde, J W Eichenberger *J. Chromatogr. Sci.*, 1981, **19** 377
183. R S Collard, M M Irwin *Talanta*, 1983, **30** 811
184. E E Hargesheimer *J. Assoc. Offic. Anal. Chem.*, 1984, **67** 1067
185. E J Gallegos *Anal. Chem.*, 1981, **53** 187
186. G Crescentini, F Mangani, A R Mastrogiacomo, A Cappioello, et al. *J. Chromatogr.*, 1983, **280** 146
187. M S Vigdergauz, L V Semenchenko, V A Ezrets, Yu N Bogoslovskii *Kachestvennyi Gazokhromatograficheskii Analiz* (Qualitative Gas-Chromatographic Analysis), Izd. Nauka, Moscow, 1978, 244 pp
188. I G Zenkevich *Zh. Anal. Khim.*, 1984, **39** 1297
189. J F Sprouse, A Varano *Int. Laboratory*, 1984, (6) 54
190. L Weber *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1986, **9** 446
191. G Castello, G D'Amato *J. Chromatogr.*, 1986, **354** 65
192. I O O Korhonen *J. Chromatogr.*, 1984, **288** 51
193. J K Haken, I O O Korhonen *J. Chromatogr.*, 1984, **284** 474
194. I O O Korhonen *Chromatographia*, 1982, **15** 505
195. I O O Korhonen *J. Chromatogr.*, 1985, **324** 181
196. I O O Korhonen, M A Lind *J. Chromatogr.*, 1985, **322** 97
197. J K Haken, I O O Korhonen *J. Chromatogr.*, 1986, **356** 79
198. J K Haken, I O O Korhonen *J. Chromatogr.*, 1985, **319** 131
199. J K Haken, B G Madden, I O O Korhonen *J. Chromatogr.*, 1985, **325** 61
200. J K Hagen, I O O Korhonen *J. Chromatogr.*, 1986, **357** 253
201. M B Evans, J K Haken *J Chromatogr.*, 1986, **351** 155
202. I O O Korhonen, M A Lind *J. Chromatogr.*, 1985, **322** 83
203. I O O Korhonen *J. Chromatogr.*, 1986, **360** 63
204. I O O Korhonen *J Chromatogr.*, 1986, **357** 107
205. I O O Korhonen *J. Chromatogr.*, 1985, **321** 467
206. J Bermejo, C G Blanco, M D Guillen *J. Chromatogr.*, 1985, **331** 237
207. I O O Korhonen, J S Knuutinen *J. Chromatogr.*, 1984, **292** 345
208. I O O Korhonen *J. Chromatogr.*, 1984, **315** 185
209. I O O Korhonen, M A Lind *J. Chromatogr.*, 1985, **328** 325
210. V D Chmil', K I Sakodynskii *Zh. Anal. Khim.*, 1984, **39** 1105
211. W A Korfmacher, R K Mitchum *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1982, **5** 681
212. M D Hale, F D Hileman, T Mazer, et al. *Anal. Chem.*, 1985, **57** 640
213. W J Dunn, M Koehler, D L Stalling, T R Schwartz *Anal. Chem.*, 1986, **58** 1835
214. J R Donelly, W D Munslow, R K Mitchum, G W Sovocool *J. Chromatogr.*, 1987, **392** 51
215. W J Dunn, D L Stalling, T R Schwartz, et al. *Anal. Chem.*, 1984, **56** 1308
216. L P Burkhard, D Weininger *Anal. Chem.*, 1987, **59** 1187
217. P A D'Agostino, L R Provost *J. Chromatogr.*, 1985, **331** 47
218. W L Saxton *J. Chromatogr.*, 1987, **393** 175
219. T R Schwartz, J D Petty, E M Kaiser *Anal. Chem.*, 1983, **55** 1839
220. G V Golovin, A I Smol'chenko, K P Fedorov, B A Rudenko *Zh. Anal. Khim.*, 1984, **39** 723
221. T R Schwartz, R D Campbell, D L Stalling, et al. *Anal. Chem.*, 1984, **56** 1303
222. A Yasuhara, M Morita, K Fuwa *J. Chromatogr.*, 1985, **328** 35
223. G L Hall, W E Whitehead, C R Mourer, T Shibamoto *J. High Resolut. Chromatogr., Chromatogr. Commun.*, 1986, **9** 266
224. J Enqvist, A Hesso *Kemia-Kemi*, 1982, **9** 176
225. A Manninen, M L Kuitunen, L Julin *J. Chromatogr.*, 1987, **394** 465
226. N S Vul'fson, V G Zaikin, A I Mikaya *Mass-Spektrometriya Organicheskikh Soedinenii* (The Mass Spectrometry of Organic Compounds), Izd. Khimiya, Moscow, 1986, 312 pp

227. I G Zenkevich, B V Ioffe *Interpretatsiya Mass-Spektrov Organicheskikh Soedinenii* (The Interpretation of the Mass Spectra of Organic Compounds), Izd. Khimiya, Leningrad, 1986, 176 pp
228. J L Labrosse, R J Anderegg *J. Chromatogr.*, 1984, **314** 83
229. J L Labrosse, R J Anderegg *J. Chromatogr.*, 1984, **314** 93
230. G W A Milne, W L Budde, S R Heller, et al. *Org. Mass. Spectrom.*, 1982, **17** 547
231. J W Eichelberger, L E Harris, W L Budde *Anal. Chem.*, 1975, **47** 45
232. Internat. Org. of Legal Metrology, Oct. 1985. *GC/MS Data System for Analysis of Org. Pollutants in Water. OITM Rep. Secr., PS 17/RS2,* 26 pp
233. V N Bochkarev, A N Polivanov, T F Slyusarenko, et al. *Zh. Obshch. Khim.*, 1981, **51** 824
234. S T Hill, M Mokotoff *J. Org. Chem.*, 1984, **49** 1441
235. I G Zenkevich, M V Drugov *Teor. Eksp. Khim.*, 1987, (2) 226
236. A A Espenbetov, Yu T Struchkov, S P Kolesnikov, O M Nefedov *J. Organomet. Chem.*, 1984, **275** 33
237. K A Balodis, R S Medne, O Ya Neiland, et al. *Zh. Org. Khim.*, 1985, **21** 2423
238. K Yonemoto, F Kakizaki, G Yamamoto, et al. *Bull. Chem. Soc. Jpn.*, 1985, **58** 3346
239. A P Rothwell, R G Cooks, T V Singh, et al. *Org. Mass Spectrom.*, 1985, **20** 757
240. K Oxinos, H Parlar, F Korte *Chemosphere,* 1981, **10** 63
241. H S Pyysalo, K Wickstroem, R Litmanen, et al. *Finn. Chem. Lett.*, 1983, (1–2) 34
242. F I Onuska *Mass Spectrom. Environ. Sci.*, New York, 1985, p. 405
243. C E Parker, P W Albro, M J Bobenrieth, et al. *J. Chromatogr. Biomed. Appl.*, 1983, **278** 1
244. Y Tondeur, P W Albro, J R Hass, et al. *Anal. Chem.*, 1984, **56** 1344
245. A L Alford-Stevens, T A Bellar, J W Eichelberger, W L Budde *Anal. Chem.*, 1986, **58** 2022
246. N Bhargava, M Anand, M M Agrawal, et al. *Indian J. Chem., Part B,* 1982, **21** 691
247. R D Minard, H R Allcock *Org. Mass Spectrom.*, 1983, **18** 178
248. P J Harris, R D Minard, H R Allcock *Org. Mass Spectrom.*, 1983, **18** 268
249. M Gleria, G Audisio, S Daolio, et al. *Macromolecules,* 1984, **17** 1230
250. P J Harris, K B Williams *Org. Mass Spectrom.*, 1984, **19** 248
251. M Gleria, S Daolio, A M Maccioni, et al. *Org. Mass Spectrom.*, 1985, **20** 686
252. P J Harris, R D Minard, H R Allcock *Org. Mass Spectrom.*, 1985, **20** 321
253. A Ouassini, R De Jaeger, J Heubel *Z. Anorg. Allg. Chem.*, 1985, **351** 188
254. T T Bamgboye, O A Bamgboye *Spectrochim. Acta,* 1985, **41** 981
255. P Castera, J P Faucher, G Guerch, et al. *Inorg. Chim. Acta,* 1985, **108** 29
256. D A Kidwell, K Biemann *Anal. Chem.*, 1982, **54** 2462
257. L W Sieck *Anal. Chem.*, 1983, **55** 38
258. C Jortay, R Flammang, A Maquestiau *Bull. Soc. Chim. Belg.*, 1985, **941** 727
259. K Hiraoka, K Morise, T Shoda *Int. J. Mass Spectrom. Ion Process.*, 1985, **67** 11
260. J A Stone, N J Moote, A C M Wojtyniak *Can. J. Chem.*, 1985, **63** 260
261. V I Khvostenko *Mass-Spektrometriya Otritsatel'nykh Ionov v Organicheskoi Khimii* (Negative-Ion Mass Spectrometry in Organic Chemistry), Izd. Nauka, Moscow, 1981, 160 pp
262. K G Das, A M Reddy, et al. *Org. Mass Spectrom.*, 1985, **20** 677
263. Y Deng, R Peng *Youji Huaxue* (Org. Chem.), 1985, (3) 254
264. I K Gregor, M Guilhaus *J. Fluorine Chem.*, 1983, **23** 549
265. R Kaufel, E Illenberger, H Baumgaertel *Chem. Phys. Lett.*, 1984, **106** 342
266. E Illenberger, H Baumgaertel, S Suezer *J. Electron. Spectrosc. Relat. Phenom.*, 1984, **33** 123
267. G K C Low, A M Duffield *Org. Mass Spectrom.*, 1985, **20** 595
268. P P Wickramanayake, M L Deinzer, A L Burlingame *Biomed. Mass Spectrom.*, 1985, **12** 127
269. J W Turk, B A Wolf, M L McDaniel *Biomed. Environ. Mass Spectrom.*, 1986, **13** 234
270. A I Parakhnenko, Yu S Nekrasov, V A Mazunov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, (6) 1307
271. S Hashimoto, E Sakurai, M Mizobuchi, et al. *Biomed. Mass Spectrom.*, 1982, **9** 546
272. S Suezer, E Illenberger, M H Baumgaertel *Org. Mass Spectrom.*, 1984, **19** 292
273. A Cavallaro, G Bandi, G Invernizzi, et al. *Chlorinated Dioxins and Related Compounds,* Impact Environ. Proc. Workshop, Rome, 1982, p. 55
274. S Daishima, Y Iida, T Kajiki *J. Chem. Soc. Jpn., Chem. Ind. Chem.*, 1984, (5) 739
275. S Daishima, Y Iida, T Kajiki *J. Chem. Soc. Jpn., Chem. Ind. Chem.*, 1984, (7) 1146
276. E A Stemmler, R A Hites *Anal. Chem.*, 1985, **57** 684
277. D L Swackhamer, M J Charles, R A Hites *Anal. Chem.*, 1987, **59** 913
278. K G Heumann, F Beer, H Weiss *Mikrochim. Acta,* 1983, **1** 95
279. C E Parker, K Yamaguchi, D L Harvan, et al. *J. Chromatogr.*, 1985, **319** 273
280. C E Parker, R W Smith, S J Gaskell, M M Bursey *Anal. Chem.*, 1986, **58** 1661
281. B L Mil'man *Zh. Anal. Khim.*, 1986, **41** 1933
282. V G Golovatyi, M A Klisenko, et al. *Tezisy Dokladov V Vsesoyuznoi Konferentsii po Analiticheskoi Khimii Organicheskikh Soedinenii* (Summaries of Papers Presented at the Fifth All-Union Conference on the Analytical Chemistry of Organic Compounds), Izd. Nauka, Moscow, 1984, p. 248
283. C D Watts, B Crathorne, M Fielding, C P Steel *Anal. Org. Micropollutants Water. Proceedings of the IIIrd European Symposium, Oslo, 1983,* p. 120
284. F C Y Wang, G E Leroi *Vac. Ultraviolet. Radiat. Phys., Proceedings of the VIIth International Conference, Jerusalem, 1983,* p. 210
285. T Heinis, R Baer, K Boerlin, M Jungen *Chem. Phys.*, 1985, **94** 235
286. K Rademann, H W Jochims, H Baumgaertel *J. Phys. Chem.*, 1985, **89** 3459
287. H O Beckmann, W Braun, H W Jochims, et al. *Chem. Phys. Lett.*, 1985, **121** 499
288. V M Orlov, V N Pustobaev, S N Mikhailov, et al. *Bioorg. Khim.*, 1984, **10** 528
289. P A Lyon, K B Tomer, M L Gross *Anal. Chem.*, 1985, **57** 2984
290. G L Larsen, R Ryhage *Xenobiotica,* 1982, **12** 855
291. D Pitre, M Grandi, P Traldi, R Self, *Arch. Pharm. Chemi. Sci. Ed.*, 1984, **317** 1037
292. J M Miller, A Fulcher *Can. J. Chem.*, 1985, **63** 2508

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The liquid-crystalline state of salt melts containing organic ions

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ABSTRACT. The present review deals with the latest achievements in the chemistry of ionic melts and liquid crystals (LC). New liquid crystals, formed by salt melts containing organic ions, have been described. The characteristics of their thermodynamic and transport behaviour, structure, and optical properties have been examined. The part played by electrostatic interactions and the parameters of the cations and anions in the stabilisation of the ionic mesophase has been demonstrated. The dependence of the production of liquid crystals in binary salt mesogenic systems on the nature of the interionic interactions has been analysed. The possible practical applications of this new class of liquid crystals have been discussed.

The bibliography contains 77 references.

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I. Introduction

The most remarkable of the states of aggregation of matter, namely the liquid-crystalline state, is produced as a result of the specific breakdown of the crystal lattice on fusion (thermotropic LC) or solution (lyotropic LC) of a mesogenic substance.

The basic problem in the chemistry of liquid crystals is to determine which characteristics of the structure of the molecules of mesogens and their interactions determine the existence of the mesomorphic phase. Ionic liquid-crystalline melts, in which the principal role in the stabilisation of the liquid-crystalline state is played by the electrostatic factor,[1] are of particular interest in this connection.

The term melt is used to describe that part of the range of the liquid state of matter which can be described by the quasi-crystalline approach.[1,2] The structure and properties of salt melts consisting of simple ions have been studied in detail. They can be regarded as unique model systems, but the intensive study of melts containing monatomic ions has been stimulated not only by the possibility of carrying out simple experiments and the unambiguous interpretation of the results, but also by their extensive practical application.[2,3] Physical chemists have recently begun to study salt melts containing polyatomic ions. This has been due not only to the necessity of developing the theory of the liquid state but also to a number of technological requirements of modern industry. Research workers have been attracted by the low melting points, the ease of formation of salt glasses, and other properties of melts containing complex ions.[4–6]

Until recently, mainly inorganic salt melts were studied although organic salts provide a much wider and more varied range of materials for study and application. Since the shape and size of the repulsion envelope of the organic ion,† and the magnitude and distribution of the density of the Coulombic charge on it, can be easily varied, organic salt melts make it possible to obtain liquids with different inter-particle interactions, with expected and sometimes unusual properties.

The main obstacle to the extensive study and application of organic salt melts has been their low thermal stability. The instability of salt melts is both "internal", determined by the energy of the interatomic bonds within the ion, and "external", determined by the perturbing influence of impurity ions, molecules, and atoms.[4]

In most cases, the instability of organic ionic melts is "external", so that it can be avoided. Ubbelohde and co-workers[7,8] determined various impurities influencing the stability of melts containing organic ions, and formulated the requirements to be satisfied in the synthesis and study of these salts. Thus the basic conditions for working with molten organic salts include the absence from the melt of molecular or atomic oxygen and impurity transition metal ions and OH^- ions.

Thorough precautions in experiments with organic salt melts have made it possible to accumulate fairly extensive data on their physicochemical properties.[9–12]

Melts formed by the salts of n-alkanoic acids have been studied most systematically. Many representatives of this class of salt show unique properties. Thus in a definite temperature range, from the melting point (T_f) to the clearing temperature of the mesophase (T_{cl}), most of them exist in a viscous optically anisotropic state completely analogous to liquid crystals.[13]

A liquid crystal is a liquid with a constant anisotropy of the physical properties, having one-dimensional (nematic, cholesteric) or two-dimensional (smectic) order in space.

Liquid crystals play an important role in present-day science and technology.[14–27] Considerable interest is shown in all new data on liquid-crystalline substances, particularly data refuting the previously accepted view that the ability to form liquid crystals or mesophases

†The repulsion envelope of a polyatomic ion is the surface extending round the spheres of repulsion of the outer atoms in the complex ion; the radius of the sphere of repulsion of an atom, according to Ubbelohde, is equal to its crystal-chemical radius for the given type of bond and coordination (see the bibliography in Ubbelohde's book[1]).

is shown only by complex organic molecules with clearly defined anisometry.[14,15]

In fact, mesogens (that is substances forming liquid crystals or mesophases) are most frequently long rod-shaped or cylindrical, and also disc-shaped, molecules. At an early date, however, Frederiks,[16] one of the founders of the physics of liquid crystals, warned against overestimation of the part played by the anisometry of mesogens: "... since there are known cases of liquids with long molecules which do not form an anisotropic liquid phase, a comparatively elongated molecule is undoubtedly not a sufficient condition for the existence of an anisotropic phase. In fact, it cannot even be stated that this is a necessary condition".

Mesogenic substances with non-traditional structure and molecular shape, such as organic and inorganic compounds with ionic structures, are now increasingly encountered among liquid crystals.[1,13,20,21] These mesogens are extending the range of existence of mesogenic substances from organic into inorganic chemistry.

The liquid-crystalline properties of salts of carboxylic acids were detected as early as 1910 by Vorlaender on fusion of the long-chain homologues of soaps.[14] The mesophases of these salts are similar to liquid soaps, and by analogy were called smectic, from the Greek work "smektos"—soap-like. It was later found that the smectic form of liquid crystals is often encountered in substances of other (non-salt-forming) classes. Having given their name to the type of liquid-crystalline system showing two-dimensional order, however, the carboxylic acid salt mesophases themselves subsequently attracted practically no attention from research workers for many decades. Many aspects of the structure of the mesophases and the mechanism of fusion of the salts of the higher homologues of aliphatic acids became clear only after the work of Vold and co-workers[28,29] and Skoulios and co-workers.[30–33]

The liquid crystals formed by soaps show no distinctive features compared with smectic liquid crystals of other types, and show the same regularities; their molecules have clearly defined anisometry (the length to width ratio is greater than 5) and have a constant dipole at right angles to the long axis of the molecule.[14]

Ubbelohde's discovery[34] of the liquid-crystalline properties of the salts of the lower homologues of the alkanoic acids (from propanoic to octanoic) was unexpected and even sensational.

Table 1. Characteristics of the polyatomic anions of various mesogenic and non-mesogenic salts.[8]

Anion	Radius of repulsion envelope, Å	Charge/(number of atoms) ratio
SCN^-	2.20	1:3
NO_3^-	2.32	1:4
ClO_4^-	2.36	1:5
$CH_3CO_2^-$	2.60	1:7
$C_2H_5CO_2^-$	2.82	1:10
$n\text{-}C_3H_7CO_2^-$	3.04	1:13
$iso\text{-}C_4H_9CO_2^-$	3.28	1:16

Firstly, the particles making up these mesophases are quasi-globular ions: inorganic cations and carboxylate anions, whose length to width ratio does not exceed 2. Thus the principal geometric requirement satisfied by the particles of all previously known mesogenic substances[14] is not satisfied in this case.

Secondly, in contrast to the classic liquid crystals formed by electrically neutral molecules, the salt mesophases have a high ratio of the electrostatic charge to the total number of atoms. Moreover, the radii of the repulsion envelopes of the carboxylate anions of the group of salts being considered differ little from those of the polyatomic anions of inorganic non-mesogenic salts (Table 1). Thus salt mesophases are anisotropic ionic melts.

Thirdly, in most cases there is a marked difference in the radii of the repulsion envelopes of the cations and the carboxylate anions, that is $r_c/r_a < 1$ (Table 2). By analogy with inorganic salts, this ratio of the dimensions of the cation and the anion should favour the stepwise positional ordering of first the cation sub-lattice and then the anion sub-lattice of the crystal, and hence lead to the existence of a highly conducting solid phase (solid electrolyte).

Table 2. Ratio of the radii of the cation and the anion and the difference in the specific conductance of the melt and the crystal at T_f for non-mesogenic salts and T_{cl} for mesogenic salts.[8]

Salt	r_c/r_a	γ_l/γ_s	Characteristic of thermal behaviour
AgCl	0.62	30	solid electrolyte
AgBr	0.57	20	ditto
$C_2H_5CO_2Na$	0.35	13	mesogenic salt
$iso\text{-}C_4H_9CO_2Na$	0.30	8	ditto
$n\text{-}C_3H_7CO_2Na$	0.32	—	»

These facts, together with electrical conductivity data (Table 2), led Ubbelohde[8] to suggest that the mesophases of the salts of the lower carboxylic acids are not true liquids but highly plastic solid forms in which only the anions are organised in a crystal lattice, while the cation sub-lattice is disordered. Measurements of the shearing stresses showed unambiguously,[35] however, that salt mesophases are true liquids throughout the temperature range of their existence from T_f to T_{cl}, and that they are liquids with constant anisotropy of the physical properties. Similar anisotropic melts with the structure of the smectic form of type A were subsequently detected among salts of aromatic acids and alkali metals[36] and the lower homologues of n-alkylammonium halides.[37]

Ionic anisotropic melts have been called ionic liquid crystals (ILC). They could be defined as thermodynamically equilibrium liquids with constant anisotropy of the physical properties, consisting of oppositely charged ions. The basic structural unit of ILC, in contrast to molecular LC, is a mesogen ion, and not a mesogen molecule. Since the existence of a mesophase requires clearly defined anisotropy of the inter-particle interactions,[15] it follows that in molecular liquid crystals, in which the predominant intermolecular interaction is van der Waals interaction, an anisotropic shape is a necessary characteristic of the mesogen molecule, whereas in ILC, in which the predominant inter-particle interaction is electrostatic, the necessary characteristic of the mesogen ion should be the anisotropy of the distribution of the Coulombic charge, and the geometry of the ion is now not the decisive factor.

Table 3. Parameters of the fusion and clearing of non-mesomorphic and mesomorphic salts and classic LC.

Compound	T_f, K	T_{cl}, K	ΔH_f, kJ mol^{-1}	ΔH_{cl}, kJ mol^{-1}	ΔS_f, J mol^{-1} K^{-1}	ΔS_{cl}, J mol^{-1} K^{-1}	$\Delta V_f/V_s$, %	$\Delta V_{cl}/V_{lc}$, %	$\Delta V^*/V_s$, %	Refs.
Non-mesomorphic salts										
$NaNO_3$	577		14.6		25.3		10.7			[1]
NaCl	1075		30.1		28.0		25.0			[1]
CH_3CO_2Na	603		17.9		29.7		3.9			[8]
Ionic liquid crystals										
n-$C_3H_7CO_2Na$	529	597	6.2	1.5	11.7	2.5	6.8	3.4	17.4	[8]
iso-$C_4H_9CO_2Na$	461	553	4.2	0.8	9.1	1.3	3.9	3.6	13.6	[8]
n-$C_4H_9CO_2Na$	408	631	10.9	2.0	21.8	3.2				[12]
n-$C_6H_{13}NH_3Cl$	490	526	6.6	2.2	13.4	4.2				[37]
n-$C_4H_9CO_2Tl$	455	487	5.4	3.0	12.1	6.3				[12]
n-$C_3H_7CO_2K$	626	677	10.8	5.0	17.3	7.4				[12]
Classic liquid crystals										
p-Azoxyanisole	391	409	29.4	0.6	75.3	1.4	11.0	0.4		[12, 27]
p-Azoxyphenetole	303	441	26.9	1.4	88.7	3.1	8.4	0.6		[14, 27]
Cholesteryl propionate	371	385	23.1	0.4	62.3	1.1				[23]
Sodium stearate	387	553	21.7	2.2	56.0	3.8				[12]
Cadmium myristate	374	400	43.0	1.6	115.0	4.0				[38]

Note. $\Delta V_f = V_m - V_s$, where V_m is the volume of the mesophase at T_f, and V_s the volume of the solid phase at T_f; $\Delta V_{cl} = V_l - V_{lc}$, where V_l is the volume of the isotropic melt at T_{cl}, and V_{lc} the volume of the mesophase at T_{cl}; $\Delta V^* = V_l - V_s$.

The properties of this new class of liquid crystal, the structural characteristics of typical representatives, and the relationship between the mesomorphism and the nature of the ionic components of the melt can now be considered.

II. The thermodynamic properties of ionic mesogens

The study of the thermodynamic functions of liquid crystals and the changes which they undergo in mesomorphic phase transformations is an important step in the determination of the nature of the inter-particle interactions and the mechanisms of the phase transformations. Most available data on the thermodynamic properties of organic salts have been fully dealt with in a review by Franzosini and Sanesi.[12] Nevertheless, the tendency of most salts with organic ions to form supercooled and metastable states complicates considerably the interpretation of the thermodynamic data obtained; a large number of ambiguous results and results which have not been reproduced have been published.

The temperatures of the phase transformations have been most fully studied; this applies to the homologous series of the alkanoates of the alkali metals, thallium, ammonium, various metals of the second main group of the periodic system, and various transition metals (zinc, cadmium, lead, manganese, etc.), and various salts of aromatic carboxylic acids.[12,36] The enthalpies and entropies of the fusion and clearing of the mesophase have been studied for the alkanoates of the alkali metals, thallium, and various transition metals, and for mono-substituted n-alkylammonium chlorides,[12,37–41] but a complete picture of the thermal change in the thermodynamic properties has been obtained for only two salts from the ILC group, sodium isovalerate and butyrate.

A comparative analysis of the parameters of the fusion and clearing of the mesophase (Table 3) for three groups of substance, namely non-mesogenic inorganic salts, ILC, and molecular LC, leads to several important conclusions.

1. Ionic mesogens have relatively low enthalpies of fusion, like molecular LC and salts without conformationally flexible chains.[42]

2. The values of ΔS_f for ionic mesogens are extremely low (9–20 J mol^{-1} K^{-1}) compared with ΔS_f for molecular LC ($\sim$70 J mol^{-1} K^{-1}) and inorganic salts ($\sim$25 J mol^{-1} K^{-1}). They are often even lower than ΔS_f for the inert gases ($\sim$14 J mol^{-1} K^{-1}).

3. The values of ΔH_{cl} and ΔS_{cl} for ILC are of the same order of magnitude as for ordinary LC.

4. The values of ΔS_{Cl} for ILC are lower than ΔS_f by factors of 2–5.

5. The relative changes in volume in the fusion and clearing of ILC are approximately equal, whereas for molecular LC the relative change in volume at T_{cl} is smaller by an order of magnitude than that at T_f. The relative change in the volume of ionic mesogens in the transformation between the crystal and the isotropic melt via the mesophase ($\Delta V^*/V_s$, see Table 3) is of the same order of magnitude as the relative change in volume in the transformation between the crystal and the isotropic melt for ordinary inorganic salts.

The low enthalpy and entropy of fusion of ILC are indications of positional ordering, characteristic of a crystal containing quasi-spherical molecules consisting of a small number of atoms.[42] However, the fact that ΔS_f for ionic liquid crystals is often lower than the value 14 J mol^{-1} K^{-1} characteristic of the formation of simple positional defects apparently indicates cooperative positional disordering of the crystal lattice at T_f.[42]

In the fusion of ionic mesogens, the features of the cooperative positional disordering may be that each group of neighbouring ions and their component atoms are displaced collectively from their equilibrium positions in the crystal, forming local structures or domains with liquid-crystalline ordering. If smectic ILC are formed on fusion, the arrangement of the ions in these domains should preserve the long-range orientational order combined with translational periodicity in two dimensions. An indirect thermodynamic indication of the preservation of partial positional

order in ILC is the extremely marked increase in volume of T_{cl} for sodium butyrate and isovalerate, comparable with the change in volume on fusion.

A characteristic feature of the ILC studied is the absence of mesomorphic polymorphism (only one LC phase exists).

The influence of the length of the aliphatic chain of the anion or cation on the thermodynamics of the mesomorphic state has been studied for the homologous series of n-alkanoates of the alkali metals, thallium, and various transition metals, and for mono-substituted n-alkylammonium chlorides.[12,36-41]

Fig. 1 gives the dependence of the thermodynamic parameters of the phase transformations (T_{cl}, ΔS_f, ΔS_{cl}) on the length of the aliphatic chain of the mesogen ion (n) in various homologous series of ILC. Analysis of these data shows that:

1) there is an odd–even alternation of the thermodynamic parameters of the transformation betweeen the ILC and the isotropic melt, which is smoothed out with increase in the length of the alkyl chain n;

2) the dependence of T_{cl} on n shows a flat maximum at n = 5–8;

3) there is no simple dependence of ΔS_f on n;

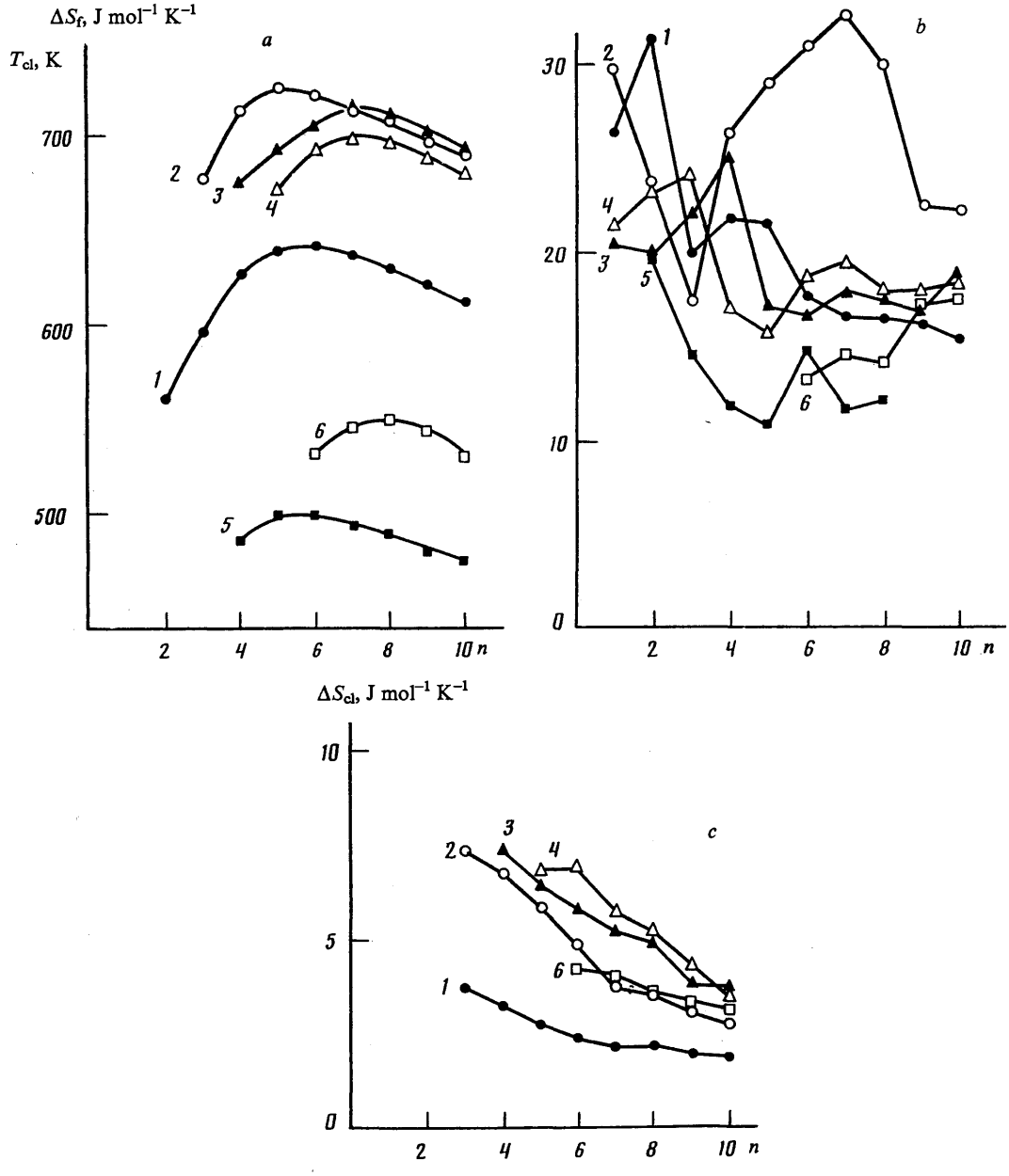


Figure 1. Dependence of the clearing temperature (*a*), the entropy of fusion (*b*), and the entropy of clearing (*c*) of the mesophase on the number of carbon atoms in the aliphatic chain of the mesogen ion for homologous series of salts: *1*, $C_nH_{2n+1}CO_2Na$; *2*, $C_nH_{2n+1}CO_2K$; *3*, $C_nH_{2n+1}CO_2Rb$; *4*, $C_nH_{2n+1}CO_2Cs$; *5*, $C_nH_{2n+1}CO_2Tl$; *6*, $C_nH_{2n+1}NH_3Cl$.[12,37]

4) ΔS_{cl} and ΔH_{cl} decrease regularly with increase in the length of the alkyl chain of the mesogen ion.

These regularities are qualitatively the same as the general regularities in the thermodynamic behaviour of known homologous series of classic smectic liquid crystals,[43] since in all cases a decisive role is played by the dimensions of the alkyl group. Thus the odd–even alternation is a consequence of the difference between the contributions of an odd and an even carbon atom to the length and polarisability of the hydrocarbon chain of the ion or molecule.

The decrease in ΔS_{Cl} and ΔH_{Cl} with increase in n may be due either to a relative increase in the ordering of the isotropic melt or to a decrease in the ordering of the mesophase close to T_{cl}. X-Ray diffraction data for thallium alkanoates[44] indicate an increase in the ordering of the alkane chains of the anions in the mesophase close to T_{cl} with increase in n.

The few published studies of the total change in the entropy of organic salts on going from the crystalline state at 0 K or 298 K to the isotropic liquid state indicate a definite increase in $\Sigma\Delta S$ with increase in the length of the alkyl group.[40] This increase in the total entropy in homologous series of flexible molecules is due predominantly to the increase in the configurational component of the entropy. Thus for the long-chain homologues of alkanoates and alkylammonium salts, the main mechanism of fusion involves disordering of the alkane chains.

For the homologues of salts with short alkyl groups ($n \leqslant 7$), in which the predominant interionic interaction is electrostatic, the mechanism of fusion is apparently slightly different, and will be discussed later in relation to structural data for ILC. The fact that the electrostatic interaction makes the principal contribution to the total energy of stabilisation of the ionic mesophase explains the high sensitivity of the thermal stability of ILC to the nature of the component ions. Thus Fig. 1*a* shows that the LC state is not realised in lithium carboxylates; in the homologous series of the salts of the other alkali metals, the existence of the mesophase depends on the length of the alkyl group; for example, the salts form a mesophase at $n \geqslant 2$ for sodium, at $n \geqslant 3$ for potassium, at $n \geqslant 4$ for rubidium, and at $n \geqslant 5$ for caesium.

Parameters of the cations and the carboxylate anions making up the salt mesophase, namely the polarising power of the cations z_c/r_c^2 and the ratio of the radii of the cations and anions r_c/r_a, have been analysed.[45] This analysis made it possible to formulate the following empirical relationship: an ionic mesophase can exist in molten salts of alkanoic acids if

$$z_c/r_c^2 \leqslant 1.05 \text{ and } r_c/r_a \leqslant 0.4. \quad (1)$$

This relationship is naturally approximate, but it applies satisfactorily to 12 homologous series of monovalent and divalent metal n-alkanoates.[45] The main value of the expressions (1) is that they show the relationship between the possible production of LC ordering in a salt melt and the nature of cations and anions.

III. The structure and optical properties of ionic mesogens

Although the structure of ILC has not yet been established in sufficient detail, a model of the structure of the ionic mesophase has now been proposed, based on the results of polarisation, X-ray diffraction, and NMR studies of sodium butyrate and isovalerate,[46–48] potassium hexanoate,[49] thallium and sodium n-alkanoates,[44,50–52] and sodium methylpentanoates.[53]

Optical polarisation studies have established unambiguously that the mesophases of the salts of lower alkanoic acids are homogeneous liquid-crystalline phases of the smectic A type;[44,48] the existence of only one smectic phase throughout the temperature range of stability of the ILC is also indicated by the ^{23}Na NMR spectra of sodium alkanoates. Thus in all the sodium salts studied, the quadrupole coupling constant, calculated from the first-order quadrupole splitting of the ^{23}Na NMR spectrum, shows a smooth temperature dependence.[47,51,53]

The basic principle of the arrangement of the ions of the salts of carboxylic acids in the condensed state is determined by the combination of the strong electrostatic interactions of the cations and the anions and the weak van der Waals interactions of the organic chains of the anions. The ionic groups should be in contact with one another, but in such a way that the bulky non-polar organic parts of the carboxylate anions are close-packed. This condition is satisfied by electrostatic "sandwich" layers of metal cations, situated close to the negatively charged carboxyl groups of the alkanoate anions (Fig. 2). This layer segregation of the ions practically excludes the unfavourable interaction of the Coulombic charges with the aliphatic chains, whose dielectric constants are low

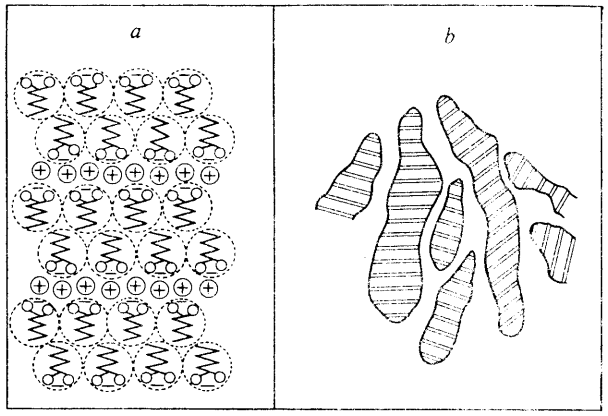


Figure 2. Schematic representation of the layer structure of an ionic liquid crystal (from published data[46–48]): *a*, relative arrangement of the carboxylate anions and the metal cations in LC domains; *b*, possible preferred orientation of the cation–anion layers forming the domains in the ionic mesophase.

Thus in a liquid-crystalline carboxylate melt, the first coordination sphere of the cation contains only anions, in accordance with Temkin's model of the structure of ionic melts,[42] whereas the first coordination sphere of the anion contains both cations and anions. The energy of the Coulombic interaction of two adjacent cations in the same electrostatic layer will naturally be much greater than the energy of this interaction between the cations belonging to two neighbouring electrostatic "sandwiches".

The arrangement of the electrostatic "sandwiches" in space may be different in different salts, since the packing of the ions is determined by the Coulombic forces acting both [illegible] sandwich"

and between neighbouring "sandwiches". The magnitude of these forces should apparently depend both on the nature of the metal cations and on the size of the hydrocarbon chain of the carboxylate anion, shielding the electrostatic interactions between neighbouring "sandwiches". In ionic liquid-crystalline melts, the Coulombic interactions involve more than ten thousand ions,[8] and this facilitates their mutual ordering. Thus the strength of the electrostatic interactions should also influence the size of the LC domains in salt melts, and the parameters of the order in the ILC.

Optical polarisation studies of lower sodium carboxylates[48] have shown that in the series of homologues from sodium butyrate to sodium heptanoate there is a considerable change in the size of the LC domains (Table 4). The size of the domains decreases with a relative increase in the organic part of the carboxylate anion in the series of related compounds, reflecting the increase in the shielding of the electrostatic field. No obvious simple criteria have yet been found, however, for estimating the absolute dimensions of the LC domains in other homologous series. Thus no complete explanation has yet been given for the marked increase (by a factor of ~ 25) in the size of the domain on going from sodium butyrate to sodium isovalerate, which is similar in many respects but which has a lower mesophase thermal stability (Table 4).

Table 4. Size of the LC domain and the thermal stability of the ionic mesophase of sodium carboxylates.

Salt	Size of domain $\times$ 10^6, m (Ref.48)	T_{cl}, K (Ref.12)
iso-$C_4H_9CO_2Na$	500	556
n-$C_3H_7CO_2Na$	20	597
n-$C_4H_9CO_2Na$	15	626
n-$C_5H_{11}CO_2Na$	10	631
n-$C_6H_{13}CO_2Na$	7	634

A characteristic feature of salt mesogens is the preservation of the long lattice constants of the crystals (d) on fusion. Thus non-branched sodium and thallium alkanoates[44,46] show an abrupt decrease in d at the melting point, and further increase in temperature leads to an even greater gradual compression of the cation–anion layers. Sodium isovalerate at the melting point shows a sharp increase in the long period, which in the mesophase remains constant and independent of temperature (Fig. 3).

According to Duruz and Ubbelohde,[46] the difference in the thermal behaviour of the long periods d of the mesophases of sodium butyrate and isovalerate is due to a difference in the thermal flexibility of the two alkane chains and the difference in their reaction to increasing torsional thermal vibrations with increase in temperature. Using data on the molar volume V, the authors cited[46] estimated the area occupied by the electrostatic cation–anion layers ($A = V/d$) in sodium butyrate and isovalerate, with the approximate assumption that these layers are packed in columns with no spaces between them. It was found that if one imagines cylinders being cut from the sequence of layers formed by identical numbers of cations and anions in the structures of the two salts, then at a temperature slightly below T_f the butyrate cylinder will be higher and will have a smaller basal area than the isovalerate cylinder. At T_f, the area of the base of the butyrate cylinder increases abruptly (by $\sim 8\%$), and its length decreases (by $\sim 1.6\%$). For the isovalerate cylinder, however, the length increases abruptly (by $\sim 7\%$), and the area of the base decreases (by $\sim 2.2\%$). Further increase in temperature from T_f to T_{cl} leads to a gradual increase in the area of the base of both cylinders, while the length of the isovalerate cylinder remains constant and that of the butyrate cylinder gradually decreases.

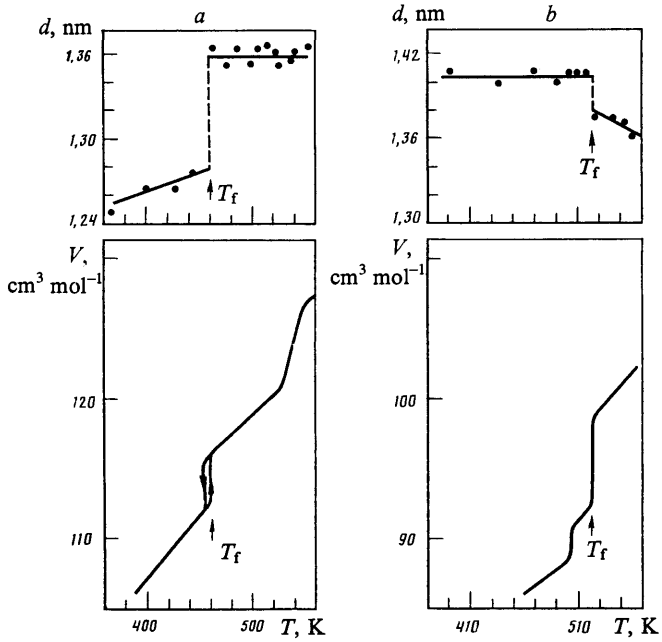


Figure 3. Temperature dependence of the lattice parameter d and molar volume V in the crystal and mesophase of sodium isovalerate (a) and butyrate (b).[46]

Thus a common feature of the thermal behaviour of salt mesophases containing organic ions is that the packing of the ions is loosened in a direction parallel to the plane of the electrostatic layers. In the direction at right angles to the plane of the smectic layers, however, the strong electrostatic attraction tends to compress the layers. The greater the possibility of a configurational change in the alkane chains of the mesogen ion, the greater the relative compression of the cation–anion layers in the mesophase. Thus for the homologous thallium n-alkanoates, the relative compression of the layers in the mesophase β ($\beta = (2L - d)/2L$, where L is the length of the carboxylate anion) is directly proportional to the length of the alkane chain of the anion n.[44] When a configurational change in the alkane chain of the anion is hindered, as in sodium isovalerate,[46] the inter-layer distance in the mesophase remains practically unchanged with increase in temperature.

The results of structural and thermodynamic studies of ILC indicate that the mechanism of the fusion of ionic mesogens involves cooperative positional disordering of the crystal lattice of the salt, accompanied by configurational ordering of the alkane chains of the

mesogen ions, and at T_{cl} the electrostatic layers probably undergo positional and other types of ordering.

A molecular model of the structure of ILC, essentially quasicrystalline, was first proposed by Ubbelohde and Duruz,[46] and was later developed in more detail from the results of polarisation and NMR studies by Jonas and co-workers.[47,48,51–53] According to this model, the structure of smectic ILC is described by a space filled by sequences of parallel cation–anion layers forming LC domains (see Fig. 2). These domains may take all possible configurations and be subjected to the orienting influence of different fields. In the opinion of Jonas and co-workers,[52] the organic chains of the anions in the LC domains either rotate "in a cone" with angle of 35° about the normal to the cation–anion layer or are ordered along the normal to the charged layer, but undergo *trans–gauche* isomerisation. Local structure formation, corresponding to the isotropically oriented layer domains, are preserved in the isotropic melts.[53] The type of ordering of the carboxylate anions in the layers may apparently be different for different salts, and, as noted by Jonas and co-workers,[53] is determined by the size and structure of the crystal lattice defects, and also by the structure of the carboxylate anions. No change in the size of the domains in carboxylate ILC with change in temperature was observed.[48]

In contrast to the above quasi-crystalline model of the structure of the mesophases of molten salts of alkanoic acids, an attempt has been made to describe them using the so-called R-theory of aqueous amphiphilic mesophases.[39] The basic postulates of this theory were analysed by Winsor.[24] The R-theory describes the structure of the mesophases on the basis of the balance between intermolecular forces which tend on the one hand to make the amphiphilic layer of molecules convex with respect to the lypophilic environment, and on the other hand to make it convex with respect to the polar medium. The postulates of this theory can obviously be applied satisfactorily only to systems with a low density of Coulombic charges, for example to the molten salts of the higher homologues of n-alkanoic acids. In ILC, where powerful Coulombic forces operate, this balance of intermolecular forces apparently does not play a decisive role in the stabilisation of the LC order.

An important characteristic of LC is the degree of long-range orientational order or the order parameter S, introduced by Tsvetkov[25] and defined by the equation:

$$S = {}^1/_2(3\overline{\cos^2\theta} - 1),$$

where θ is the angle between the direction of the director‡ of the LC and the long axis of the molecule, and $\cos^2\theta$ is the value obtained by averaging over all orientations of the molecules. In an ideal crystal, $S = 1$, and in an isotropic liquid, $S = 0$. For molecular LC, the maximum value of S in nematic crystals is 0.6–0.8, and the value for smectic crystals reaches 0.9 and changes little with change in temperature.

In the ionic smectic melts of sodium isovalerate and n-alkanoates, the order parameter is much smaller than in molecular smectics, and depends on temperature. Thus with increase in temperature from T_f to T_{cl}, the value of S changes from 0.65 to 0.1 in sodium isovalerate and from 0.38 to 0.1 in sodium butyrate.[47,48]

‡The director of the LC is the unit vector which indicates the direction of the preferred orientation of the long molecular axes, coinciding with the optical axis of the LC (for more details see Pikin's book[26]).

A characteristic feature of ILC is negative birefringence.[48,50] Pelzl and Sackmann[50] studied the birefringence of the LC phases formed by homologous thallium n-alkanoates. They established that the lower homologues (n = 5–9) show negative birefringence, which decreases with increase in the length of the alkane chain and with decrease in the temperature of the mesophase. For the middle homologues (n = 10–12), the sign of the birefringence changes from negative to positive. The higher homologues ($n > 12$) show only positive birefringence, which increases with increase in the length of the alkane chain of the anion and with decrease in the temperature of the mesophase. The difference between the optical behaviour of the lower and higher homologues of the n-alkanoates can be attributed to the characteristics of the structures of their smectic mesophases.

The magnitude and sign of the birefringence of LC are determined by the magnitude of the anisotropy of the polarisability. For salt mesophases, the anisotropy of the polarisability is determined by two structural factors: 1) the monoaxial layer arrangement of the polar groups, and 2) the group and mutually consistent configuration of the alkane chains between the cation–anion planes. The first factor determines the negative anisotropy of the polarisability, that is the polarisability in a direction perpendicular to the optical axis ($\alpha_\perp$), which is greater than the polarisability in a direction parallel to the optical axis ($\alpha_\parallel$), that is $(\alpha_\parallel - \alpha_\perp) < 0$, and the second factor determines the positive anisotropy of the polarisability, that is $(\alpha_\parallel - \alpha_\perp) > 0$.[50] In ILC, where the ratio of the charge to the number of atoms is high, the first factor predominates, so that negative birefringence is observed, whereas for the long-chain homologues of thallium alkanoates, the second factor is decisive, and positive birefringence is observed.[50]

As already noted, increase in the temperature of the mesophase of the salts of n-alkanoic acids leads to compression of the cation–anion layers and to loosening of the packing of the ions in a direction parallel to the cation–anion layers, and this leads to a decrease in $\alpha_\parallel$ and an increase in $\alpha_\perp$. Since the refractive index for the extraordinary ray n_e is directly proportional to $\alpha_\parallel$, and the refractive index for the ordinary ray n_o is directly proportional to $\alpha_\perp$, increase in temperature leads to an increase in the negative value of the birefringence $(n_e - n_o)$ for ILC, and to a decrease in its positive value for the LC phases of the higher homologues of thallium alkanoates. Thus the optical behaviour of ionic mesophases is described satisfactorily in terms of the above quasi-crystalline model of their structure.

IV. The transport properties of ionic mesophases

The transport properties of LC materials are very sensitive to their anisotropy and orientation. Unfortunately, for ILC there are practically no published data on completely oriented single-domain specimens, although these studies are necessary to establish the relationship between the dynamics and structure of the ionic mesophases.

Viscosity. ILC apparently have very high viscosities, since they are smectic forms (usually type A). Approximate data are available for only two mesophases, sodium butyrate and isovalerate.[12] Close to T_{cl}, the viscosity of both mesophases is ~10 Pa.s; on going to the isotropic melt, the viscosity decreases to ~0.04 Pa.s for sodium isovalerate and to ~0.01 Pa.s for sodium butyrate. Thus the viscosities of the isotropic melts of ionic mesogens are comparable with those of molten inorganic salts.[1,2,5]

Nuclear magnetic relaxation times and diffusion. Jonas, Bonekamp, and co-workers[47,51–54] have carried out NMR studies (^{1}H, ^{2}H, ^{23}Na) of the smectic mesophases of molten sodium carboxylates throughout the temperature range of stability of the LC phases. It was established that the mechanism of proton relaxation in the salt mesophase reduces to the self-diffusion of the anions and fluctuations in the ordering of their orientation; the first mechanism determines the frequency dispersion of the spin–lattice proton relaxation time T_1, and the second determines that of the spin–rotation relaxation time $T_{1\rho}$. The values of the self-diffusion coefficients D for the butyrate and isovalerate anions in the mesophase, estimated by the authors cited, are about 10^{-7} to 10^{-6} cm^2 s^{-1}, which coincides with the values predicted by theory for smectics of type A.[55]

The temperature dependence of the coefficients of self-diffusion of the anions in the mesophase and in an isotropic melt obey the Arrhenius law, with a break at T_{cl}. The NMR data can be used to estimate the averaged coefficient of three-dimensional diffusion.[54] It is assumed, however, that in smectic domains there is two-dimensional diffusion, which, according to the calculations,[54] is characterised by a value of D 1.5 times that measured by NMR. These differences in the absolute values of the diffusion coefficients, however, do not influence the estimation of the activation energy of diffusion, which has the values 37.7 kJ mol^{-1} and 37.2 kJ mol^{-1} for the butyrate and isovalerate anions respectively.

For sodium isovalerate, good agreement was established between the activation energies of viscosity and diffusion in the isotropic melt (50.6 kJ mol^{-1} and 48.1 kJ mol^{-1} respectively).

The absolute value of D calculated from the viscosity data using the Stokes–Einstein equation is smaller by two orders of magnitude than the values of D measured by NMR.[54] The explanation apparently is that the viscosity of the salt mesopahse is determined by slow interactions between the LC domains, whereas the rate of NMR relaxation reflects the rapid diffusion within domains of macroscopic dimensions.

The spin–lattice relaxation times T_1 (^{23}Na NMR) in the mesophases of molten sodium carboxylates increase regularly with increase in temperature, and have values of 10^{-4}–10^{-2} s. Because of the large difference in the dimensions of the carboxylate anion and the sodium cation, the correlation times (τ_c) for the fluctuations in the electric field gradient at the sodium cation, calculated by Bonekamp and co-workers,[47] reflect the fluctuations as a consequence of the diffusion of the sodium cation, and not the anion. The values of the activation energy for τ_c (16.7 kJ mol^{-1} for sodium butyrate and 32.3 kJ mol^{-1} for sodium isovalerate), obtained by Bonekamp and co-workers,[47] are much smaller than the values of the activation energy of diffusion of the anion. Thus the principal charge carrier in the ionic mesophases of molten carboxylates is the cation, and the conductivity in the mesophase of sodium butyrate should be higher than that in the mesophase of sodium isovalerate.

Electrical conductivity. A basic characteristic of the liquid-crystalline phases of salt melts is their intrinsic ionic conductivity.[8,56–59] In the isotropic melts of the carboxylates of monovalent and divalent metals, the activation energy of the electrical conductivity is not sensitive to change in the length of the alkane chain of the anion n.[57,58,60] At the same time, the absolute value of the electrical conductivity of the melt (measured at a temperature 5 K above T_{cl}) decreases regularly with increase in n.[57] These data indicate that the predominant charge carriers in carboxylate melts are the metal cations. This is also indicated by the size of the ionic components and by the NMR relaxation data for the salt mesophases. In the isotropic melt–mesophase and mesophase–crystal transformations, there is an abrupt change in the electrical conductivity, and the magnitude of these sharp stepwise changes depends on the length of the alkane chain of the anion and is greatest for the lower homologues of the alkanoates.[56,57]

The values of the specific conductance of the ILC studied are 10^{-1}–10 S m^{-1}, but most published electrical conductivity data relate to multi-domain non-oriented LC specimens. The results obtained by Duruz and Ubbelohde,[61] and also by Meisel and co-workers,[56,57] indicate marked anisotropy of the electrical conductivity of ILC. Thus the electrical conductivity of the mesophase of sodium isovalerate, obtained by cooling the isotropic melt with the application of a magnetic field ($\sim$10 kG) perpendicular to the electrical field, was found to be twice that of the mesophase obtained by cooling the isotropic melt in the absence of a magnetic field.[61] It has been shown[57] that the electrical conductivity of thallium carboxylates is influenced by differences in the degree of orientation of the LC phase, obtained by applying mechanical shearing stresses to the mesophase or by producing it in the field of a varying temperature gradient.

The most convincing proof of the anisotropy of ion transport, however, was obtained by Meisel and co-workers,[57] who determined the electrical conductivity of a homeotropically oriented (smectic layers parallel to the supports) LC specimen of thallium laurate in two mutually perpendicular directions. According to their data, the electrical conductivity of the mesophase in a direction parallel to the smectic cation–anion layers was much greater than that in the perpendicular direction (by a factor of $\sim$3). The electrical conductivity along the cation–anion layers in the oriented single-domain salt mesophase was found to be even higher than in the isotropic melt at a higher temperature, and at the point corresponding to the change from the mesophase to the isotropic melt, a marked abrupt decrease in the electrical conductivity was observed. In the direction perpendicular to the smectic layers, however, the electrical conductivity in the mesophase was much lower than that in the isotropic melt, and on going from the mesophase to the isotropic melt the usual abrupt increase in conductivity was observed. These data, and the values of the activation energies of the electrical conductivity in the salt mesophase (in the case of isovalerate, 7.6 kJ mol^{-1} for the non-oriented mesophase and <4 kJ mol^{-1} for the oriented mesophase), lead to the following conclusions.[61]

1. Charge transfer in the salt mesophases apparently involves the movement of ions along channels in the electrostatic layers.
2. The barriers preventing this movement are due to changes in the local electrostatic potential, so that they are extremely low (<4 kJ mol^{-1}) and comparable with the barriers controlling the migration of the ions in aqueous electrolytes.
3. The less oriented the LC specimen, the higher the activation energy of the electrical conductivity, as a consequence of the additional barriers preventing the transfer of ions from one LC domain to another.

The fact that the electrical conductivity in the oriented single-domain mesophase in a direction parallel to the smectic layers is higher than that in the less viscous isotropically-liquid phase at a higher temperature is apparently due to the marked difference in the heights of the energy barriers controlling ion migration in these two phases (the activation energy of the electrical conductivity in the isotropic carboxylate melt is $\sim$28 kJ mol^{-1}).

The further study of the anisotropy of the electrical conductivity of oriented thin-layer single-domain ILC specimens will yield new data on the dynamics and structure of this unusual class of LC materials, which will be useful for their practical application.

V. Binary systems of ionic mesogens

As already noted, a characteristic of the ionic mesophase is that its stabilisation depends to a considerable extent on electrostatic factors. For salts of carboxylic acids, it follows from Fig. 1*a* and the empirical relationship (1) that a decisive role in the stabilisation of the mesophase is played by the size of the ions and the polarising power of the cation. The relationship between the nature of the interionic interactions in the salt melt and the stability of the mesophase is most clearly revealed in binary salt systems, in which the formation of mixed melts is accompanied by a change in the nature of the interionic interactions.[45]

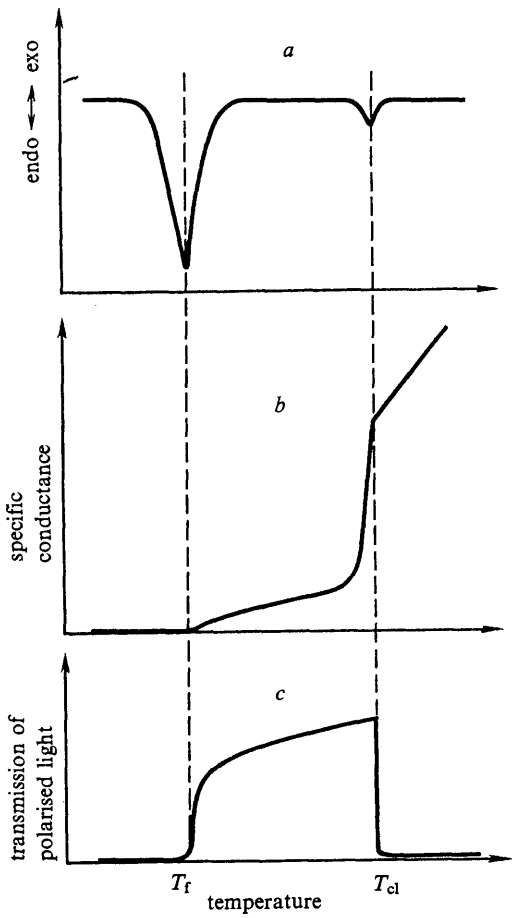


Figure 4. General form of the temperature dependence of the physicochemical properties of ionic mesogenic systems observed on heating; thermodynamic transitions from the crystal to the mesophase at T_f and from the mesophase to the isotropic melt at T_{cl}: *a*, differential thermal analysis curve; *b*, temperature dependence of the specific conductance; *c*, temperature dependence of the intensity of polarised light passed through a specimen of a salt LC system.[45]

In general, the formation of multicomponent systems provides interesting possibilities for extending the range of existence of the LC phase and even for the production of a mesophase in mixtures of components which are potentially mesogenic but individually non-mesomorphic, as a result of a marked decrease in T_{cl} for the system.[23] This last feature was first pointed out and confirmed experimentally in the early nineteen-huundreds by Bogoyavlenskii and Vinogradov.[62,63] Fifty years later, it was confirmed repeatedly by many workers.[23] The study of the stability of the mesophase with change in the ionic composition of the LC melt is of particular interest.

Mirnaya[45] studied the temperature range of existence of a binary salt mesophase by three independent methods: by studying the differential thermal analysis (DTA) curve, the temperature dependence of the specific conductance, and the transmission of polarised light by the LC specimen. Fig. 4 shows that all three methods made it possible to determine reliably the melting point of the crystal and the clearing temperature of the mesophase; DTA gives T_{cl} most accurately, and the other two methods are highly sensitive to the change from the isotropic liquid to the mesophase.

Unfortunately, very few binary salt mesogenic systems have been studied, and most of these contain the butyrate anion as the mesogen ion. All the salt LC systems studied can be provisionally divided into two groups.

The first group consists of systems in which continuous LC solutions are formed. They are characterised by a smooth change in T_{cl} with change in concentration, with positive or *S*-shaped deviations from additivity. These systems include binary mixtures of salts with a common mesogen anion and symmetrically charged cations, for example Na, K$|C_3H_7CO_2$; Na, Cs$|C_3H_7CO_2$; Cs, $NH_4|C_3H_7CO_2$; and Na, Tl$|C_3H_7CO_2$ (Fig. 5).

The second group consists of systems in which the formation of the mixed melt leads to marked destabilisation and disappearance of the mesophase. These systems include binary systems with a common mesogen anion and asymmetrically charged cations, for example K, Zn$|C_3H_7CO_2$; Na, Mg$|C_3H_7CO_2$, and also systems with a common cation, for example Na$|C_3H_7CO_2$, NO_3; Na$|C_3H_7SO_2$, SCN (Fig. 6).

In the ionic mesogenic systems studied, T_{cl} in most cases deviates considerably from additivity, whereas in molecular LC systems of two components without specific interaction, T_{cl} obeys the additivity law, that is it is a linear function of the composition:[14,24]

$$T_{cl} = T_1 + x_2(T_2 - T_1),$$

where T_1 and T_2 are the clearing temperatures of the mesophases of the individual components, and x_2 the mole fraction of the second component. In only a few cases are slight deviations from additivity ΔT_{cl} (mainly negative) observed, when the molar volumes of the components differ considerably. This behaviour of molecular LC mixtures is described satisfactorily by the statistical theory of Luckhurst and Humphries.[64]

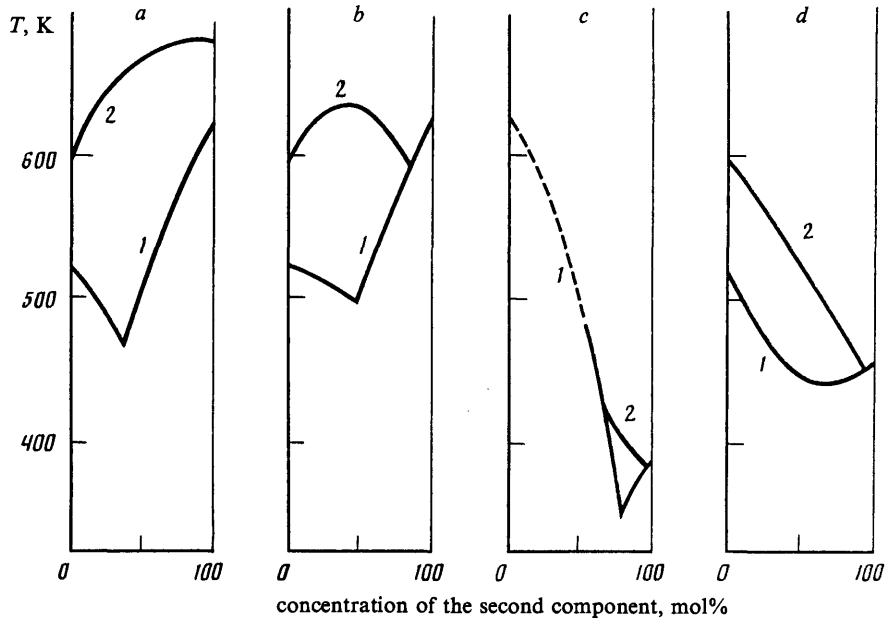


Figure 5. Melting point (*1*) and clearing temperature (*2*) of the mesophase in binary salt systems: *a*, $C_3H_7CO_2Na-C_3H_7CO_2K$; *b*, $C_3H_7CO_2Na$–$C_3H_7CO_2Cs$; *c*, $C_3H_7CO_2Cs$–$C_3H_7CO_2NH_4$; *d*, $C_3H_7CO_2Na$–$C_3H_7CO_2Tl$.[45]

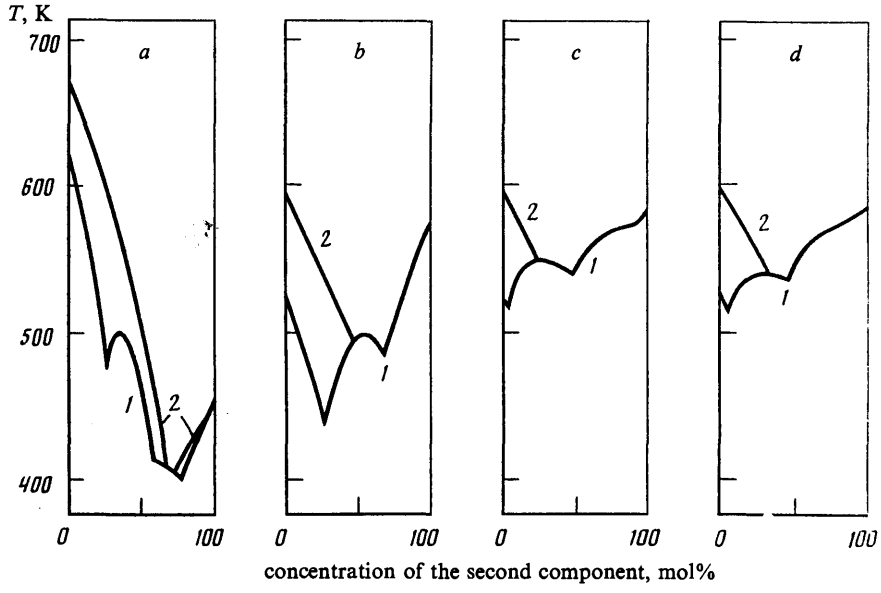


Figure 6. Melting point (*1*) and clearing temperature (*2*) of the mesophase in binary salt systems: *a*, $C_3H_7CO_2K$–$(C_3H_7CO_2)_2Zn$; *b*, $C_3H_7CO_2Na$–$(C_3H_7CO_2)_2Mg$; *c*, $C_3H_7CO_2Na$–$NaNO_3$; *d*, $C_3H_7CO_2Na$–NaSCN.[45]

The formation of continuous LC solutions in salt systems of the first group made it possible to estimate the thermal stability of a mixed ionic mesophase using the approximate model of ionic solid solutions.[65] This approach led to the following expression:

$$\Delta T_{cl} = 2x_1x_2E/R,$$

where R is the universal gas constant, and E the energy of stabilisation of the mesophase, which is the orientational component of the enthalpy of mixing of the system corresponding to one mole of the vapour of the interacting non-equivalent cations.

In systems in which one or both of the components containing the mesogen ion are individually non-mesomorphic, ΔT_{cl} was estimated using the values of the latent T_{cl}, determined by extrapolation.[45,66]

The value of E is extremely sensitive to the nature of the interionic interactions in the mesomorphic systems. Thus in the systems formed by alkali metal carboxylates with a common mesogen anion, for example Na, K|$C_3H_7CO_2$ or Na, Cs|C_3H7CO_2, where the predominant type of inter-particle interaction is the Coulombic interaction of the non-equivalent cations, $E > 0$. This leads to a unique characteristic of systems of this type, namely the marked positive deviation of T_{cl} from additivity, reaching several tens of degrees. The energy of stabilisation in these systems is practically independent of the concentration of the components, and shows a linear correlation with the parameter of the interionic interactions Δ^2 [$\Delta = (r_1 - r_2)/(r_1 + r_2)$, where r_1 and r_2 are the cation–anion distances in the individual components].[65] The authors cited[65] established the interesting fact that the stabilisation of the ionic mesophase in the binary system, is higher, the greater the difference in the sizes of the metal cations of the two salts.

For salt melts, the parameter of the interionic interactions determines the intensity of the enthalpy changes on formation of the mixed melt,[67] so that the stabilisation of the carboxylate mesophase takes place as a result of the enthalpy factor, that is the increase in the energy of the orientational interaction of the non-equivalent ions relative to the energy of their thermal motion.

Another type of binary mesogenic system in the first group corresponds to the systems formed by monovalent metal and ammonium carboxylates with a common mesogen anion, for example Ca, $NH_4|C_3H_7CO_2$ (see Fig. 5). A distinguishing feature of interionic interactions in these systems is the formation of hydrogen bonds (H-bonds) between the ammonium cations and the carboxylate anions. A linear change in E with change in concentration was established for systems of this type.[68] The relative increase in the concentration of the monovalent metal cation in the mixed melt leads to an increase in E, and a directly proportional relationship is observed between the value of E and the increase in the ^{1}H NMR chemical shift (δ) of the ammonium ion as a result of the formation of H-bonds in the system.[45]

Thus the energy of stabilisation of the mixed salt mesophase is higher, the greater the number of ions forming H-bonds in the melt, and the greater strength of these bonds.[45,68] Naturally, the formation of H-bonds in the salt melt will facilitate the production of LC order only if appreciable anisotropy of the electrostatic interactions is preserved or created in the system.

In the systems formed by ammonium and monovalent metal butyrates, the values of the energies of formation of the H-bonds and the stabilisation of the mesophase are determined by the nature of the metal cation. The strength of the H-bond between a carboxylate anion and the ammonium cation in a salt melt is a complex function of two parameters of the metal cation, namely its size and its polarising power.[69] Increase in the polarising power of the metal cation is accompanied by a decrease in the strength of the H-bond as a result of the decrease in the electron-donor power of the carboxyl group of the anion, and increase in the size of the metal cation is accompanied by an increase in the steric barriers preventing the formation of the H-bond. According to Mirnaya and co-workers,[68] in the salt mesophases studied the last factor predominates, and with increase in the size of the metal cations in the LC melt, the energy of stabilisation of the mesophase generally decreases.

The first group of salt mesogenic systems also includes the binary systems formed by thallium and alkali metal carboxylates with a common mesogen ion, for example Na, Tl|$C_3H_7CO_2$ (see Fig. 5). In these systems, one component, namely the thallium(I) carboxylate, provides a non-Coulombic component of the cation–anion bond, so that their behaviour is determined by both the Coulombic and the exchange repulsion interaction. In the presence of the strongly polarising lithium and sodium cations, the covalent character of the bond formed by the thallium cation with the counter-ion decreases, whereas in the presence of other alkali metal cations it increases, the increase being greater, the larger these cations.[70] The increase in the covalent character of the bond formed by the thallium cation with the butyrate anion in the salt mesomorphic melt is equivalent to an increase in the probability of formation in the melt of long-lived paired cation–anion associates, that is uncharged quasi-globular particles, which decrease the electrostatic stabilisation of the LC phase; E may then have negative values and actually determine the energy of destabilisation of the mesophase. It is this factor which apparently is responsible for the destabilisation of the ionic mesophase observed in the systems formed by thallium and alkali metal carboxylates,[45] since the stability of the mesophase decreases with increase in the size of the alkali metal cation (Fig. 7). With increase in the concentration of the alkali metal salts in systems of this type, stabilisation of the ionic mesophase takes place in addition to its destabilisation. The stabilisation is due to an increase in the anisotropy of the electrostatic interactions with increase in the total number of Coulombic charges, and also to the decrease in the total energy of the system. At definite component ratios in the systems formed by thallium and alkali metal carboxylates, the stabilisation of the salt mesophase predominates, so that the overall concentration dependence of E is S-shaped (Fig. 7).

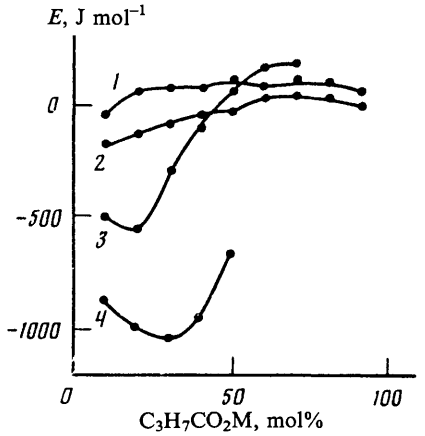


Figure 7. Concentration dependence of the energy of stabilisation of the ionic mesophase in the binary systems $C_3H_7CO_2Tl$–$C_3H_7CO_2M$, where M = Na (*1*), K (*2*), Rb (*3*), Cs (*4*).[45]

Unlike the mesogenic systems of the first group, where the formation of the mixed mesophase in most cases stabilises the LC phase, the mesogenic systems of the second group are characterised by breakdown of the LC order when the components are mixed. This behaviour is similar to that of molecular LC systems with one non-mesomorphic component. For the latter, the decrease in the thermal stability of the mesophase when the

non-mesomorphic component is added is greater, the greater the volume and mass and the smaller the anisometry of the non-mesogen molecules.[23,43]

In salt mesogenic systems with a common cation, for example $Na|C_3H_7CO_2$, NO_3 or $Na|C_3H_7CO_2$, SCN (see Fig. 6), the introduction of the anions of the second component into the cation–anion layers of the LC domains depresses T_{cl}. The rate of the decrease in the thermal stability of the salt mesophase is greater, the higher the symmetry and the larger the size of the added anion. Thus the anions studied[45] can be arranged in the following order of increasing ability to break down the LC order in molten sodium butyrate:

$$iso\text{-}C_4H_9CO_2^- < C_2H_5CO_2^- < SCN^- < NO_3^- < CH_3CO_2^-.$$

The mechanism of the observed breakdown in the LC order in the binary systems formed by carboxylates with a common mesogen anion and asymmetrically charged cations, such as K, $Zn|C_3H_7CO_2$ or Na, $Mg|C_3H_7CO_2$ (Fig. 6), is apparently the same as in systems with a common cation. This is due to appreciable local ion association and complex formation in these salt melts.[45] Thus as a result of the formation of the fairly stable anionic complexes $[Zn(C_3H_7CO_2)_4]^{2-}$, the K, $Zn|C_3H_7CO_2$ system can be regarded as a system with a common cation, in which one anion is the mesogenic butyrate anion, and the other the non-mesogenic anionic complex, that is $K|C_3H_7CO_2$, $[Zn(C_3H_7CO_2)_4]$.

The non-mesogenic character of the ionic complexes formed in salt melts is related to their quasi-globular form and the isotropic distribution of the Coulombic charge. These factors are responsible for the fundamental difference between ionic mesogenic systems and molecular systems in relation to the influence of complex formation on the thermal stability of the LC phase. In molecular LC systems with donor–acceptor interaction between the components, the thermal stability of the mesophase increases, apparently as a result of the increase in the anisotropy of the intermolecular interactions when molecular complexes with a higher anisotropy of the molecular form,[71,72] compared with the individual components, are formed. In individual cases, the donor–acceptor interaction between the components may be insufficient for the formation of a molecular compound, but when the nematic or isotropic solution is cooled, this interaction may lead to partial ordering of the molecules and to the formation of smectic or nematic phases, not observed for the components.[73,74] Thus complex formation in binary molecular systems makes it possible not only to obtain new LC phases but also to increase their stability.

Molten salt systems in which the ionic complex formed is mesogenic can also probably exist, and this should lead to an increase in the stabilisation of the ionic mesophase or to the appearance of LC order in a salt melt consisting of two individually non-mesomorphic components. Salt systems of this kind are not yet known, although searches are being carried out in this direction.[45,75]

Glass formation is an interesting characteristic of LC melts of salts of carboxylic acids with asymmetrically charged ions.[45] Among the great variety of problems in the physics and chemistry of liquid crystals, a unique position is now occupied by the problems of obtaining and detecting metastable LC phases, or, in Shubnikov's words, the problems of "obtaining homogeneous mesomorphic systems of sufficiently large volume in the supercooled vitreous solid state".[76] The aim in the production of these LC glasses is to extend the range of the practical application of LC to lower temperatures, and also to study the fundamental properties of the LC state.[26,77] The research interest is due to the fact that in LC glasses, all the characteristics of the macro-structure corresponding to the mesomorphic form will be revealed more clearly as a consequence of the marked decrease in the mobility of the LC molecules. The preparation and study of known molecular LC glasses is complicated, however, by the fact that their softening temperatures are usually much lower than room temperature.[26] In contrast to molecular systems, in ionic LC systems LC glasses with high softening temperatures (> 300 K) are formed.[45]

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In conclusion it should be noted that binary ionic systems provide additional possibilities for controlling the stability of the ionic mesophase and for the production of new LC phases as a consequence of the high sensitivity of the salt mesophase to the nature of its component ions. High- and medium-temperature smectic ILC (range of existence 313–673 K) have now been studied, but it is also possible to produce low-temperature ILC using an appropriate combination of cations and anions in the salt melt.

It is not difficult to predict the future practical applications of this new class of LC. In contrast to classic smectics, ionic smectic LC should show optical sensitivity with respect to even weak electric fields. This is due to the high values of the components of the dielectric constant tensor of the ionic melt, the appreciable anisotropy of the electrical conductivity, and the small size of the cations and anions making up the ILC. In addition to the long-term memory and the possibility of local erasure of information,[18] characteristic of ordinary smectics, a basis for new non-traditional applications of ILC should be provided by the characteristic ionic channel electrical conductivity and its sensitivity to the degree of orientation of the LC specimen, and also by the possibility of controlling the optical properties of ILC by ion exchange and electrochemical transformations. The use of ILC as an anisotropic medium for the synthesis of organic and inorganic compounds, and also as an isotropic vitreous matrix for various spectroscopic purposes, is also of interest.

References

1. A R Ubbelohde *The Molten State of Matter* (Translated into Russian), Izd. Metallurgiya, 1982, 376 pp
2. Yu K Delimarskii *Khimiya Ionnykh Rasplavov* (The Chemistry of Ionic Melts), Izd. Naukova Dumka, Kiev, 1980, 328 pp
3. D Inman, D G Lovering (Editors) *Ionic Liquids*, Plenum Press, New York–London, 1981, p.450
4. A R Ubbelohde *J. Chim. Phys., Numéro spécial*, 1969, 59
5. H Rawson *Non-metallic Solids. Vol. 2. Inorganic Glass-forming Systems* (Translated into Russian), Izd. Mir, Moscow, 1970, 312 pp
6. C A Angell, J C Tucker *Phys. Chem. Process Metallurgy: Abstr. of Richardson Conf. L: Inst. Mining Metallurgy Publ.*, 1974, p. 207
7. F J Hazlewood, E Rhodes, A R Ubbelohde *Trans. Faraday Soc.*, 1966, **62** 3101
8. J J Duruz, H J Michels, A R Ubbelohde *Proc. R. Soc. London A*, 1971, **322**(1550) 281
9. J E Gordon *Techniques and Methods of Organic and Organometallic Chemistry*, Acad. Press, New York, 1969, p. 51

10. J E Lind, Jr. *Advances in Molten Salt Chemistry,* Plenum Press, New York–London, 1973, Vol. 1, p. 1
11. P Tissot *Molten Salt Techniques* (Edited by D G Lovering, R J Gale), Plenum Press, New York–London, 1983, Vol. 1, p. 137
12. *Thermodynamic and Transport Properties of Organic Salts,* (Edited by P Franzosini, M Sanesi), Pergamon Press, New York, etc., 1980, 370 p
13. A R Ubbelohde *Rev. Int. Htes Temp. Refract.,* 1976, **13** 5
14. G W Gray *Molecular Structure and the Properties of Liquid Crystals,* Acad. Press, London–New York, 1962, 314 pp
15. Yu B Amerik, B A Krentsel' *Khimiya Zhidkikh Kristallov i Mezomorfnykh Polimernykh Sistem* (The Chemistry of Liquid Crystals and Mesomorphic Polymeric Systems), Izd. Nauka, Moscow, 1981, 288 pp
16. V K Frederiks *Zh. Fiz. Khim.,* 1936, 7(6) 889 [English translation in *Russ. J. Phys. Chem.,* 1936(6)]
17. *Primenenie Zhidkikh Kristallov v Vychislitel'noi Tekhnike* (The Use of Liquid Crystals in Computer Technology), Izd. Naukova Dumka, Kiev, 1980, 172 pp
18. S A Gadzhiev, A Kh Zeinally, A N Nasrullaev, D F Aliev *Termo- i Elektro-opticheskie Svoistva Smekticheskikh Kristallov* (The Thermo- and Electro-optical Properties of Smectic Crystals), Preprint Akad. Nauk Azerbaidzhan. SSR, Baku, 1985, 24 pp
19. S M Arakelyan, Yu S Chilingaryan *Nelineinaya Optika Zhidkikh Kristallov* (The Non-linear Optics of Liquid Crystals), Izd. Nauka, Moscow, 1984, 360 pp
20. V A Shcherbakov, L L Shcherbakova *Radiokhimiya,* 1984, 26(5) 708
21. L L Shcherbakova, V A Shcherbakov *IV Vsesoyuznoe Soveshchanie po Spektroskopii Koordinatsionykh Soedinenii. Tezisy Dokladov* (Summaries of Papers Presented at the Fourth All Union Conference on the Spectroscopy of Coordination Compounds), Krasnodar, 1986, p. 64
22. P G De Gennes *The Physics of Liquid Crystals* (Translated into Russian), Izd. Mir, Moscow, 1977, 400 pp
23. S I Zhdanov (Editor) *Zhidkie Kristally* (Liquid Crystals), Izd. Khimiya, Moscow, 1979, 328 pp
24. *Liquid Crystals and Plastic Crystals,* (Edited by G W Gray, P A Winsor), Wiley, New York, 1974, Vol. 1, 383 p; Vol. 2, 314 p
25. A S Sonin *Vvedenie v Fiziku Zhidkikh Kristallov* (Introduction to the Physics of Liquid Crystals), Izd. Nauka, Moscow, 1983, 319 pp
26. S A Pikin *Strukturnye Prevrashcheniya v Zhidkikh Kristallakh* (Structural Transformations in Liquid Crystals), Izd. Nauka, Moscow, 1981, 336 pp
27. A P Kapustin *Eksperimental'nye Issledovaniya Zhidkikh Kristallov* (Experimental Studies of Liquid Crystals), Izd. Nauka, Moscow, 1978, 368 pp
28. R D Vold, M J Vold *J. Am. Chem. Soc.,* 1939, **61** 808
29. M J Vold, M Macomber, R D Vold *J. Am. Chem. Soc.,* 1941, **63** 168
30. A E Skoulios, V Luzzati *Nature,* 1959, **183** 1310
31. A E Skoulios, V Luzzati *Acta Crystallogr.,* 1961, **14** 278
32. B Gallot, A E Skoulios *Acta Crystallogr.,* 1962, **15** 826
33. B Gallot, A E Skoulios *Mol. Cryst.,* 1966, **1** 263
34. A R Ubbelohde, H J Michels, J J Duruz *Nature,* 1970, **228** 50
35. A R Ubbelohde, H J Michels, J J Duruz *J. Phys. E: Sci. Instrum.,* 1972, **5** 283
36. D Demus, H Sackmann, K Seibert *Wiss. Z. Univ. Halle, M,* 1970, **19**(5) 47
37. V Busico, A Scopa, M Vacatello *Z. Naturforsch., A,* 1982, 37(12) 1466
38. I Konkoly-Thege, I Ruff, S O Adeosun, S J Sime *Thermochim. Acta,* 1978, **24** 89
39. S O Adeosun, S J Sime *Thermochim. Acta,* 1976, **17** 351
40. S O Adeosun *J. Therm. Anal.,* 1978, **14** 235
41. S O Adeosun *Can. J. Chem.,* 1979, **57**(2) 151
42. A R Ubbelohde *Melting and Crystal Structure* (Translated into Russian), Izd. Mir, Moscow, 1969, 420 pp
43. A G Morachevskii, E P Sokolova, in Ya M Kolotyrkin (Editor) *Fizicheskaya Khimiya. Sovremennye Problemy* (Physical Chemistry. Current Problems), Izd. Khimiya, Moscow, 1984, p. 77
44. J Lindau, S Diele, H Krüger, H-D Dörfler *Z. Phys. Chem. (Leipzig),* 1981, **262**(5) 775
45. T A Mirnaya, Candidate's Thesis, Institute of General and Inorganic Chemistry, Ukrainian SSR Academy of Sciences, Kiev, 1984
46. J J Duruz, A Ubbelohde *Proc. R. Soc. London,* 1972, **330**(1580) 1
47. J E Bonekamp, T Eguchi, S Plesko, J Jonas *J. Chem. Phys.,* 1983, **79** 1203
48. J E Bonekamp, B Hegemann, J Jonas *Mol. Cryst. Liq. Cryst.,* 1982, **87** 13
49. H J Michels, A R Ubbelohde *J. Chem. Soc., Perkin Trans. II,* 1972, (12), 1879
50. G Pelzl, H Sackmann *Mol. Cryst. Liq. Cryst.,* 1971, **15** 75
51. J E Bonekamp, I Artaki, M L Phillips, et al. *J. Phys. Chem.,* 1983, **87** 4991
52. M L Phillips, T M Barbara, S Plesko, J Jonas *J. Chem. Phys.,* 1986, **4** 5143
53. S Plesko, M L Phillips, R Cassell, J Jonas *J. Chem. Phys.,* 1984, **80** 5806
54. M Wolfe, J E Bonekamp, J Jonas *J. Chem. Phys.,* 1979, **70** 3993
55. G J Krüger *Phys. Rep.,* 1982, **82** 229
56. J Roth, T Meisel, K Seybold, Z Halmos *J. Therm. Anal.,* 1976, **10** 223
57. T Meisel, K Seybold, J Roth *J. Therm. Anal.,* 1977, **12** 361
58. S O Adeosun, S J Sime *J. Chem. Faraday, Trans. I,* 1979, **75** 953
59. S O Adeosun, M O Illori, H A Ellis *Thermochim. Acta,* 1980, **39** 125
60. M E Ekwunife, M U Nwachukwu, F P Rinehart, S J Sime *J. Chem. Soc., Faraday Trans. I,* 1975, **71** 1432
61. J J Duruz, A R Ubbelohde *Proc. R. Soc. London,* 1976, **347**(1650) 301
62. A Bogoyavlenskii, N M Vinogradov *Z. Phys. Chem.,* 1907, **60** 433
63. A Bogoyavlenskii, N M Vinogradov *Z. Phys. Chem.,* 1908, **64** 229
64. R L Humphries, G R Luckhurst *Chem. Phys. Lett.,* 1973, **23** 567
65. T A Mirnaya, V D Prisyazhnyi *Ukr. Khim. Zh.,* 1983, **49** 1023
66. J M Lohar, D S Shan *Mol. Cryst. Liq. Cryst.,* 1974, **25** 145
67. J Braunstein *Ionic Interactions,* Vol. 1, *Equilibrium and Mass Transport,* S Petrucci (Editor), Acad. Press, New York–London, 1971, p. 179

68. T A Mirnaya, V D Prisyazhnyi, V N Mirnyi *Ukr. Khim. Zh.*, 1984, **50** 359
69. V N Mirnyi, V D Prisyazhnyi, T A Mirnaya *Termodinamicheskie i Elektrokhimicheskie Svoistva Ionnykh Rasplavov* (The Thermodynamic and Electrochemical Properties of Ionic Melts), Izd. Naukova, Dumka, Kiev, 1984, p. 54
70. Y Nakamura, Sh Shimokawa, Y Kitazawa, M Shimoji *Proc. I Intern. Symp. on Molten Salt Chemistry and Technology, Kyoto, Japan*, 1983, p. 387
71. J W Park, C S Bak, M M Labes *J. Am. Chem. Soc.*, 1975, **97** 4398
72. A C Griffin, R F Fisher, S J Havens *J. Am. Chem. Soc.*, 1978, **100** 6329
73. K Araya, Y Matsunaya *Bull. Chem. Soc. Jpn.*, 1980, **53** 3079
74. R S Gupta, R A Vora *Mol. Cryst. Liq. Cryst.*, 1984, **106** 147
75. V Busico, T Tartaglione, M Vacatello *Thermochim. Acta.*, 1983, **62** 77
76. A V Shubnikov *Kristallografiya*, 1960, **5**(1) 3
77. O P Kevdin, Candidate's Thesis, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1983

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Thermodynamics of extraction by solutions of amines and salts of substituted ammonium bases

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ABSTRACT. Extraction systems containing amines and their salts are widely used to concentrate and separate metals. From the theoretical viewpoint, these systems are among the most complex, because of the variety of intermolecular interactions in the organic phase. The explanation and quantitative description of the observed regularities of extraction became possible only as a result of progress in the study of the thermodynamics of binary and multicomponent solutions of salts of substituted ammonium bases in non-polar organic solvents, which make it possible to distinguish the contribution of each type of interaction to the non-ideal character of the solutions. All known "anomalous" features are due to the influence of the hydration of the salts of the substituted ammonium bases on their activity.

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I. Introduction

The extraction of acids and metal salts by solutions of substituted ammonium bases is widely used in the processing of irradiated nuclear fuel, in hydrometallurgy, and in the analytical chemistry of various elements. The extensive published experimental material on extraction equilibria in various systems has been summarised in monographs,[1–7] reviews,[8–21] and reference works.[22,23] At the same time, systems containing the salts of substituted ammonium bases are very complex, and until recently for a number of systems there was even lack of agreement about the composition of the compounds extracted; contradictory data have been published on the state of the retracting agents in organic solvents, obtained from inter-phase distribution data and from independent physicochemical measurements.

An examination of the results of a large number of studies of the extraction properties of amines and their salts, and also the properties of solutions of salts of substituted ammonium bases in organic solvents, shows that the principal reason for these discrepancies is the lack of data on the influence of various factors on the activity of the salts.

The present review examines the thermodynamics of solutions of salts of substituted ammonium bases in organic solvents, the influence of various factors (molecular association, hydration, and solvation) on the activity coefficients of the salts, and the use of the observed regularities for the explanation and quantitative description of the extraction equilibrium. The review does not deal with molecular-statistical models of the solutions, except for models of an ideal associated solution (IAS), which can be regarded as one of the methods for describing deviations from ideal behaviour, so long as no physical significance is assigned to the calculated values of the association constants.

The thermodynamic methods for describing the deviations from ideal behaviour in solutions of substituted ammonium bases are general, and make it possible to predict the equilibrium in extraction systems containing reagents of different classes. The material in the present review is useful for explaining the properties of ion-selective electrodes with liquid and solidified membranes based on the salts of completely substituted onium bases, and also for describing the kinetics of the reactions taking place in the synthesis of organic compounds in two-phase systems containing inter-phase transfer catalysts.

II. Regularities of the extraction of acids and metal salts

The extraction of acids and metal salts by solutions of amines in organic solvents usually involves chemical reactions between molecules of the extracting agent and the substance being extracted. A knowledge of the stoichiometry of the reaction involved in the formation of the compound being extracted is a necessary condition for an understanding of the regularities of the extraction and the description of the extraction equilibrium.

The extraction of monobasic inorganic acids from their sufficiently dilute aqueous solutions by solutions of amines in non-polar solvents, when the electrolytic dissociation of the salt formed in the process can be neglected, is usually described by the reaction

$$R_3N(org) + H^+ + X^- \rightleftarrows R_3NHX(org), \quad (1)$$

where R represents an organic group or a hydrogen atom, and X^- an anion. In the extraction of polybasic acids H_mX, normal $(R_3NH)_mX$ and acid R_3NH_mX salts are formed, the concentration of which depends on the equilibrium acidity, the nature of the organic solvent, and the strength of the acid and the base. For example, in the extraction of phosphoric acid by solutions of primary amines, normal phosphates are formed, whereas in extraction by tertiary amines, normal phosphates are not formed.[4] In the extraction of sulphuric acid by solutions of N,N-dioctylaniline, only the hydrogen sulphate $R_3NH_2SO_4$ is formed,[24] whereas in the extraction of sulphuric acid by the more basic tri-n-octylamine (TOA), various physicochemical methods have detected not only TOA sulphate and hydrogen sulphate

but also a compound with the intermediate composition $(R_3N)_3.(H_2SO_4)_2$.[25] Compounds with complex compositions are also formed in various other cases. Micro-quantities of peroxomolybdates are extracted by a trialkylmethylammonium sulphate as R_4NHMoO_6. The composition of the complex extracted at high molybdenum concentrations corresponds to the formula $(R_4NHMoO_6)_2H_2MoO_6$.[26]

The kinetics of the extraction of hydrochloric, perchloric, and sulphuric acids by solutions of TOA, tri-n-decylamine, and tri-n-laurylamine have been studied using a diffusion cell with stirring and with brief contact between the phases.[27] Since the rate of extraction is independent of the pH of the aqueous solutions and the concentration of the anion of the acid, it was concluded that the reversible protonation of the amine takes place at the inter-phase boundary.

The extent of the extraction of acids according to reaction (1) increases in the order $HCl < HBr < HI < HClO_4$, that is with decrease in the proton affinity and the hydration energy of their anions in aqueous solution. When different amines are used, the extraction of the acids decreases with increase in the degree of substitution: primary > secondary > tertiary amine.[28] Since the electronegativity of the hydrogen atom is lower than that of alkyl groups, the observed order of extractability is the opposite of that expected.[29] This contradication is apparently due to association of the amine salts as a result of the formation of hydrogen bonds between the non-substituted hydrogen atoms of the bases and the anions of the other salts. The existence of these interactions in solution has not yet been confirmed experimentally, but X-ray diffraction studies of crystals of the salts showed that they contain intermolecular hydrogen bonds.[29] Moreover, it has been established spectrophotometrically that hydrogen bonds are formed between the N–H groups of primary amines and the anions of the salts of quaternary ammonium bases R_4NX.[30]

The extraction of acids is influenced considerably by the nature of the organic diluent used and by the presence in the systems of a modifier (usually an alcohol or tri-n-butyl phosphate) added to prevent the formation of a second organic phase in the extraction. The distribution coefficients of acids usually increase with increase in the polarity of the organic solvents. Alcohols and other protogenic solvents generally facilitate the extraction of acids when normal salts are formed, and lower the distribution coefficients slightly when acid salts are formed.

The description of the extraction equilibrium is complicated considerably by the extraction of super-stoichiometric quantities of acid by the amine salts according to the equation

$$R_3NHX(org) + lH^+ + lX^- \rightleftarrows R_3NHX.lHX(org). \quad (2)$$

In the extraction of weak acids, for example hydrofluoric acid, the ratio of the concentrations of the acid and the amine in the organic phase increases continuously with increase in the concentration of the acid in the aqueous phase. A similar phenomenon is observed in the extraction of strong acids from their concentrated solutions. In this case, however, the extraction isotherm usually shows a clearly defined inflection corresponding to the point of complete neutralisation of the mine according to reaction (1). The extraction of super-stoichiometric quantities of the acid increases with decrease in the radius of the anion of the acid in the order perchlorate < iodide < bromide < chloride, and also on going from the salts of secondary amines to the salts of quaternary ammonium bases. Similar regularities are characteristic of the extraction of water by solutions of ammonium salts.

In the extraction of mineral acids by salts of onium bases, containing the anions of organic acids (HA), according to the reaction

$$R_4NA(org) + H^+ + X \rightleftarrows R_4NX(org) + HA(org) \quad (3)$$

the organic acid and the salt R_4NX are formed.[31,32] There is a close analogy between the regularities of the distribution of mineral acids in systems containing R_4NA and the regularities of extraction by neutral reagents with dissociation of the compound extracted in the organic phase.[33] By changing the nature of the components and the composition of the organic phase, it is possible to control the values of the distribution coefficients of inorganic acids and metal salts over a wide range at the stages of extraction and re-extraction. In particular, mixtures of TOA chloride with various acids (*p*-t-butylphenol, octanoic acid, di-2-ethylhexyl hydrogen phosphate, 5-t-butyl-2-hexadecylbenzenesulphuric acid) effectively extract H_2PtCl_6 and H_2PdCl_4. Conditions under which platinum and palladium in these systems can be re-extracted with water have been found.[34]

When aqueous solutions containing the anions of a mineral acid HY are treated with solutions of ammonium salts, anion exchange takes place:

$$R_4NX(org) + Y^- \rightleftarrows R_4NY(org) + X^-. \quad (4)$$

The degree of extraction of the ions of monobasic acids decreases in the order $ClO_4^- > I^- > NO_3^- > C_6H_5COO^- > Br^- > Cl^- > HSO_4^- > HCO_3^- > CH_3COO^- > F^- > OH^-$.[10] A similar lyophilic series is observed for liquid and solidified ion-selective electrodes based on quaternary ammonium salts.

Reaction (1) usually precedes the extraction of metal salts by ammonium salts, which may involve addition

$$qR_3NHX(org) + M^{z+} + zX^- \rightleftarrows (R_3NH)_qMX_{z+q}(org), \quad (5)$$

or anion exchange

$$qR_3NHX(org) + MX_{z+q}^{q-} \rightleftarrows (R_3NH)_qMX_{z+q}(org) + qX^-. \quad (6)$$

The final equilibrium products of reactions (5) and (6) are identical, that is these reactions are thermodynamically indistinguishable. Studies of the kinetics of extraction showed that it takes place according to reaction (6) when acido-complexes of the metals predominate in the aqueous phase, and according to reaction (5) in their absence.[13,17] From an analysis of data on the extraction of uranyl chloride by solutions of trioctylmethylammonium chloride it was suggested that metals may be extracted by a cation-exchange mechanism by molecules of the extracting agent combined with super-equivalent acid.[35]

Equilibria (5) and (6) are influenced considerably by the nature of the organic diluent. The influence of the diluent on the distribution coefficient of the metal salt depends markedly on the nature of the cation and anion of the onium salt.

Metal salts may also be extracted by other mechanisms. Thus in the extraction of the platinum metals, the amines are coordinated to the metal atoms.[2] The formation of bonds between the nitrogen atoms of the amines and the metal being extracted is most characteristic of primary amines. In particular, it has been established by different methods that in the extraction of divalent zinc from thiocyanate solutions by primary amines, the amine complexes $(RNH_2)_2Zn(SCN)_2$ are formed.[36] Long-chain primary aliphatic amines, unlike tertiary and secondary amines, effectively extract hydrolysed forms of aluminium sulphate.[37] In the systems formed by R_3NHX and R_4NX with platinum metals, the extraction equilibrium is often displaced towards the formation of polynuclear complexes, whose concentration increases with decrease in the concentration of the extracting agent.[38] The extraction of alkali metal carbonates by solutions of quaternary ammonium carbonates is accompanied by appreciable inter-phase distribution of water, and this has been attributed to the extraction of the salts by a hydrate–solvate mechanism.[39]

A characteristic feature of extraction systems containing salts of substituted ammonium bases is the marked positive deviations of the organic phase from ideal behaviour, due to molecular association and solvation of the salts. Until recently there was no method for taking account of the influence of various interactions on the activity of the components of the organic phase, so that extraction isotherms had been described only for various simple systems, and many observed phenomena could not be explained even qualitatively.

The extraction constant for the extraction of acids according to Eqn. (1) is given by the expression

$$K = \frac{\overline{C}_s \overline{y}_s}{\overline{C}_a \overline{y}_a a_{HX}} = \frac{\overline{y}_s}{\overline{y}_a}, \qquad (7)$$

where C represents the molar concentrations of the components, K and $\tilde{K}$ the thermodynamic and effective extraction constants respectively, y the activity coefficient, a_{HX} the activity of the acid in the aqueous solution, the subscripts s and a denote the amine salt and the amine respectively, and the bar above the symbols denotes the concentrations and activities of the components of the organic phase. Data on the activity of water (a_w) and the activity coefficients of electrolytes in aqueous solution are given, for example, by Mikulin.[40] The characteristics of the calculation of the activity of the components in mixed electrolyte solutions have been examined by a number of authors.[40–43]

The extraction constant for the extraction of metals according to reaction (5) can also be written as

$$K = \frac{\overline{C}_c y_c}{\overline{C}_s^q \overline{y}_s^q a_{MX_z}} = \tilde{K} \frac{\overline{y}_c}{\overline{y}_s^q} = \overline{K} \frac{\overline{y}}{\overline{y}_s^q \gamma_\pm^{z+1}}, \qquad (8)$$

where $\overline{K}$ is the apparent constant calculated without allowance for the mean ionic activity coefficients in the aqueous phase $\gamma_\pm$, a_{MX_z} the activity of the metal salt in the aqueous phase, and the subscript c denotes the metal complex extracted.

The stoichiometric coefficient q is often determined by studying the extraction of micro-quantities of the metal at a constant composition of the aqueous phase and varying concentration of the extracting agent $\overline{C}_s$. Eqn. (8) then becomes

$$\lg D = \text{const} + q \lg \overline{C}_s + \lg(\overline{y}_s^q / \overline{y}_c), \qquad (9)$$

where D is the distribution coefficient of the metal, and const $= \lg(K[X^-]^z \gamma_\pm^{z+1})$. The plot of $\lg D$ against $\lg \overline{C}_s$ will obviously be linear, with slope q, only if the ratio of the activity coefficients $\overline{y}_s^q / \overline{y}_c$ remains constant in the range of concentrations $\overline{C}_s$ studied.

To understand the influence of macro-components on the extraction of micro-quantities of substances by solutions of quatarnary ammonium salts, it is of fundamental importance to take account of the electrolytic dissociation of the salts and the complexes formed in the organic phase.[44] The dissociation constants of simple and complex high-molecular-weight ammonium salts in benzene and nitrobenzene have been determined and tabulated.

Experimental data on the extraction of mineral acids by amine solutions show that the effective extraction constants depend markedly on the concentration $\overline{C}_s$.[20] It is usually assumed that the values of $\overline{y}_a$ are close to 1, and the increase in $\tilde{K}$ with increase in the concentration of the amine salt is attributed to the decrease in $\overline{y}_s$ as a result of association of the salts:

$$n R_3NHX(org) \rightleftarrows (R_3NHX)_n(org). \qquad (10)$$

The association constant is

$$\beta_n = \overline{C}_s(n) / [\overline{C}_s(1)]^n, \qquad (11)$$

where $\overline{C}_s(1)$ and $\overline{C}_s(n)$ are respectively the concentrations of the monomer and the n-mer of the amine salt. The association constants have been determined either from independent data (cryoscopic, ebullioscopic, etc.) or from distribution data (two-phase potentiometric titration). In the last case, the following equilibrium was studied[16]

$$n R_3N(org) + n H^+ + n X^- \rightleftarrows (R_3NHX)_n(org), \qquad (12)$$

with equilibrium constant

$$K_n = \overline{C}_s(n) / \overline{C}_a^n a_{HX}^n = K^n \beta_n. \qquad (13)$$

The concentration of the amine salt is

$$\overline{C}_s = \sum_n \beta_n [\overline{C}_s(1)]^n = \sum_n K^n \beta_n \overline{C}_a^n a_{HX}^n. \qquad (14)$$

The extraction of sulphuric acid has been studied in most detail. The earliest study of the extraction of sulphuric acid by benzene solutions of TOA[45] established that the effective extraction constant remains constant only as far as a TOA sulphate concentration of 0.02 M, after which it increases. The deviations from ideal behaviour were attributed to the "polymerisation" of TOA sulphate in benzene.

The use of the equilibrium-displacement method to determine the composition of the compound formed in the extraction of uranyl sulphate by amine sulphates[13,14] established that the distribution coefficient of uranium is proportional to the concentration of "free" amine sulphate to the approximate power 0.5. At the same time, according to saturation data, one molecule of uranyl sulphate reacts with two molecules of TOA sulphate.[18,46] This discrepancy was also attributed to the formation of associates, present in a stable colloidally dispersed state. Independent physicochemical studies showed, however, that in anhydrous benzene solutions, TOA sulphate is monomeric[25,47] and undergoes association to only a slight extent when water is added to the organic phase.[48,49] This weak association can explain only a small fraction of the deviation from ideal behaviour in the organic phase of the extraction systems studied.

The effective extraction constants for the extraction of monobasic inorganic acids by amine solutions also depend markedly on the concentration of the ammonium salts formed. The experimental data are often represented on coordinates $\lg \overline{C}_s$–$\lg(\overline{C}_a a_{HX})$. If it is then assumed that the deviations from ideal behaviour are due only to the association of the amine salt in the organic phase and that Eqns. (10) to (14) are applicable, then for the slope of the tangent to the curve on these coordinates it is possible to write

$$\frac{\partial \lg \overline{C}_s}{\partial \lg(\overline{C}_a a_{HX})} = \frac{\sum_n n K^n \beta_n \overline{C}_a^n a_{HX}^n}{\sum_n K^n \beta_n \overline{C}_a^n a_{HX}^n} = \overline{n}, \qquad (15)$$

where $\overline{n}$ is the average degree of association of the amine salt in the organic phase.

Experimental data[8,20] show that at low concentrations of the ammonium salt, the slope is close to 1 (linear section), that is there is no association. With further increase in $\overline{C}_s$, the slope gradually begins to increase, and at a certain concentration the tangent becomes perpendicular to the abscissa. From this it was concluded that the average degree of association had become infinite, and this was interpreted as corresponding to the formation of a colloidal solution. With further increase in $\lg(\overline{C}_a a_{HX})$, however, the curve deviates to an even greater extent towards the ordinate, and the slope becomes negative, indicating that Eqn. (15) and the entire concept developed cannot be used to describe the extraction in this range. According to

independent data,[20] at concentrations corresponding to the vertical position of the tangent the average degree of association is not even close to infinity.

For a long time there was no accepted explanation for this phenomenon. For example, Diamond[8] suggested that the "anomalous" relationships are due to a change in the properties of the pure solvent resulting from the presence of a large number of ions, so that the solvent acquires the properties of a completely new substance with better extraction characteristics. Later,[50] he concluded that the "anomalous" relationship is due entirely to the behaviour of the "free" amine, and that increase in the concentration of the salt leads to an increase in the activity coefficient of the amine and a marked decrease in the ratio of the activity coefficients of the components of the organic phase. Others[51] suggested that "the increase in the dielectric constant of the solution with increase in the concentration of the ammonium salt leads to a decrease in the association and an increase in the extraction constant. The superposition of these effects gives different curves, including the anomalous curve".

Similarly, no unambiguous explanation was found for the nature of the dependence of the extraction of metal salts on the structure of the cations of the substituted ammonium salts. The extraction of metal salts from nitric acid solutions increases in the order primary < secondary < tertiary < quaternary alkylammonium.[5] In sulphuric acid solutions, at least for the actinides(IV) and (VI), the opposite relationship is observed, and was described as "curious".[19]

The influence of modifiers on the extraction equilibrium is often examined using the model of an ideal associated solution. According to this model, the deviations of the solutions from ideal behaviour are due to the formation of associates or solvates, whose solution behaves as an ideal solution, and the equilibria between them obey the law of mass action. Thus it is assumed that in the presence of alcohols or other solvating additives (B), mixed associate–solvates are formed

$$n\mathrm{R_3NHX(org)} + p\overline{\mathrm{B}} \rightleftarrows (\mathrm{R_3NHX})_n\mathrm{B}_p\mathrm{(org)}. \qquad (16)$$

and the equilibrium constant is written as

$$\beta_{np} = \frac{[(\mathrm{R_3NHX})_n\mathrm{B}_p]}{[\overline{C}_s(1)]^n[\overline{C}_B(1)]^p}. \qquad (17)$$

Eqns. (16) and (17) are more general than Eqns. (10) and (11). Similar equations can be written for the extraction of metals. This approach has not yet been used systematically to describe the influence of modifiers on extraction by amines. Eqns. (16) and (17) are most frequently used when $n = 1$.[14,15] These equations, however, can hardly explain various "anomalous" features of extraction, for example the fact that the distribution coefficient of the metal passes through a maximum with increase in the alcohol concentration.[52]

An explanation of these and various other "anomalous" features became possible after the development of methods for taking systematic account of the influence of various interactions on the activity of the salts of substituted ammonium bases.

III. Determination of the activity of the components in ammonium salt solutions

The organic phase of amine extraction systems is a multicomponent solution, which in the general case contains a diluent, an amine, neutral and acidic amine salts, water, a modifier, and the metal complexes extracted. A characteristic of these solutions is that the amines and the ammonium salts formed in the extraction are non-volatile substances, sparingly soluble in water. There are at present no direct methods for determining the thermodynamic activity of substances of this kind. The activity of the ammonium salts is therefore usually determined by indirect methods from the activity of the other components of the solution.

1. Experimental methods

Most frequently, in solutions of ammonium salts, the activity of the solvent is determined. Since existing methods are not of equal value, it is necessary to consider them briefly. The direct method involving measurement of the vapour pressure of the solvent is rarely used,[53,54] since it requires extremely complex apparatus and does not make it possible to study sufficiently dilute solutions in which the mole fraction of the solute $x_2 < 0.01$. The most accurate and sensitive method for determining the activity of the solvent is apparently the cryoscopic method. It has been used to study solutions in benzene with a molality down to 0.0003.[55–57] The chief disadvantage of the cryoscopic method is the need to carry out the studies at the freezing point of the solvent. It is thus practically impossible to determine the influence of the nature of the solvent and temperature on the activity of the components of the solution. Of the diluents usually employed in extraction, only benzene is widely used for cryoscopic measurements. Isolated studies have been carried out using cyclohexane and *p*-xylene.[58]

The ebulliometric method using a manostat has the advantage over the cryoscopic method that it makes it possible to carry out studies with a large number of volatile solvents at different temperatures. Ebulliometry is widely used to study solutions of polymers. The instruments developed for these purposes make it possible to carry out measurements in solutions with solute concentrations down to 0.0003 mol kg^{-1} and even lower.[59–61]

Isothermal distillation, and the isopiestic method, are applicable only to solutions with concentrations not lower than 0.01 mol kg^{-1}. Studies by these methods were previously carried out at temperatures close to room temperature (25–50 °C) using the solvents benzene, tetrachloromethane, cyclohexane, and chloroform.[20,62–64] Methods of measurement were subsequently developed for studying solutions in less volatile solvents (toluene, chlorobenzene, butylbenzene, and chloronaphthalene) at temperatures up to 130 °C.[65]

The above methods make it possible to determine directly only the activity of the solvent a_1. Nevertheless, in many papers, the experimental data are given as the average degrees of association of the solute $\bar{n}$:

$$\bar{n} = \ln x_1/\ln a_1 = 1/\varphi, \qquad (18)$$

where x_1 is the mole fraction of the solvent, and φ the osmotic coefficient. The values of $\bar{n}$ give a clear picture of the deviations from ideal behaviour in solution, and are widely used in the theory of IAS. This theory has been justifiably criticised for the insufficient clarity of the physical ideas on which it is based. However, so long as a physical significance is not given to the association (solvation) constants calculated from Eqns. (11), (13), and (17), then the theory of IAS can be regarded as a method for describing deviations from ideal behaviour, where the activity of the solute is equal to the concentration of its monomer.

Another component of the organic phase of amine extraction systems whose activity can easily be determined is water. In practice, however, the opposite approach is used; the dependence of the concentration of water in the organic phase on its activity a_w is determined. Titration with the Karl Fischer reagent is usually employed for this purpose, although other methods are also known. The saturation of the organic phase with water at a definite water activity is often carried out by the isopiestic method with

thermostatting.[12] The previously popular method involving the equilibration of the organic phase with an aqueous salt solution with known a_w has a number of unsatisfactory features, and is now seldom used.

The activity of the other components of the organic phase of amine extraction systems has not yet been determined experimentally. The determination of the activity of a number of susbstances used as modifiers is possible in principle.

2. Methods for calculating the activity of the components

The activity of the components of the solution is most frequently calculated from the activity of the solvent using the Gibbs–Duhem equation in the form

$$\frac{10^3}{M_1} d\ln a_1 + \sum_{i=2}^{n} m_i d\ln a_i = 0 \qquad (19)$$

or

$$\frac{10^3}{M_1} d\ln f_1 + \sum_{i=2}^{n} m_i d\ln f_i = 0, \qquad (20)$$

where m_i, a_i, and f_i represent respectively the molality, activity, and molar activity coefficient of the ith component of the solution, the subscript 1 refers to the solvent, and M_1 is the molecular mass of the solvent.

For binary solutions, integration of Eqn. (20) gives the expression

$$\ln f_2/f_2^0 = -\frac{10^3}{M_1}\int_0^{m_2} \frac{1}{m_2}\frac{\partial \ln f_1}{\partial m_2} dm_2, \qquad (21)$$

where $f_2^0$is the activity coefficient in the infinitely dilute solution. The absolute activity coefficients (standard state the pure substance) of the solute cannot be determined using the Gibbs–Duhem equation, so that the concentration activity coefficients are generally determined using $f_2^0 = 1$.

Eqn. (21) is practically never used to calculate activity coefficients, since as $m_2 \to 0$, the right-hand side becomes indeterminate. To avoid this difficulty, the concept of osmotic coefficient is used. Substituting Eqn. (18) in Eqn. (20) and integrating gives the following equation for the concentration activity coefficient:

$$\ln f_2 = \varphi - 1 - \int_0^{m_2} \frac{1-\varphi}{m_2} dm_2. \qquad (22)$$

The calculation of the activity coefficients from Eqn. (22) is usually carried out by graphical integration of the function $(1 - \varphi)/m_2$, extrapolating it to $m_2 = 0$.

The use of cross relationships has been proposed[66] for calculating the activities of the components in muiltcomponent solutions. Thus for solutions with components i, j, and k it is possible to write

$$\left(\frac{\partial \ln a_i}{\partial r_{kj}}\right) r_{ij} = \left(\frac{\partial \ln a_k}{\partial r_{ij}}\right) r_{kj} \qquad (23)$$

and

$$\left(\frac{\partial \ln f_i}{\partial r_{kj}}\right) r_{ij} = \left(\frac{\partial \ln f_k}{\partial r_{ij}}\right) r_{kj}, \qquad (24)$$

where $r_{ij} = x_i/x_j$ is the relative concentration. A particular case of r_{ij} is the molal concentrations

$$m_i = \frac{10^3}{M_1} r_{i1} = \frac{10^3}{M_1}\frac{x_i}{x_1}.$$

The method involving the calculation of the Gibbs free energy of the solution from the partial molar Gibbs free energy of one of the components,[67] and various other methods,[68–70] have been used in the calculation of the activities of the components of metallic alloys, but have not yet been used to interpret the results of the study of an extraction equilibrium.

It should be emphasised that different methods of calculation should theoretically give the same results. In practice, however, errors which are different for different methods are unavoidably introduced in the calculations. The well-founded selection of a method of calculation applicable to the systems being discussed in order to achieve the smallest uncertainty is as yet impossible, because of the lack of accurate experimental data.

3. Binary solutions

A knowledge of the activities in binary solutions is necessary for calculating the activities in more complex systems. Of the large number of binary solutions which may be formed with the participation of the components of the organic phase of amine extraction systems, only solutions of the amine salt (or amine)–non-polar solvent type have as yet been studied.

Only slight deviations from ideal behaviour have been observed in solutions of water[71] and amines[20,62] in non-polar organic solvents, so that the concentration activity coefficients of these substances in the binary solutions can be taken as 1.

Appreciable association takes place in solutions of alcohols in non-polar organic solvents. The activity coefficients of alcohols in binary solutions can be readily calculated from experimental data using Eqn. (22). A large number of studies have been devoted to binary solutions of substituted ammonium salts, whose degree of association varies over a wide range. Analysis of the experimental data[15] has shown that the association of ammonium salts increases in the following cases: 1) with increase in the radius of the anion (for a given cation) in the order fluoride < chloride < bromide < thiocyanate < nitrate < iodide < perchlorate; 2) with decrease in the length of the group of the ammonium cation; 3) with decrease in temperature; 4) with decrease in the dielectric constant of the solvent in the order of nitrobenzene > chloroform > benzene > xylene > tetrachloromethane > cyclohexane > alkanes; and 5) with decrease in the degree of replacement at the nitrogen atom for salts with a given anion in the order tertiary < secondary < primary amines. The salts of quaternary ammonium bases occupy an intermediate position between the salts of tertiary and secondary amines. Since the publication of the review cited,[15] a large number of new studies[1,3,5] of the association of ammonium salts have been published, confirming the above features.

It is assumed that the formation of intermolecular hydrogen bonds generally facilitates the association of salts of primary and secondary amines. The main factor responsible for the association of the salts of tertiary amines and quaternary ammonium bases, which have extremely high dipole moments,[1] is the electrostatic attraction between the molecules (chiefly dipole–dipole interaction), although in some cases (acid salts) intermolecular hydrogen bonds are also probably formed. Thus the dipole moments of the molecules of the hydrogen sulphates of tertiary amines are lower than those of the molecules of the chlorides or bromides of the same amines, although the latter are associated to a smaller extent than the hydrogen sulphates.[1,72]

There are comparatively few published data on the association of complex ammonium salts with metal salts in binary solutions. This is partly due to the insufficient stability of many complex salts, as a consequence of which it is necessary to introduce simple ammonium salts to displace the equilibrium in the solution. For stable complex

salts, the degree of association varies over a wide range, from 1 for the complex of uranyl sulphate with trioctylammonium sulphate in benzene[72] to 10 or more for tetraheptylammonium tetrachloro- and tetrabromoferrates.[62] NMR[73] has established that the association of the acido-complexes of lanthanide nitrates with the nitrates of tertiary amines increases with decrease in the length of the n-alkyl groups in the cations of the salts, and also on going from symmetrical to unsymmetrical cations.

A high degree of association makes it difficult to calculate the activity coefficients of ammonium salts from Eqn. (22). Thus in solutions of tridodecylammonium bromide in cyclohexane at a minimum concentration of 0.0077 M, the average degree of association $\bar{n} = 1.83$,[62] which corresponds to $\varphi = 0.546$. At the same time, for reliable extrapolation to infinite dilution in the calculation using Eqn. (22), it is necessary that the values of φ be close to 1 or at least greater than 0.9 at the minimum concentration of the solute. In the study of binary solutions of ammonium salts, this condition can be satisfied extremely rarely (the measurements have to be carried out in the concentration range 10^{-4}–10^{-3} M). Attempts have therefore been made to approximate the dependence of $\ln f_1$ or φ on the concentration of the solute by various functions, and then to carry out the integration of Eqns. (21) and (22).

For this purpose, the following polynomial expansion has been used[62]

$$\lg f_2 = A + Bm_2 + Cm_2^2 + Dm_2^3, \qquad (25)$$

where the subscript 2 refers to the ammonium salt, and the coefficients A, B, C, and D are non-zero. Since it follows from the definition of the concentration activity coefficient that $\lg f_2 = 0$ for $m_2 = 0$, Eqn. (25) can be regarded as an interpolation equation, applicable only in the range of concentrations studied in the work cited.[62] As noted by the authors cited,[62] the values of $\lg f_2$ calculated from Eqn. (25) may differ from the true values by a certain constant amount as a consequence of the inaccuracy of the extrapolation to infinite dilution in the integration of the Gibbs–Duhem equation. The value of $\Delta \lg f_2$ may reach about 0.15.[74]

A different approach was used by Gal and co-workers,[63] who represented the function under the integral sign in Eqn. (22) in the form of the polynomial

$$\frac{1-\varphi}{m_2} = A + Bm_2 + Cm_2^2 + Dm_2^3 + Em_2^4. \qquad (26)$$

This expansion is obviously preferable to that in Eqn. (25), since substituting Eqn. (26) in Eqn. (22) and integrating gives for $\lg f_2$ a polynomial which becomes zero for $m_2 = 0$. The dependence of $(1-\varphi)/m_2$ on m_2, however, is given by a curve resembling a hyperbola. For these relationships, the approximation by the polynomial is not effective, and the values of the coefficients of the polynomial are extremely sensitive to change in the range of the approximation. An extensive verification of the applicability of Eqn. (26) has not yet been carried out. It may be noted that the inverse function $m_2/(1-\varphi)$ is close to linear.

The following equation has been proposed[75] for solutions of ammonium salts in non-polar solvents

$$m_2^2/\ln f_1 = b_0 + b_1 m_2. \qquad (27)$$

This equation is useful for extrapolating data to infinitely dilute solutions, since significant deviations from linearity are observed only at high concentrations. Substituting Eqn. (27) in Eqn. (21) and integrating gives the equation

$$\ln f_2 = -\frac{10^3}{M_1 b_1}\left[\ln\left(1 + \frac{b_1}{b_0} m_2\right) + \frac{b_1 m_2}{b_0 + b_1 m_2}\right]. \qquad (28)$$

Thus the calculation of the activity coefficients in binary solutions of ammonium salts reduces to the determination of two empirical parameters, b_0 and b_1. This makes Eqns. (27) and (28) preferable to other equations used to describe the thermodynamic functions in these solutions. The values of the parameters b_0 and b_1 for a number of solutions have been published.[1] When $m_2 \ll 10^3/M_1$, Eqn. (27) becomes

$$\frac{m_2}{1-\varphi} = \frac{M_1}{10^3}(b_0 + b_1 m_2). \qquad (29)$$

Many authors use the theory of IAS to describe the deviations from ideal behaviour in binary solutions of ammonium salts. The calculation of the association constants for the same solutions using this theory leads to ambiguous results, however. For example, two alternative descriptions of the tridodecylammonium chloride–*o*-xylene system have been published.[76,77]

The activity coefficients (or the association constants, which to some extent are equivalent) in binary solutions are often used to describe the extraction equilibrium. This approach has been successful in a number of cases.[78] To avoid errors, however, before using the activity coefficients found in binary solutions, it should be established that the introduction of other components into the solution does not influence the values of the activity coefficients. For this it is necessary to develop methods for calculating the activity coefficients in multicomponent solutions of ammonium salts.

4. Calculation of the activities of solutes from the activities of the solvent in multicomponent solutions

The most complex problem is the calculation of the activities of substances in multicomponent solutions from the activities of the solvent. This problem can be simplified and reduced to the calculation of the change in the activity of a solute when another substance is added to the solution. The two most important cases may be noted. To explain the "anomalous" dependence of $\lg \bar{C}_s$ on $\lg(\bar{C}_a a_{HX})$ it has been suggested that the activity coefficient of the amine $\bar{y}_a$ increases when an amine salt is added to the solution.[50] Experimental data also indicate that the metal complex extracted may react with the amine salt in the organic phase. This interaction must be taken into account in the determination of q by the equilibrium-displacement method.

In the extraction of iron(III) chloride, only tetrachloroferrate ions $FeCl_4^-$ are present in the organic phase.[79] The values of q found by the equilibrium-displacement method, however, depending on the conditions of the experiment, lie in the range 1–2, due to the formation of $FeCl_5^{2-}$ ions or to the reaction of the tetrachloroferrate and the amine chloride.

In the extraction of lanthanide nitrates by amine nitrates, the dependence of $\lg D$ on $\lg \bar{C}_s$ is not linear,[80] and the deviation from linearity cannot be attributed entirely to the change in the activity coefficients of the salt $\bar{y}_s$. Finally, in some cases, reaction between the extracted complexes of different metals is possible.

The following equation was obtained[81] for calculating the activity coefficients in these systems by transforming the Gibbs–Duhen equation and the cross relationship (23)

$$\ln \gamma_2 = -\frac{10^3}{M_1}\int_0^{m_3}\frac{1}{m_3}\left[\frac{M_1}{10^3} + \left(\frac{\partial \ln a_1}{\partial m_2}\right)_{m_3=0;m_2}\right] dm_3, \qquad (30)$$

where γ is the activity coefficient when the concentration is expressed as the molality, and the subscript $m_2 = 0$ indicates that the derivative is taken as the concentration $m_2 \to 0$. Eqn. (30) can be used to calculate the change in the activity coefficients of micro-quantities of a solute when a third component is introduced.

Eqn. (30) has been used to determine the influence of an amine salt on the activity of an amine.[82] Three-component tetrachloromethane–tridodecylamine–tridodecylammonium bromide solutions were chosen as model systems; for these solutions, the slope of the plot of $\lg \overline{C}_s$–$\lg(\overline{C}_a a_{HX})$ becomes equal to infinity at $0.05\ M < \overline{C}_s < 0.1\ M$.[20]

Ebulliometric measurements showed that at a concentration $m_s = m_3 = 0.0482$ mol kg^{-1}, the expression in square brackets under the integral sign in Eqn. (30) is practically equal to zero, and the activity coefficients $\gamma_2 = \gamma_a$ do not differ significantly from 1. Thus the suggestion by Diamond and Bucher[50] that γ_a depends significantly on the concentration of the amine salt is not confirmed in this system, and it is necessary to look for another explanation of the anomalous dependence of $\lg \overline{C}_s$ on $\lg(\overline{C}_a a_{HX})$.

The ebulliometric method has been used to study the chloroform–tridodecylammonium chloride–tridodecylammonium tetrachloroferrate system.[83] The binary solutions based on these components are close to ideal, but in the ternary solutions, strong interaction between the solutes is observed. Thus the activity coefficients of micro-quantities of the amine tetrachloroferrate γ_c, calculated from Eqn. (30), decrease rapidly with increase in the concentration m_s, and at $m_s = 6 \times 10^{-3}$ mol kg^{-1}, $\gamma_c = 0.49$.

The systems formed by a solvent (tetrachloromethane or benzene) with tridodecylammonium nitrate and the complex of cerium or europium nitrate with tridodecylammonium nitrate have been studied in most detail.[85] Eqn. (30) was used to calculate the dependence of the activity coefficients of micro-quantities of the complex salts γ_c on the concentration of the amine nitrate, and it was shown that γ_c is smaller for the europium salts than for the cerium salts.[84] The values of γ_c were then used to describe the dependence of the distribution coefficient of micro-quantities of cerium and europium on the tridodecylammonium concentration at a constant composition of the aqueous phase. The extraction constants (more accurately, the products $K\gamma_{\pm}^4$) remained practically constant with change in the concentration of the extracting agent by a factor of 20, whereas neglect of γ_c led to a systematic drift of the constants (for example, in the extraction of europium, the apparent extraction constant changed by a factor of 2–3 in the concentration range studied).

Eqn. (30) can be used to calculate the activity coefficients of a solute only when its concentration is very low (micro-component). An equation has been derived,[85] making it possible to calculate the change in the activity coefficients of a solute when another substance is introduced into the solution over a wide range of concentrations For this purpose, the cross relationship (24) was intregated with replacement of the variables r_{12} and r_{13} by m_2 and m_3 respectively:

$$\ln f_2 = -\frac{10^3}{M_1}\int_0^{m_s}\left(\frac{\partial \ln f_1}{\partial m_2}\right)_{m_s}\frac{dm_3}{m_3}. \qquad (31)$$

It can be shown that as $m_2 \to 0$, Eqn. (31) becomes Eqn. (30). The calculation using Eqn. (31) is difficult, since the dependence of $\ln f_1$ on m_2 in solutions of amine salts is not linear. To eliminate this difficulty, Eqn. (31) was transformed to the equation[85]

$$\ln f_2 = \ln f_2^0 - \frac{10^3}{M_1}\int_0^{m_s}\left[\frac{\partial \ln (f_1/f_1^0 f_1^*)}{\partial m_2}\right]_{m_s}\frac{dm_3}{m_3}, \qquad (32)$$

where the superscripts 0 and * indicate that the activity coefficients were determined for binary solutions with $m_3 = 0$ or $m_2 = 0$. Eqn. (32) has been used to calculate the activity coefficients γ_c of the complexes of cerium and europium nitrates with tridodecylammonium nitrate. When the amine salt is added in the concentration range studied, γ_c is independent of the metal concentration.[85]

Allowance for the intermolecular association of the amine salts in the IAS model made it possible to develop mathematical models for the extraction of lanthanides from nitric acid solutions containing a salting-out agent by solutions of the nitrates of tertiary amines[86] and quaternary ammonium bases.[87]

IV. The influence of solvation of the extraction equilibrium

The solvation of ammonium salts by protogenic solvents in non-polar media has been studied in sufficient detail,[1,5,12,15] For example, infrared spectroscopy has shown that the reaction of the molecules of alcohols or water with the anions of the salts increases with increase in the degree of replacement at the nitrogen atom of the bases, and also with increase in the proton affinity of the anions.[88,89] Allowance for the influence of solvation on the extraction equilibrium using IAS theory does not explain the "anomalous" extraction relationships. The concepts of non-stoichiometric hydration and solvation of the salts[1] have proved to be more fruitful for describing the extraction equilibrium and understanding the essential features of the inter-particle interactions accompanying the extraction of acids and metal salts in systems containing solutions of amines and ammonium salts.

1. The hydration of ammonium salts

For many systems containing ammonium salts, in which the solubility of water (m_w) is relatively high, the distribution of water is described by the equation[90]

$$m_w = m_w^0 a_w (1 + k_r m_2), \qquad (33)$$

where m_w^0 is the solubility of water in the pure solvent at an equilibrium activity of water $a_w = 1$, and k_r the hydration parameter, related to the degree of hydration h by the expression

$$h = k_r m_w^0 a_w. \qquad (34)$$

An equation describing the activity of a solute in a ternary solution[1] was obtained from Eqn. (34) using cross relationships of the type (23) and (24):

$$\ln a_2 = \ln a_{20} - k_r m_w^0 a_w = \ln a_{20} - h, \qquad (35)$$

where a_{20} is the activity of the solute in the binary ammonium salt–solvent solution not containing water. Eqn. (35) was previously obtained by other methods.[91–93] Eqns. (33) and (35) were generalised to the case of multicomponent solutions.[94]

Thus the degree of hydration is a quantitative measure of the influence of the hydration of a solute on its activity on going from the binary solutions to solutions saturated with water at an equilibrium a_w. For the case being considered, where the distribution of water in the pure solvent and in the solution of the extracting agent obeys Henry's law, it is possible to write:

$$\Delta\mu_{2,hydr} = -RTh, \qquad (36)$$

that is the degree of hydration reflects the change in the partial molar Gibbs free energy of the ammonium salt when the solute is transferred from its dry solution to a solution containing water. Eqn. (35) can be transformed to the equation

$$\gamma_{hydr} = \exp(-h). \qquad (37)$$

It follows from Eqn. (37) that hydration lowers the activity coefficient of solutes if solutions of unit molality with the properties of infinitely

dilute solutions in the dry solvent are taken as the standard state. For the case being considered, the degree of hydration h is equal to the number of water molecules combined with a molecule of the solute in the organic solvent.[95] Thus for given values of m_w^0, hydration leads to lower values of γ_{hydr}, the higher the solubility of water in the organic phase of the extraction system.

In a number of cases it is more convenient to take as standard state a solution with the properties of an infinitely dilute solution, saturated with water at $a_w = 1$. The dependence on a_w of the activity coefficient γ_{21}, determined relative to this standard state, then has the form

$$\gamma_{21} = \gamma_2 \exp[h_\infty(1 - a_w)], \quad (38)$$

where h_∞ is the degree of hydration in the infinitely dilute solution at $a_w = 1$. In other words, the concentration activity coefficients in solutions saturated with water at $a_w = 1$ are equal to the concentration activity coefficients in the binary dry solutions. The equality of the activity coefficients determined in this way was established experimentally in a study of the extraction of hydrochloric and hydrobromic acids by trilaurylamine solutions.[78] This equality is observed in a relatively narrow range of change in the concentration of the trilaurylammonium salt, in which the distribution of water obeys Henry's law satisfactorily. The applicability of Eqns. (35)–(38) to ammonium salt solutions was confirmed by determining the activity of the salts in ternary solutions.[12,91] The range of change in h for the salts studied is fairly large. The greatest decrease in activity (by five orders of magnitude) was observed when water was added to solutions of methyltrioctylammonium sulphate.

Published data on the hydration of ammonium salts have been summarised.[1] The molar ratio of the concentrations of water and the salt in the solutions saturated with water depends on many factors. For quaternary ammonium salts it varies from 2 to 15, increasing with decrease in the molecular mass and symmetry of the cation.[96] In solutions of TOA sulphate and the salts of unsymmetrical ammonium bases, in which the solubility of water is high, the distribution of water shows appreciable deviations from Henry's law. These deviations are also observed in solutions of weakly hydrated amine salts, but at high concentrations of these salts. The deviations increase with decrease in the polarity of the organic solvents used.[90,91]

When there are deviations from Henry's law, the isotherm for the distribution of water can be described by the equation

$$m_w = \sum_{n_1,n_2} b_{n_1,n_2} a_w^{n_1} m_2^{n_2}, \quad (39)$$

where b_{n_1,n_2} is an empirical coefficient.

Substituting Eqn. (39) in the cross relationship (23)

$$(\partial \ln a_2/\partial \ln a_w) = -(\partial m_w/\partial m_2)_{a_w} \quad (40)$$

and integrating gives the expression

$$\ln a_2 = \ln a_{20} - \sum_{n_2,n_2} \frac{n_2}{n_1} b_{n_1,n_2} a_w^{n_1} m_2^{n_2-1}. \quad (41)$$

If all the terms with $n_1 \gg 2$ and $n_2 \gg 2$ are neglected, Eqn. (41) becomes Eqn. (35). For practical calculations, in the description of the influence of "non-linear" hydration, the following semi-empirical equation[97] is used instead of Eqn. (41)

$$\gamma_2 = \gamma_{20} \exp(-h_{int}), \quad (42)$$

and the integral degree of hydration h_{int}, reflecting the actual contribution of hydration to the decrease in the activity of the solute, is calculated from the isotherms for the distribution of water into the solution of the salt and into the pure solvent. With allowance for Eqn. (42), Eqn. (38) becomes

$$\gamma_{21} = \gamma_2 \exp(h_\infty - h_{int}). \quad (43)$$

Thus by using the values of h_{int} and h_∞ it is possible to change from the activities determined relative to solutions in the dry solvent to the activities determined relative to solutions saturated with water at a water activity a_w. In general, $h_{int} \geqslant h_\infty$, and the value of γ_{hydr} decreases with increase in the concentration of the salt.

Eqns. (35)–(43) make it possible to determine the regularities of the influence of hydration on the extraction equilibrium. Thus hydration is revealed most strongly in systems which include polybasic acids, and also ammonium salts containing methyl substituents. The contribution of hydration to the non-ideal behaviour of the organic phase of extraction systems decreases with decrease in the concentration of the salts and the proton affinity of their anions and with increase in the polarity of the solvents used.

As noted in section II, the most familiar "anomalous" relationship in extraction by amines is the discrepancy between the data on the degree of association of the ammonium salts obtained by analysing the distribution on the one hand, and independent physicochemical measurements on the other. The anomalies found[20] in the analysis of data on the extraction of monobasic acids by solutions of trilaurylamine on coordinates $\lg \overline{C}_s$–$\lg(\overline{C}_a a_{HX})$ are observed to an even greater extent[91] for the sulphuric acid–water–benzene–TOA system, that is the anomalies increase with increase in the solubility of water in the extracts. The solubility of water in solutions of TOA sulphate does not obey Henry's law even for dilute solutions, and the integral degree of hydration increases with increase in the salt concentratrion. For this system over a wide range of change in the salt concentration, $\gamma_{20} \simeq 1$. The activity coefficient of TOA sulphate in the ternary solutions was determined by two methods: from the combined results of cryoscopic and isopiestic measurements, and also by calculation using Eqn. (42) and the isotherms for the distribution of water in salt solutions with different concentrations.[12] The extraction constants for the extraction of sulphuric acid by benzene solutions of TOA, calculated with allowance for the values of γ_2, are practically constant. This shows that in the sulphuric acid–water–benzene–TOA extraction system at low concentrations of the acid, the main factor responsible for the non-ideal behaviour of the organic phase is the hydration of TOA sulphate.[91]

The solubility of water increases considerably with increase in the concentration of trilaurylammonium halides. Thus the "anomalous" relationships observed by Mueller and Diamond[20] are also apparently due to hydration of the salts, and not their association.

Allowance for the influence of hydration on the activity of TOA sulphate also made it possible to eliminate the contradiction between data on the composition of the extracted complex of uranyl sulphate obtained by the saturation and equlibrium-displacement methods.[98] The slope of the plot of $\lg D$ against $\lg a_2$ is close to 2, indicating the formation of the complex $(R_3NH)_4UO_2(SO_4)_3$ in this system. The composition of the complex found in this way is identical to that established by the saturation method.

In a number of studies,[99–101] the activity coefficients of various ammonium salts were found from the isotherm of the surface pressure at the interface between water and a solution of the salt in an aromatic hydrocarbon. With change in the anion of the salt R_3NHX, the values of γ_2 decrease in the order perchlorate < iodide < bromide < chloride. From this it was concluded that the salts whose anions are least effectively extracted are most highly associated.[17,18] This does not agree, however, with data on the association of the salts in dry solutions, obtained by independent methods.[99] It is understandable that

the inversion of this series is due to hydration of the salts, which increases sharply with increase in the proton affinity of their anions and which makes a larger contribution to the non-ideal behaviour of the solutions than association of the salts.

The inversion of the order of activity of the salts in ternary solutions compared with the binary solutions is also observed in other cases. Thus as a consequence of the marked differences in the hydration of ammonium salts with different degrees of substitution, the observed extraction features often cannot be explained on the basis of the reactivity of the amines and the ammonium salts in their dry solutions.

It was pointed out above that the extraction of metals from sulphuric acid solutions increases in the order quaternary < tertiary < secondary alkylammonium. At the same time, spectroscopic studies show that the electron-donor properties of the anions of ammonium salts increase with increase in the degree of substitution at the nitrogen atom of the bases.[102] This "anomalous" dependence of the extraction of metal salts from sulphuric acid solutions on the nature of the cation of the ammonium salt is often related to a steric effect.[8,9] It has been shown, however, that the observed regularity is also due to the influence of hydration on the activity of the ammonium salts.[1] Thus at identical concentrations of secondary and quaternary alkylammonium sulphates, their degrees of hydration differ by approximately 7 units. From the stoichiometry of the complex formed, it can be shown that a decrease in the distribution coefficient should be observed in this order as a result of the difference in the hydration of the salts. For uranyl sulphate, for example, it decreases by a factor of approximately 10^6.[103] The difference actually observed in the extracting power of ammonium salts of the series being considered is appreciably lower, because of the increase in reactivity with increase in the degree of replacement at the nitrogen atom of the bases.

Methyldialkylamines and dimethylalkylamines are weaker bases than trialkylamines, so that the extraction constants for the extraction of acids by these compounds should be slightly lower. In fact, the extraction constant for the extraction of nitric acid by TOA solutions is slightly higher than that for extraction by solutions of methyldioctylamine.[104] The opposite picture is observed, however, for the extraction of hydrochloric and sulphuric acids.[5] The "anomalous" increase in the extraction constants for extraction by methyl-substituted tertiary amines corresponds quantitatively to the difference in the degrees of hydration of the chlorides and sulphates of these amines and those of the corresponding TOA salts in non-polar solvents.[12]

Thus the "anomalous" features observed up to the present in systems containing amines and ammonium salts can be explained only by taking account of the influence of hydration on the activity of the components of the organic phase. In extraction systems containing amines, the part played by hydration generally increases with decrease in the intensity of the acid–base reaction between the components. Hydration has a levelling action on the extraction of inorganic acids. The distribution of the salts between the phases is usually accompanied by displacement of water from the organic phase. Thus hydration facilitates the extraction of inorganic acids by amines, but depresses the extraction of metal salts.

2. The solvation of ammonium salts

To interpret data on the extraction equilibrium in systems containing modifiers, it is necessary to have data on the activity of the components in ternary solvent–ammonium salt–alcohol and solvent–alcohol–water systems and in quaternary solvent–ammonium salt–water–alcohol systems.

In the thermodynamic study of ternary solvent–ammonium salt–alcohol solutions, usually only the activity of the solvent is determined, and the activity of the salt is calculated using the cross relationships (23) and (24). The close analogy between the phenomena of the hydration of ammonium salts and their solvation by alcohols makes it possible to simplify the calculation of the activity of the salt. Eqn. (33) can then be written as:[105,106]

$$m_{al}\gamma^*_{al} = a_{al}(1 + k_s m_2), \tag{44}$$

where a_{al} and m_{al} represent respectively the activity and molality of the alcohol in the ternary solution, γ^*_{al} the activity coefficient of the alcohol in the binary solution ($m_2 = 0$) at the same concentration m_{al}, and k_s the solvation parameter.

Since it is difficult to determine the activity of alcohols in ternary solutions, Eqn. (44) cannot be confirmed experimentally. Only the equations for the activity of the ammonium salt and the solvent, obtained using Eqn. (44), can be verified.

In the derivation of the equation for the activity of the ammonium salt,[105] the cross relatonship (23) was used in the form

$$(\partial \ln a_2/\partial m_{al})_{m_2} = (\partial \ln a_{al}/\partial m_2)m_{al}. \tag{45}$$

Differentiating Eqn. (45) with respect to m_2 and integrating with respect to m_{al} gave the equation

$$\ln a_2 = \ln a_2^0 - \frac{k_s}{1 + k_s m_2} m_{al}. \tag{46}$$

Substituting Eqns. (44) and (46) in the Gibbs-Duhem equation (19) and integrating gives the following equation for the activity of the solvent.[106]

$$\frac{10^3}{M_1} \ln \frac{a_1}{a_1^0 a_1^*} = \frac{k_s m_s m_{al}}{1 + k_s m_2}, \tag{47}$$

where a_1^0 and a_1^* are the activities of the solvent in the corresponding binary solutions for $m_{al} = 0$ and $m_2 = 0$. Eqns. (44), (46), and (47) have been generalised to multicomponent solutions.[94]

Eqn. (47) has been used for the treatment of the results of cryoscopic measurements[49] in the three-component benzene–trioctylammonium sulphate–n-octanol and benzene–trioctylammonium sulphate–methanol systems by the isomolar-series method. These results were prevoiusly described assuming that a trioctylammonium disolvate is formed.[49] The calculated values of the stability constants of the disolvates varied from 393 to 783 for the first system, and from 1020 to 4800 for the second. The range of change in the solvation parameters k_s calculated from the same data was much smaller: from 11.6 to 17.1 for the first system, and from 21.1 to 25.4 for the second. Thus Eqn. (47) provides a better description of the experimental data on the solvation of the ammonium salts than equations based on stoichiometric considerations.

At low alcohol concentrations, Eqn. (47) is simplified and becomes

$$\frac{10^3}{M_1} \ln \frac{a_1}{a_1^0} = -\frac{m_{al}}{1 + k_s m_2}. \tag{48}$$

Eqn. (48) has been used to calculate solvation parameters from ebulliometric data. The results, given in Table 1, show that the solvation parameters of the ammonium salts decrease with increase in temperature, and also with increase in the radius of the anion and the length of the alkyl group of the cation of the salt. To compare data on the influence of "inert" solvents, the solvation parameters of the salts were calculated on the molar concentration scale $k'_s = k_s/d_0$, where d_0 is the density of the solvent. With change in the solvent, the values of k'_s decrease in the order n-pentane < cyclohexane < tetrachloromethane < benzene, that is with increase in the polarity of the solvent. Similar relationships were previously observed for the hydration of ammonium

salts,[15,90] indicating that the phenomena of solvation and hydration are similar. Certain differences are also observed, however; in the solvation by alcohols of trioctylammonium sulphate and methyldioctylammonium and tetrapentylammonium chlorides, a phenomenon analogous to the non-linear hydration detected for these systems is not observed.

Table 1. Solvation parameters k_s of ammonium salts by n-tetradecanol.

Salt	Temperature, °C	k_s	Δk_s	Refs.
Solvent tetrachloromethane				
$(C_{12}H_{25})_3NHCl$	78.6	8.95	0.97	[105]
$(C_{12}H_{25})_3NHCl$	45	15.83	0.79	[105]
$(C_{12}H_{25})_3NHCl$	35	37.8	2.0	[108]
$CH_3(C_8H_{17})_2NHCl$	78.6	11.04	0.19	[106]
$(C_{12}H_{25})_3NHBr$	35	23.98	0.98	[108]
$(C_8H_{11})_4NCl$	78.6	48.3	2.8	[109]
$[(C_{12}H_{25})_3NH]_2ZnCl_4$	35	15.6	1.3	[107]
$(C_8H_{13})_4NI$	78.6	7.41	0.24	[105]
$(C_8H_{13})_4NI$*1	78.6	7.30	0.19	[107]
$(C_8H_{13})_4NI$*2	78.6	7.45	0.65	[107]
$(C_8H_{17})_4NI$	78.6	6.91	0.40	[109]
$(C_4H_9)_3C_8H_{17}NI$	78.6	9.65	0.44	[109]
$(C_4H_9)_3C_8H_{17}NI$	78.6	22.0	2.90	[107]
$[(C_{12}H_{25})_3NH]_2CoCl_4$	78.6	20.8	1.8	[107]
Solvent benzene				
$[(C_8H_{17})_3NH]_2SO_4$*3	5.5	14.46	0.74	[106]
$[(C_8H_{17})_3NH]_2SO_4$*4	5.5	23.20	0.60	[106]
$[C_6H_5(C_{10}H_{21})NH_2]SO_4$*3	5.5	3.93	0.22	[106]
$(C_{12}H_{25})_3NHCl$	80.6	4.2	1.3	[108]
$(C_{12}H_{25})_3NHCl$	35	14.20	0.43	[108]
$(C_{12}H_{25})_3NHBr$	35	9.75	0.55	[108]
$(C_4H_9)_4NI$	80.6	4.15	0.41	[108]
$(C_8H_{17})_4NI$	80.6	3.64	0.26	[108]
$(C_4H_9)_3C_8H_{17}NI$	80.6	4.88	0.57	[108]
$(C_8H_{17})_3C_8H_{17}NBr$	80.6	8.1	1.7	[108]
$(C_8H_{11})_4NCl$	80,6	22.3	1.1	[108]
Solvent cyclohexane				
$(C_{12}H_{25})_3NHCl$	35	30.4	2.9	[108]
$[(C_{12}H_{25})_3NH]_2CoCl_4$	35	11.3	1.3	[107]
Solvent n-pentane				
$(C_{12}H_{25})_3NHCl$	36	28.4	2.5	[108]
$[(C_{12}H_{25})_3NH]_2ZnCl_4$	36	12.0	1.8	[107]

*1Solvation by n-decanol; *2by n-hexadecanol; *3by n-octanol; *4by methanol.

There are few published data on the hydration of alcohols in non-polar solvents. The solubility of water increases slightly in the presence of alcohols. The distribution of water at relatively low alcohol concentrations is described by Eqn. (33), and the degree of hydration of the alcohols is usually low. Thus for $a_w = 1$, the degree of hydration of n-octanol h_{al} in benzene is 0.052[110] or 0.049,[107] and that in tetrachloromethane is 0.043.[110] These data show that the addition of alcohols to non-polar solvents does not lead to a significant change in the activity of water in the organic phase.

The Gibbs–Duhem equation for a four-component solvent–ammonium salt–water–alcohol system can be written as

$$\frac{10^3}{M_1}\frac{\partial \ln a_1}{\partial m_{al}}dm_{al}+m_2\frac{\partial \ln a_2}{\partial m_{al}}dm_{al}+m_w\frac{\partial \ln a_w}{\partial m_{al}}dm_{al}+m_{al}\frac{\partial \ln a_{al}}{\partial m_{al}}dm_{al}=0, \quad (49)$$

The possibility of transforming this equation to a form convenient for calculations is determined by the nature of the dependence of the solubility of water on the alcohol concentration. The experimental study of the hydration of ammonium salts in the presence of alcohols shows the existence of two types of dependence of m_w on m_{al}.[107,110–112] For some systems at low alcohol concentrations and a constant activity of water the following equation is applicable:

$$m_w = m_w^0 + hm_2 + h_{al}m_{al}. \quad (50)$$

For other systems, when an alcohol is added, m_w decreases at first, after which it passes through a minimum and then increases slowly. The degree of displacement of water by the alcohol increases with increase in the proton affinity of the anion of the salt.[112] The last section of the curve can be described by Eqn. (50). In systems of the first type, $h \leqslant 1$, whereas in systems of the second type, the minimum solubility of water corresponds to $h \simeq 1$.

For systems in which the hydration of the salts is described by Eqn. (50), the derivative $\partial \ln a_w/\partial m_{al} \simeq 0$, since the values of h_{al} are usually low. In this case, Eqn. (49) becomes the Gibbs–Duhem equation for a three-component system. This means that in these sysems, the hydration and solvation of the ammonium salts take place independently of one another, and in the calculation of the influence of alcohols on the activity of the ammonium salts in the presence of water it is possible to use the same equations and solvation parameters as for anhydrous solutions.

The solubility of water in solvent–ammonium salt–metal complex–alcohol systems can also in a number of cases be described by Eqn. (50). The following equation has been proposed[107] for the description of the influence of solvation on the activity of the components in systems of this kind:

$$m_{al}\gamma_{al}^* = a_{al}(1 + k_{2s}m_2 + k_{3s}m_3), \quad (51)$$

where k_{2s} and k_{3s} are the solvation parameters of the ammonium salt and the metal complex respectively. This equation has been used[107,113] for the description of the extraction of micro-quantities of metals, and this has made it possible to eliminate the influence on the equilibrium of the change in the concentration of the extracting agent as saturation takes place. In this case, $m_3 \to 0$, and from Eqn. (51), using the cross relationship (45), it is possible to obtain the expressions

$$\ln(a_2/a_2^0) = -k_{2s}m_{al}/(1 + k_{2s}m_2) = \ln(\gamma_2/\gamma_2^0) \quad (52)$$

and

$$\ln(a_3/a_3^0) = -k_{3s}m_{al}/(1 + k_{2s}m_2) = \ln\gamma_3, \quad (53)$$

where γ_2 and γ_3 are the activity coefficients of the ammonium salt and the metal complex respectively in the presence of the alcohol, γ_2^0 the activity coefficient of the ammonium salt in the binary solution, and $\gamma_3^0 = 1$. At a constant composition of the aqueous phase and a constant concentration of the ammonium salt, substituting Eqns. (52) and (53) in Eqn. (9) gives the equation

$$\ln D = \ln D_0 - \frac{qk_{2s} - k_{3s}}{1 + k_{2s}m_2}m_{al}, \quad (54)$$

where D_0 is the distribution coefficient of micro-quantities of the metal in the absence of the alcohol.

Eqn. (54) has been used to describe the influence of n-tetradecanol on the extraction of micro-quantities of iron(III), cobalt(II), and zinc chlorides by solutions of tridodecylammonium chloride in tetrachloromethane.[107,113] In these systems the introduction of the alcohol has practically no influence on the hydration of the extracting agent. The

treatment of the experimental data was carried out using the linear regression equation

$$\ln D = \ln D_0 - bm_{al}. \quad (55)$$

The calculation using Eqn. (55) and the solvation parameters given in Table 1 gives values of b which are practically identical to those obtained from experimental distribution data.

The description of systems in which the addition of an alochol leads initially to a decrease in the hydration of the ammonium salt is even more complex.[52] In this case the distribution coefficient of the metal salt passes through a maximum with increase in the alcohol concentration. The position of the maximum coincides with the position of the minimum on the curve giving the dependence of the concentration of water in the organic phase on the alcohol concentration. The ascending branch of the dependence of the distribution coefficient of the metal salt on the alcohol concentration is due to the increase in the activity of the ammonium salt as a result of the decrease in its hydration when the alcohol is added, and the descending branch is due to the decrease in the activity of the salt as a result of its solvation. This descending branch of the curve is described by equations of type (54) and (55). The calculated increase in the activity of the ammonium salt corresponds to the observed increase in the distribution coefficient of the metal salt.

Thus the non-stoichiometric model of the hydration and solvation of ammonium salts developed by the present authors makes possible a fairly simple description and interpretation of data on the extraction equilibrium. The results obtained using this model are consistent with the results of independent physicochemical measurements.

References

1. G A Yagodin, S Z Kogan, V V Tarsasov, et al. in G A Yagodin (Editor) *Osnovy Zhidkostnoi Ekstraktsii* (Principles of Liquid Extraction), Izd. Khimiya, Moscow, 1981, 440 pp
2. L M Gindin *Ekstraktsionnye Protsessy i ikh Primenenie* (Extraction Processes and Their Application), Izd. Nauka, Moscow, 1984, 144 pp
3. E V Komarov, A A Kopyrin, V V Proyaev *Teoreticheskie Osnovy Ekstraktsii Assotsiirovannymi Reagentami* (The Theoretical Principles of Extractions by Associated Reagents), Energoatomizdat, Moscow, 1984, 128 pp
4. I A Shevchuk *Ekstraktsiya Organicheskimi Osnovaniyami (Ionnye Assotsiaty)* [Extraction by Organic Bases (Ionic Associates)], Izd. Vishcha Shkola, Kiev, 1978, 170 pp
5. V S Shmidt *Ekstraktsiya Aminami* (Extraction by Amines), Atomizdat, Moscow, 1980, 262 pp
6. Y Marcus, A S Kertes *Ion Exchange and Solvent Extraction of Metal Complexes*. Wiley-Intersci., London, 1969, 1037 pp
7. T Sekine, Y Hasegawa *Solvent Extraction Chemistry. Fundamental and Applications*, Marcell Dekker: New York, 1977, 919 pp
8. R M Diamond in collected papers *The Chemistry of Extraction* (Translated into Russian), Atomizdat, Moscow, 1971, p. 180
9. R R Grinstead in collected papers *The Chemistry of Extraction* (Translated into Russian), Atomizdat, Moscow, 1971, p. 249
10. I M Ivanov, L M Gindin, G N Chichagova *Khimiya Protsessov Ekstraktsii* (The Chemistry of Extraction Processes), Izd. Nauka, Moscow, 1972, p. 207
11. E V Komarov, V N Komarov *Usp. Khim.*, 1974, **43** 632 [English transaltion in *Russ. Chem. Rev.*, 1974(4)]
12. V V Sergievskii *Itogi Nauki i Tekhniki. Neorganicheskaya Khimiya* (Progress in Science and Technology. Inorganic Chemistry), Vol. 5, Izd. VINITI, Moscow, 1976, p. 5
13. V V Tarasov, G A Yagodin *Itogi Nauki i Tekhniki. Neorganicheskaya Khimiya* (Progress in Science and Technology. Inorganic Chemistry), Vol. 4, Izd. VINITI, Moscow, 1974, p. 5
14. V S Shmidt, V N Shesterikov, E A Mezhov *Usp. Khim.*, 1976, **36** 2167 [English translation in *Russ. Chem. Rev.*, 1976(12)]
15. Yu G Frolov, A V Ochkin, V V Sergievskii *Nekotorye Teoreticheskie Voprosy Ekstraktsii Aminami* (Some Theoretical Questions in Extraction by Amines), Izd. Mosk. Khim. Tekh. Inst. im. D I Mendeleeva, Moscow, 1969, 125 pp
16. E Hoegfeldt *Ion Exchange* (Translated into Russian), Izd. Mir, Moscow, 1968, p.512
17. V V Tarasov, G A Yagodin, A A Pichugin *Itogi Nauki i Tekhniki. Neorganicheskaya Khimiya* (Progress in Science and Technology. Inorganic Chemistry), Vol. 11, Izd. VINITI, Moscow, 1984, p. 3
18. C F Coleman, J W Roddy in collected papers *The Chemistry of Extraction* (Translated into Russian), Atomizdat, Moscow, 1971, p. 196
19. D S Flett *Solvent Extraction in Metallurgical Process*, Antwerpen, 1972, p. 24
20. W Müller, R M Diamond *J. Phys. Chem.*, 1966, **70** 3469
21. W Müller *Chem. Ztg.*, 1971, **95** 499
22. E A Mezhov in A M Rozen (Editor) *Ekstraktsiya Aminami, Solyami Aminov i Chetvertichnykh Ammonievykh Osnovanii: Spravochnik po Ekstraktsii* (Extraction by Amines and Salts of Amines and Quarternary Ammonium Bases: A Reference Book on Extraction), Vol. 2, Atomizdat, Moscow, 1977, 304 pp
23. Y Marcus, A S Kertes, E Yanir *Equilibrium Constants of Liquid–liquid Distribution Reactions, Part 2, Alkylammonium Salt Extractants*, Butterworths: London, 1974, 85 pp
24. Yu G Frolov, V V Sergievskii, G I Nasonova *Zh. Neorg. Khim.*, 1973, **18** 1705 [English translation in *Russ. J. Inorg. Chem.*, 1973(6)]
25. Yu G Frolov, V V Sergievskii *Tr. Mosk. Khim. Tekhn. Inst. im. D I Mendeleeva*, 1963(43), 58
26. G M Vol'dman, E A Mironova *Zh. Neorg. Khim.*, 1988, **33** 172 [English translation in *Russ. J. Inorg. Chem.*, 1988(1)]
27. V V Tarasov, A A Pichugin, A P Novikov, et al *ISEC '88: Int. Solv. Extr. Conf. Moscow, 18–24 July 1988, Conf. Pap. M.*, 1988, **11** 40
28. G Scibona, F Orlandini, P R Danesi *J. Inorg. Nucl. Chem., 1966,* **28** 1701
29. G Tsoucaris *Acta Crystallogr.*, 1961, **14** 917

29a. A M Rozen *ISEC '88, Inst. Solv. Extr. Conf. Moscow, 18–24 July 1988, Conf. Pap. M.*, 1988, **1** 62

30. G D Titskii, M K Turovskaya, L M Litvinenko *Zh. Org. Khim.*, 1983, **19** 2349
31. A I Khol'kin, V I Kuz'min, N V Protasova *Zh. Neorg. Khim.*, 1986, **31** 1245 [English translation in *Russ. J. Inorg. Chem.*, 1986(5)]
32. A I Khol'kin, V I Kuz'min , N V Protasova, et al. *ISEC '88, Int. Solv. Extr. Conf. Moscow, 18–24 July 1988, Conf. Pap. M.*, 1988, **1** 70
33. A M Rozen, A I Khol'kin *Dokl. Akad. Nauk SSSR*, 1988, **301** 661
34. V S Belova, A I Khol'kin, P Mühl, et al *ISEC '88, Int. Solv. Extr. Conf. Moscow, 18–24 July 1988, Conf. Pap. M.*, 1988 **3** 191
35. V I Goncharov, L Kh Genov, V V Sergievskii, G A Yagodin *Radiokhimiya*, 1979, **21** 563

36. S Le, D Li, J Ni *ISEC '88, Inst. Solv. Extr. Conf. Moscow, 18–24 July 1988, Conf. Pap. M.*, 1988, **3** 238
37. A M Chekmarev, S V Chizhevskaya, M Mrnka, et al. *ISEC '88, Int. Solv. Extr. Conf. Moscow, 18–24 July 1988, Conf. Pap. M.*, 1988, **3** 266
38. S N Ivanova, I A Druzhinina, A P Zubareva, et al. *ISEC '88, Inst. Solv. Extr. Conf. Moscow, 18–24 July 1988, Conf. Pap. M.*, 1988, **3** 198
39. S I Stepanov, O N Fedotov, V V Sergievskii, et al. *Zh. Neorg. Khim.*, 1984, **29** 2080 [English translation in *Russ. J. Inorg. Chem.*, 1984(8)]
40. G I Mikulin (Editor) *Voprosy Fizicheskoi Khimii Rastvorov Elektrolitov* (Problems in the Physical Chemistry of Electrolyte Solutions), Izd. Khimiya, Leningrad, 1968, 418 pp
41. A S Solovkin *Vysalivanie i Kolichestvennoe Opisanie Ekstraktsionnykh Ravnovesii* (Salting-out and the Quantitative Description of Extraction Equilibria), Atomizdat, Moscow, 1969, 124 pp
42. Yu G Frolov *Usp. Khim.*, 1981, **50** 429 [English translation in *Russ. Chem. Rev.*, 1981(3)]
43. V V Sergievskii, V A Shur, V V Dubrovskaya *Itogi Nauki i Tekhniki. Rastvory. Rasplavy* (Progress in Science and Technology. Solutions and Melts), Vol. 3, Izd. VINITI, Moscow, 1986, p. 3
44. V V Bagreev, Yu A Zolotov, C Fischer, et al. *ISEC '88, Int. Solv. Extr. Conf. Moscow, 18–24 July 1988, Conf. Pap. M.*, 1988, **1** 87
45. K A Allen *J. Phys. Chem.*, 1956, **60** 239
46. C F Coleman, K B Brown, J G Moore, D J Crouse *Ind. Eng. Chem.*, 1958, **50** 1756
47. W J McDowell, K A Allen *J. Phys. Chem.*, 1959, **63** 747
48. V V Fomin, P A Zagorets, A F Morgunov *Zh. Neorg. Khim.*, 1959, **4** 700 [English translation in *Russ. J. Inorg. Chem.*, 1959(3)]
49. Yu G Frolov, V V Sergievskii *Tr. Mosk. Khim. Tekhn. Inst. im. D I Mendeleeva*, 1965(49), 190
50. J J Bucher, R M Diamond *J. Phys. Chem.*, 1975, **79** 2259
51. E V Komarov, I M Balashova *Teor. Eksp. Khim.*, 1974, **10** 122
52. A V Ochkin, A N Kudrov *Radiokhimiya*, 1984, **26** 402
53. K P Mishchenko, G M Poltoratskii *Voprosy Termodinamiki i Stroeniya Vodnykh i Nevodnykh Rastvorov Elektrolitov* (Problems in the Thermodynamics and Structure of Aqueous and Non-aqueous Solutions of Electrolytes), Izd. Khimiya, Leningrad, 1968, p. 351
54. V G Yurkin, A M Rozen *Zh. Fiz. Khim.*, 1973, **47** 492 [English translation in *Russ. J. Phys. Chem.*, 1973(2)]
55. F M Batson, C A Kraus *J. Am. Chem. Soc.*, 1934, **56** 2017
56. D A Rothrock, C A Kraus *J. Am. Chem. Soc.*, 1937, **59** 1699
57. D T Copenhafer, C A Kraus *J. Am. Chem. Soc.*, 1951, **73** 4557
58. V Edinakova, J Heida, M Vogt, et al. *Sb. VSCHT Praze.*, 1983, **28** 133
59. N H Ray *Trans. Faraday Soc.*, 1952, **48** 809
60. J G van Pelt *Recl. Trav. Chim. Pays-Bas*, 1960, **80** 1023
61. T Daniels, R S Lehrie *J. Polym. Sci. C.*, 1965, 4533
62. A S Kertes, G Markovits *J. Phys. Chem.*, 1968, **72** 4202
63. I J Gal, I Paligoric-Obrenovic, V G Antonijevic *J. Inorg. Nucl. Chem.*, 1970, **32** 1645
64. A S Kertes, O Levy, G Markovits *J. Phys. Chem.*, 1970, **72** 3568
65. J David-Auslaender, H Gutmann, A S Kertes, M Zangen *J. Sol. Chem.*, 1974, **3** 251
66. H A C McKay *Nature*, 1952, **169** 464
67. L S Darken *J. Am. Chem. Soc.*, 1950, **72** 2909
68. K Wagner *The Thermodynamics of Alloys* (Translated into Russian), Izd. Metallurgizdat, Moscow, 1957, 179 pp
69. R Schuhmann, Jr. *Acta. Metall.*, 1955, **3** 219
70. N A Gokcen *J. Phys. Chem.*, 1960, **64** 401
71. S D Christian, A A Taha, B W Gash *Quart. Revs.*, 1970, **24** 20
72. K A Allen *J. Phys. Chem.*, 1958, **62** 1119
73. S O Popov, V V Bagfreev *Zh. Neorg. Khim.*, 1986, **31** 635 [English translation in *Russ. J. Inorg. Chem.*, 1986(3)]
A M Chekmarev, A V Ochkin, V V Sergievskii, et al. *ISEC '80, Int. Solv. Extr. Conf. Liege. Belgium, 6–12 September 1980, Conf. Pap. Belquium*, 1980, **2** 80–158
75. P A Zagorets, A V Ochkin *Tr. Mosk. Khim. Tekhn. Inst. im. D I Mendeleeva*, 1965(49), 206
76. D Dyrssen, M de J Tavares in collected papers *The Chemistry of Extraction* (Translated into Russian), Atomizdat, Moscow, 1971, p. 279
77. E Högfeldt, M de J Tavares *Trans. Royal Inst. Technol.*, 1968, **228** 27
78. O Levy, G Markovits, A S Kertes *J. Inorg. Nucl. Chem.*, 1971, **33** 551
79. S Lindenbaum, G E Boyd *J. Phys. Chem.*, 1963, **67** 1238
80. A V Ochkin, V E Lazarevich, A Yu Dmitriev, P A Zagorets *Radiokhimiya*, 1978, **20** 53
81. A V Ochkin *Zh. Fiz. Khim.*, 1980, **54** 1984 [English translation in *Russ. J. Phys. Chem.*, 1980(8)]
82. A V Ochkin, V E Lazarevich *Zh. Fiz. Khim.*, 1979, **53**(5) 1317 [English translation in *Russ. J. Phys. Chem.*, 1979(5)]
83. A V Ochkin, V E Lazarevich *Izv. Vys. Ucheb. Zaved SSSR, Khim. i Khim. Tekhnol.*, 1982, **25** 1413
84. A V Ochkin, V E Lazarevich *Radiokhimiya*, 1982, **24** 299
85. A V Ochkin *XI Vsesoyuznaya Konferentsiya po Kalorimetrii i Khimicheskoi Termodinamike. Tezisy Dokladov* (Summaries of Papers Presented at the Eleventh All Union Conference on Calorimetry and Chemical Thermodynamics), Novosibirsk, 1986, Part 1, p. 201
86. A A Kopyrin, M A Afonin, V V Proyaev *ISEC '88, Inst. Solv. Extr. Conf. Moscow, 18–24 July 1988, Conf. Pap. M.*, 1988, **3** 145
87. M Cerna, J Stastova, V Rod *ISEC '88, Int. Solv . Extr. Conf. Moscow, 18–24 July 1988, Conf. Pap. M.*, 1988, **3** 149
88. Yu G Frolov, V V Sergievskii, G I Sergievskaya *Zh. Neorg. Khim.*, 1968, **13** 1909 [English translation in *Russ. J. Inorg. Chem.*, 1968(7)]
89. A A Lipovskii, T A Dem'yanova *Zh. Prikl. Spektrosk.*, 1968, **9** 239
90. Yu G Frolov, V V Sergievskii, A V Ochkin, A P Zuev *Radiokhimiya*, 1972, **14** 578
91. Yu G Frolov, V V Sergievskii, A P Zuev *Atomnaya Energiya*, 1973, **35** 109
92. C Klofutar, S Paljk, M Ostanek *J. Inorg. Nucl. Chem.*, 1976, **38** 1045
93. A V Ochkin *Zh. Fiz. Khim.*, 1978, **52** 1321 [English translation in *Russ. J. Phys. Chem.*, 1978(5)]
94. A V Ochkin, V V Sergievskii *ISEC '88, Inst. Solv. Extr. Conf., Moscow, 18–24 July 1988, Conf. Pap. M.*, 1988, **1** 127
95. H A C McKay, A R Mathieson *Trans. Faraday Soc.*, 1951, **47** 428
96. C F Coleman *J. Chem. Eng. Data.*, 1964, **13** 267
97. Yu G Frolov, V V Sergievskii *Radiokhimiya*, 1974, **16** 445
98. V V Sergievskii, G A Yagodin *Zh. Neorg. Khim.*, 1980, **25** 1420 [English translation in *Russ. J. Inorg. Chem.*, 1980(5)]

99. A N Popov *Zh. Fiz. Khim.*, 1979, **53** 1001 [English translation in *Russ. J. Phys. Chem.*, 1979(4)]
100. V L Kheifets, A L Shneerson *Zh. Prikl. Khim.*, 1977, **50** 528
101. V L Kheifets, A L Shneerson *Zh. Prikl. Khim.*, 1977, **50** 534
102. V V Sergievskii, Yu G Frolov *Zh. Strukt. Khim.*, 1967, **8** 891
103. Yu G Frolov, V V Sergievskii, A P Zuev, L B Fedyanina *Zh. Fiz. Khim.*, 1973, **47** 1956
104. V P Shvedov, A A Kopyrin, V S Titov *J. Radioanal. Chem.*, 1972, **12** 421
105. A V Ochkin *Zh. Fiz. Khim.*, 1980, **54** 1862 [English translation in *Russ. J. Phys. Chem.*, 1980(7)]
106. A V Ochkin *Zh. Fiz. Khim.*, 1981, **55** 1354 [English translation in *Russ. J. Phys. Chem.*, 1981(5)]
107. A N Kudrov *Candidate's Thesis*, Mendeleev Moscow Institute of Chemical Technology, Moscow, 1983
108. A V Ochkin, A N Kudrov *Zh. Fiz. Khim.*, 1984, **58** 1260 [English translation in *Russ. J. Phys. Chem.*, 1984(5)]
109. A V Ochkin, A N Kudrov *Zh. Fiz. Khim.*, 1982, **56**, 1048 [English translation in *Russ. J. Phys. Chem.*, 1982(4)]
110. I M Ivanov, V P Zaitsev *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1978(4), 18
111. V P Zaitsev, I M Ivanov, V A Shchipachev *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1979(6), 69
112. I M Ivanov, V P Zaitsev *ISEC '88, Int. Solv. Extr. Conf. Moscow, 18–24 July 1988, Conf. Pap. M.*, 1988, **1** 138
113. A V Ochkin, A N Kudrov *VII Vsesoyuznaya Konferentsiya po Khimii Ekstrasktsii. Tezisy Dokladov* (Summaries of Papers Presented at the Seventh All Union Conference on the Chemistry of Extraction), Izd. Nauka, Moscow, 1984, p. 106

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α-Halo-α-nitrocarboxylic acids and their derivatives

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ABSTRACT. The methods for synthesising α-halo-α-nitrocarboxylic acids and their functional derivatives are reviewed. Reference is made to IR, NMR, and Raman spectroscopic data, calculation methods, and X-ray diffraction analysis, and information on the acidity and electron- and proton-donor capacities of the compounds is given. Reactions involving C–H and C–Hal bonds, carboxyl and nitro groups, the mechanisms of the most important reactions, and data on the toxicity and physiological activity are discussed.

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I. Introduction

α-Halo-α-nitrocarboxylic acids and their derivatives are polyfunctional compounds which are interesting from the point of view of studying the relationship between structure and properties. Distinctive (anomalous) behaviour of fluorine, chlorine, and bromine atoms on the carbon atom bonded to the nitro group has been found and elucidated for these compounds. A nontrivial mutual effect between the nitro and carboxyl groups and halogens, which manifests itself in the spectroscopic characteristics, structure, and chemical properties of these compounds, has been demonstrated. They have proved to be successful model compounds for studying the mechanisms of decarboxylation and the formation of halo-oximes, nitroso compounds, and phosphoryloximes. Reactions typical for them are the reductive decarboxylation with elimination of a single oxygen atom from the nitro group, deuterium exchange between cyclic transition states, the formation of heterocycles with complete or partial conversion of functional groups, redox phosphorylation, sulphonation–dehalogenation, etc.

Compounds of this group have become readily available as a result of the development of convenient methods for preparing them from accessible feedstocks. There are extensive possibilities for converting them to various nitro and nitroso compounds, oximes, hydroxylamines, amines, amino acids, and other compounds that have various properties of use for practical application and are difficult to synthesise by other methods. As a result of this, they have attracted the attention of chemists in recent years.

Compounds of this group include fungicides, insecticides, bactericides plant growth regulators, and also compounds that possess anti-choline esterase and hypotensive activity, amine oxidase inhibitors, and certain other physiologically active compounds that have potential for introduction into the national economy. All this is an indication of their important practical significance.

The first examples of this series of compounds were obtained at the beginning of the century. However, a systematic study of them was only carried out during the last 30 years because of the development of practicable synthetic methods. Specific information about α-halo-α-nitrocarboxylic acids and their derivatives is given in monographs[1–4] and review articles.[5–7] However, there are no reviews in the literature specially devoted to such an important group of compounds. The present article is the first attempt to correlate the studies on the preparative methods, properties, and use of α-halo-α-nitrocarboxylic acids and their derivatives. Literature sources from the last 30 years as well as earlier studies are covered here.

II. Synthetic methods

1. Replacement of a hydrogen atom in α-nitrocarboxylic acid derivatives by chlorine

Halogenation of salts of *aci*-nitro compounds is a general method for the preparation of α-halonitrocarboxylic acid derivatives and halonitroalkanes.[4,7,8]

$$O_2NCHY + MOH \rightarrow M^+[O_2N{=}CY]^- \xrightarrow[-MX]{X_2} O_2NCXY,$$

R = H, alkyl, NO_2, halogen; X = F, Cl, Br;
Y = CO_2R, CN, $CONH_2$ etc.; M = Na, K, NH_4, Ag etc.

When salts of *aci*-nitrocarboxylic acid derivatives are treated with bromine or chlorine, bromodinitroacetonitrile,[9] methyl bromonitroacetate,[10] dimethyl and diethyl bromonitromalonates,[11] dibromonitroacetonitrile,[12] ethyl bromo-, chloro-, dibromo-, and bromochloro-nitroacetates, ethyl α-bromo- and α-chloro-α-nitropropionates and -butyrates,[13] dichloronitroacetonitrile,[14,15] and α-bromo- and α-chloro-α-nitropropionamides[16] are obtained. Bromonitromalonamide, *N*-methylbromonitroacetamide, and dibromonitroacetamide were synthesised by treatment with bromine water.[17] It was shown subsequently using IR spectroscopy that *N*,α-dibromonitroacetamide rather than α,α-dibromonitroacetamide is formed under these conditions.[18] Dichloronitroacetamide[19] and ethyl chloronitromalonate[20] are obtained in a similar manner. The bromination of the sodium salt of dinitroacetonitrile was successfully carried out using bromine in a mixture of water and dichloromethane, while chlorination of the same salt could only be achieved using hydrochloric acid and hydrogen peroxide.[21] Treatment of the sodium salts with chlorine led to the synthesis of chloronitromalonamide,

chloronitroacetamide, fluorochloronitroacetamide, and ethyl fluoro-chloronitroacetate.[22] It was possible to obtain methyl α-bromo-α-nitropropionate and methyl α-bromo-α-nitro-β-phenylpropionate as well as ethyl α-bromo-α-nitrobutyrate in methanol solution.[23] When halogenation was carried out in a water–methanol solution, it was possible to increase the yields of ethyl dichloro- and bromo-chloro-nitroacetates.[24] Ethyl bromonitroacetate was synthesised in high yield in an alcohol–ether mixture.[25] Bromination of the potassium salts of dinitrodicarbonitriles in an ether–CCl_4 mixture at 0 °C gave a number of dibromodinitrodinitriles.[26,27]

$$\left[\begin{array}{cc} NO_2 & NO_2 \\ \| & \| \\ NCC(CH_2)_n & CCN \end{array}\right]^{2-} 2K^+ \xrightarrow[-2KBr]{2Br_2} NCCBr(NO_2)(CH_2)_nC(NO_2)BrCN,$$
$n = 2, 4, 6$.

The diastereomers were separated by fractional crystallisation from aqueous ethanol. α-Bromo-α-nitrobutyronitrile and α-bromo-α-nitrocapronitrile were obtained in a similar manner. Bromination of the dipotassium salt of α,α′-dinitroadiponitrile in an alkaline medium at the same temperature followed by acidification was accompanied by elimination of one nitrile group and hydrolysis of the other to an amide.[27] The same product is formed by alkaline hydrolysis of α,α′-dibromo-α,α′-dinitroadiponitrile.

$$\left[\begin{array}{cc} NO_2 & NO_2 \\ \| & \| \\ NCC(CH_2)_2 & CCN \end{array}\right]^{2-} 2K^+ \xrightarrow[-2KBr]{2Br_2} \begin{array}{cc} NO_2 & NO_2 \\ | & | \\ NCCBr & (CH_2)_2CBrCN \end{array}$$
$$\xrightarrow{1)\ Br_2,\ OH^-,\ 0°;\ 2)\ H^+\ 1)\ KOH\ aq.;\ 2)\ H^+}$$
$$O_2NCHBr(CH_2)_2CBr(NO_2)CONH_2$$

The bromination of $K^+[C_2H_5C(NO_2)CONH_2]^-$ and $[CH_2CH_2C(NO_2)CONMe_2]_2^-2K^+$ salts under similar conditions gives the corresponding α-bromo-α-nitroamides, while the potassium salt of *N,N*-dimethylnitroacetamide is converted to a dibromo-substituted product. Formation of the latter is accounted for by the following scheme:[28]

$$K^+[O_2N{=}CHCONMe_2]^- \xrightarrow[-KBr]{Br_2} O_2NCHBrCONMe_2 \xrightarrow[-O_2NCH_2CONMe_2]{K^+[O_2N=CHCONMe_2]^-}$$
$$\rightarrow K^+[O_2N{=}CBrCONMe_2]^- \xrightarrow[-KBr]{Br_2} O_2NCBr_2CONMe_2.$$

Bromination of the sodium salt of ethyl α-nitro-β-hydroxypropionate has been reported.[25]

$$Na^+[O_2N{=}C(CH_2OH)CO_2Et]^- \xrightarrow[-NaBr]{Br_2} O_2NCBr(CH_2OH)CO_2Et.$$

Ethyl dibromonitroacetate was obtained when the mercury salt of ethyl nitroacetate was treated with bromine.[29] Treatment of the Na and K salts of dinitroacetonitrile with equimolar quantities of chlorine fluorosulphate gives chlorodinitroacetonitrile.[30]

$$[NC(NO_2)_2C]^-M^+ + ClOSO_2F \xrightarrow[-MCl]{} NC(NO_2)_2CCl.$$

When a twofold excess of chlorine fluorosulphate is used, a product derived from addition to the C≡N bond is formed, and this undergoes methanolysis to give methyl chlorodinitroacetate.[30] The fluorinated analogue of a chlorodinitroimidate is obtained by reaction between fluorodinitroacetonitrile and chlorine fluorosulphate.

$$[C(NO_2)_2CN]^-Na^+ + 2\,ClOSO_2F \rightarrow ClC(NO_2)_2C(NCl)—OSO_2F \xrightarrow{MeOH}$$
$$\rightarrow ClC(NO_2)_2CO_2Me,$$
$$FC(NO_2)_2CN + ClOSO_2F \rightarrow FC(NO_2)_2C(NCl)—OSO_2F.$$

Reaction of chlorine fluorosulphate with ethyl dinitrocyanoacetate leads to replacement of the CN group by Cl:

$$NCC(NO_2)_2CO_2Et + ClOSO_2F \xrightarrow{-20\ to\ -30°} ClC(NO_2)_2CO_2Et.$$

A halogenation method using *N*-chloro- or *N*-bromo-succinimide is also known.[31]

$$O_2NCH(Me)CO_2Et \xrightarrow[dioxan–water]{O,\ argon} O_2NCCl(Me)CO_2Et.$$
70%

Fluorination of alkali salts of carboxylic acid nitro derivatives has been used less frequently. Fluorodinitroacetate esters are formed when salts of dinitroacetate esters are treated with fluorine over KF. Under the same conditions nitroacetate esters give a mixture of three products.[32]

$$[O_2N{=}CHCO_2Et]^-Na^+ \xrightarrow[-NaF]{F_2} O_2NCF_2CO_2Et + O_2NCHFCO_2Et +$$
$$+ O_2NCH_2CO_2Et.$$

This process results from the intermediate formation of the sodium salt of fluoronitroacetate ester and its reaction with fluorine.

$$[O_2N{=}CHCO_2Et]^-Na^+ + O_2NCHFCO_2Et \rightarrow O_2NCH_2CO_2Et +$$
$$+ [O_2N{=}CFCO_2Et]^-Na^+,$$
$$[O_2N{=}CFCO_2Et]^-Na^+ \xrightarrow[-NaF]{F_2} O_2NCF_2CO_2Et.$$

When similar conditions are used over CaF_2 fluorodinitroacetonitrile is obtained in 70% yield,[33] having been synthesised previously in low yield when an aqueous solution of the potassium salt of dinitroacetonitrile was treated with F_2.[34]

Fluorination of the potassium salt of ethyl dinitroacetate with a mixture of fluorine and nitrogen gave ethyl fluorodinitroacetate with a small amount of fluorodinitromethane.[35]

$$[(O_2N)_2CCO_2Et]^-K^+ \xrightarrow{F_2} (O_2N)_2CFCO_2Et + (O_2N)_2CHF.$$

Fluoronitromalonate ester is obtained by fluorination of the potassium salts of oximes with perchloryl fluoride[36]

$$KON{=}C(CO_2R)_2 + FClO_3 \rightarrow O_2NCF(CO_2R)_2.$$

The ammonium salts of dinotroacetamides are converted to fluorinated products in low yield.[37,38]

$$[(O_2N)_2CCONH_2]^-NH_4^+ \xrightarrow{FClO_3} (O_2N)_2CFCONH_2,$$
5.6%
$$[(O_2N)_2CCONHEt]^-\overset{+}{N}H_3Et \xrightarrow{FClO_3} (O_2N)_2CFCONHEt.$$
14%

Fluorination of dinitronitrile salts in Cellosolve gives a product from fluorination and addition to the C≡N group. It is thought that the process takes place via the formation of dinitrofluoroacetonitrile.[38]

$$[(O_2N)_2CCN]^-Na^+ \xrightarrow{FClO_3} [(O_2N)_2CFCN] \xrightarrow{HOCH_2CH_2OMe}$$
$$\rightarrow (O_2N)_2CFC(NH)—OCH_2CH_2OMe.$$

The potassium salts of nitroacetic acid derivatives can be fluorinated with both fluorine and perchloryl fluoride[39]

$$[O_2N{=}CRCO_2R']^-K^+ \xrightarrow{F_2(FClO_3)} O_2NCFRCO_2R',$$
$R = H,\ SAr;\ R' = Et,\ PhCH_2$.

A satisfactory result was obtained when diethyl nitromalonate was fluorinated in DMF in the presence of sodium hydride.[40]

$$O_2NCH(CO_2Et)_2 + NaH + FClO_3 \xrightarrow{DMF} O_2NCF(CO_2Et)_2.$$

2. Nitration of halo-olefins

The synthesis of α-halo-α-nitrocarboxylic acids and their derivatives by nitration of halo-olefins with mixtures of nitric and sulphuric acids is a more versatile and practicable method.

$$X^1X^2C{=}CX^3X^4 \xrightarrow{HNO_3/H_2SO_4} O_2NCX^1X^2C(=O)Y,$$

X^1, X^2, X^3, X^4 = H, F, Cl or Br; Y = F, Cl, Br or OH.

Nitration of a number of halo-olefins with a small excess of a mixture of nitric and sulphuric acids in the molar ratio 1 : 1 at 15–60 °C results in the formation of α-halo-α-nitrocarboxylic acids or their chlorides in 35–85% yield.[41–46] Nitration of trichloroethylene, giving chloronitroacetyl chloride, is accompanied by the formation of chlorocyanogen, dichloroacetyl chloride, and pentachloroethane.[42,43] Fluorochloronitroacetic acid is obtained from symmetrical difluorodichloroethylene.[44] Nitration of $ClF_2CCCl{=}CCl_2$ and $F_3CCCl{=}CCl_2$ gives the acid chlorides $ClF_2CCCl(NO_2)COCl$ and $F_3CCCl(NO_2)COCl$. The accumulation of chlorine atoms at the "allyl" position of 1,1,2-trichloropropylene results in a competing reaction—the formation of trichloroacrylic acid.[45]

$$Cl_2C{=}CClCCl_2F \rightarrow Cl_2C{=}CClCO_2H.$$

For perchloropropylene this reaction becomes the main process. Nitration of tetrafluoroethylene and trifluorochloroethylene leads to difluoronitroacetic acid.[46] Under these conditions perchloroethylene is converted to trichloroacetyl chloride,[46] while 1-fluoro- and 1-bromo-2,2-dichloroethylene are converted to fluoro- and bromonitroacetyl chloride respectively.[47,48] The nitration of vinylidene chloride, which leads to nitroacetyl chloride, requires an excess of the olefin undergoing nitration and cooling to –5 to 0 °C.[49]

The use of a nitric–sulphuric acid mixture comprising 5–10% nitric acid and not containing radical species, according to EPR data, creates favourable conditions for conducting an ionic reaction. It was possible to carry out the nitration of perchloroethylene to dichloronitroacetyl chloride under these conditions and to increase the yield of fluoronitroacetic acid and difluoronitroacetic acid to 85 and 92% respectively.[50] 1,1-Dichloropropene, 1,1-dichloro-3-methylbutene, and 1,1,1-trichloro-3-methylbutene have been nitrated using such a mixture.[51] Pure chloronitroacetyl chloride is obtained from trichloroethylene using a nitration mixture prepared from 60% HNO_3 and oleum.[52]

According to kinetic data, the rate of nitration is affected by the composition of the nitration mixture, the temperature, and the intensity of mixing.[53] A nitric acid content of 10–20% in the nitration mixture achieves the highest rate of reaction. According to the data of vibrational spectroscopy and ^{14}N NMR spectroscopy, at such a proportion HNO_3 is completely converted to a nitronium cation NO_2^+.[50,54–56] The process occurs at the phase boundary and can be given by a first-order equation (with respect to consumption of trichloroethylene and liberation of heat). The high value of the energy of activation (16.7 kcal mol^{-1}) indicates that a process with an ion-molecular mechanism is taking place. The proposed mechanism of ionic nitration appears to be a general one for the nitration of unsaturated compounds and is distinct from the nitration of aromatic compounds, which takes place with zero kinetic order with respect to the contents of the nitration mixture.[57–59] The process can be represented by the following scheme:[41,42,53]

$$ClHC{=}CCl_2 \xrightarrow{NO_2^+} [ClHC{=}CCl_2] \rightarrow [ClHC(NO_2){-}\overset{+}{C}Cl_2] \xrightarrow{H_2SO_4}$$
$$\rightarrow [ClHC(NO_2){-}CCl_2OSO_3H] \xrightarrow{-HOSO_2Cl} O_2NCHClCOCl.$$

The reaction starts with attack by the nitronium cation on the double bond (nitration with nitric acid gives trichloronitroethylene[60]). The carbocation formed is stabilised by the addition of bisulphate anion, and the subsequent elimination of chlorosulphonic acid gives chloronitroacetyl chloride.

3. Preparation of α-nitroperfluorocarboxylic acids from the products of nitration of fluoro-olefins with nitrogen dioxide

The hydrolysis and alcoholysis of 2-nitroperfluoroalkyl nitrites, obtained by nitration of perfluoroalkenes with nitrogen dioxide, is the most studied and most frequently used method for obtaining α-nitroperfluorocarboxylic acids and their derivatives.[6,61–70]

$$F_2C{=}CFX \xrightarrow{N_2O_4} O_2NCF_2CFXONO \rightarrow O_2NCF_2COF \rightarrow$$
$$\xrightarrow[(ROH)]{H_2O} O_2NCF_2COOH\,(R).$$

Difluoronitroacetic acid is formed by nitration of both perfluoroethylene and trifluorochloroethylene.[61] The process is a free-radical one. Reaction of 2-nitroperfluoroethyl nitrite with sulphuric or chlorosulphonic acid gives difluoronitroacetyl fluoride, which is also an intermediate in the hydrolysis and alcoholysis of 2-nitrotrifluoroethyl nitrite.[63]

$$O_2NCF_2CF_2ONO \xrightarrow{H_2SO_4,\ ClSO_3H} [O_2NCF_2CF_2OH] \rightarrow$$
$$\rightarrow O_2NCF_2COF \xrightarrow[(ROH)]{H_2O} O_2NCF_2CO_2H\,(R).$$

Hydrolysis and alcoholysis of nitroperfluoropropyl nitrite does not give the expected α-nitroperfluoropropionic acid or its esters but yields nitroperfluoroacetone hydrate or its hemiketals.[65] Difluoronitrothioacetic acid and difluoronitroacetate thioesters are also obtained when 2-nitrotetrafluoroethyl nitrite is treated with hydrogen sulphide or mercaptans.[68–70]

$$O_2NCF_2CF_2ONO + HSR \rightarrow O_2NCF_2COSR + HF + FNO.$$

Hydrolysis of the reaction products gives difluoronitroacetic acid.

Reaction of 2-nitronitrosotetrafluoroethane with hydroxylamine also gives difluoronitroacetic acid.[71,72] The reaction takes place with evolution of HF and N_2.[72,73]

$$O_2NCF_2CF_2NO + H_2NOH \rightarrow [O_2NCF_2CF_2N(OH)NHOH \xrightarrow{-H_2O}$$
$$\rightarrow O_2NCF_2CF_2N{=}NOH \xrightarrow{-N_2} O_2NCF_2CF_2OH \xrightarrow{-HF}$$
$$\rightarrow O_2NCF_2COF] \xrightarrow[-HF]{H_2O} O_2NCF_2CO_2H.$$

Alkaline hydrolysis of 2-nitronitrosotetrafluoroethane is accompanied by the formation of 1,2-dinitrotetrafluoroethane.[74]

$$O_2NCF_2CF_2NO \xrightarrow{OH^-} O_2NCF_2CO_2H + O_2NCF_2CF_2NO_2 + N_2 + F^-.$$

Difluoronitroacetyl fluoride is formed in small quantities during the nitration of perfluorobutadiene.[74]

$$F_2C{=}CFCF{=}CF_2 \xrightarrow{N_2O_4} O_2NCF_2CF{=}CFCF_2NO_2 \xrightarrow{N_2O_4} O_2NCF_2COF.$$

Difluoronitroacetic acid is isolated in the oxidation of 1,4-dinitro-1,1,4,4-tetrafluoro-2-butene. Addition of alkali gives difluoronitromethane.[76]

$$O_2NCF_2CH{=}CHCF_2NO_2 \xrightarrow[\text{KOH}]{H_2O,\ KMnO_4} O_2NCF_2COOH,\ O_2NCF_2H$$

Reaction of α-ethoxy-β-nitroperfluoropropane and α-ethoxy-β-nitroperfluoroisobutane with $AlCl_3$ followed by treatment with ethanol gives ethyl α-nitroperfluoropropionate and ethyl α-nitroperfluoroisobutyrate.[77,78]

$$CF_3CX(NO_2)CF_2OEt \xrightarrow{AlCl_3} CF_3CX(NO_2)COX \xrightarrow{EtOH} CF_3CX(NO_2)CO_2Et,$$
$$X = F,\ CF_3.$$

Various esters and amides of α-halo-α-nitrocarboxylic acids are synthesised by esterification or aminolysis of acid halides or esters obtained by nitration of halo-olefins.[1,3,43,44,46–49,51,62–64,67,77–86]

4. Other methods for synthesising functional derivatives of α-halo-α-nitrocarboxylic acids

The prolonged passage of nitryl chloride through a cooled ether solution of ethyl diazoacetate yields ethyl chloronitroacetate.[82]

$$N_2CHCO_2Et + O_2NCl \rightarrow O_2NCHClCO_2Et.$$

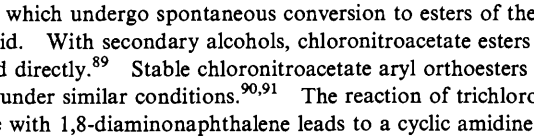
Certain problems have arisen in the preparation of halo-nitroacetate aryl esters. Difluoronitroacetate phenyl esters are not formed from 2-nitrotetrafluoroethyl nitrite and they were obtained from difluoronitroacetyl chloride.[79] Because it was not possible to obtain bromo- and chloro-nitroacetate phenyl esters by esterification of acid chlorides or by transesterification of their alkyl esters, they were synthesised from the corresponding nitroacetate esters, which in turn were obtained by nitration of acetoacetate esters synthesised from phenol and diketene.[87]

$$CH_2{=}C(O){-}CH_2{-}C(=O) + HOPh \rightarrow CH_3COCH_2CO_2Ph \xrightarrow{HNO_2}$$
$$\rightarrow O_2NCH_2CO_2Ph \xrightarrow{X_2} O_2NCHXCO_2Ph$$
$$X = Cl \text{ or } Br.$$

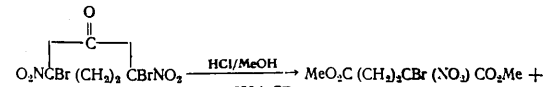
Chlorination of α-nitrocarboxylic acid hydrazides or their derivatives gave chlorodinitroacetyl and α-chloro-α-nitropropionyl chlorides, which were converted to methyl esters.[81]

$$[O_2N{=}CRCONHNH_2]^-H_3^+NNH_2 \xrightarrow{Cl_2} O_2NCClRCOCl \xrightarrow{MeOH} O_2NCClRCO_2Me.$$

The reaction of α-oximinocarboxylate esters with nitrosyl chloride leads to a mixture of chloronitrocarboxylate esters and chloronitroso esters.[88] When ethyl α-chloro-α-nitrosopropionate and ethyl α-chloro-α-nitrosobutyrate are oxidised with peroxytrifluoroacetic acid, the corresponding α-halonitro esters are isolated in good yield.[88] Chloronitroacetamide is obtained by alkaline hydrolysis of chloronitromalonamide, while fluorochloronitroacetamide is obtained by aqueous hydrolysis of the intermediate fluorochloro-nitromalonamide.[22] When trichloronitroethylene is reacted with primary alkoxides, unstable orthoesters of chloronitroacetic acid are formed, which undergo spontaneous conversion to esters of the same acid. With secondary alcohols, chloronitroacetate esters are obtained directly.[89] Stable chloronitroacetate aryl orthoesters are formed under similar conditions.[90,91] The reaction of trichloronitro-ethylene with 1,8-diaminonaphthalene leads to a cyclic amidine.[92]



Treatment of cyclic α,α′-dinitroketone with a methanol solution of hydrogen chloride gives a mixture of dimethyl 2-bromo-2-nitro-glutarate and methyl 2,5-dibromo-2,5-dinitropentanoate.[93] It has been suggested that the first product is formed from the second by a modified Nef reaction.



Reaction of dichloro- and dibromo-nitroacetamides with PCl_5 gives a number of *N*-phosphorylated amides and imidoyl chlorides of dichloro- and dibromo-nitroacetates — $Cl_2C(NO_2)CONHPOCl_2$, $Cl_2C(NO_2)CONHPO(OEt)_2$, $Br_2C(NO_2)CONHPOCl_2$, $Cl_2C(NO_2)CCl{=}NPOCl_2$, and $Br_2C(NO_2)CCl{=}NPOCl_2$.[19]

When difluoronitroacetic acid is treated with SO_3, the mixed anhydride $O_2NCF_2COOSO_3H$ is formed, and it undergoes alcoholysis to give difluoronitroacetate esters.[94,95] The mixed anhydride synthesised by the reaction of 2-nitrotetrafluoroethyl nitrite with glacial acetic acid is converted on treatment with alcohols to acetates and difluoronitroacetic acid.[96,97]

α-Nitroperfluoropropionate esters are synthesised by oxidation of α-nitrosoperfluoropropionate esters.[78]

$$ONCF(CF_3)CO_2Et \xrightarrow{N_2O_5} CF_3CF(NO_2)CO_2Et.$$

Polyfluorinated alcohols deposited as a thin layer on the surface of inert supports (NaF or CaF_2) when treated with dilute fluorine (−15 to −10 °C) form a mixture of aldehydes and esters.[98]

$$O_2NCF_2CH_2OH \xrightarrow{F_2} O_2NCF_2CHO + O_2NCF_2CO_2CH_2CF_2NO_2.$$

Amidines[99] and oximes[100] are obtained by aminolysis of nitroperfluoroalkyl nitrites. Corresponding esters are synthesised when difluoronitroacetic anhydride is treated with dihydric alcohols.[101]

The silver[6] and mercury[102–104] salts of difluoronitroacetic acid are known. The former, in contrast to the latter is unstable on standing and is rapidly decomposed with water.

$$O_2NCF_2COOH + Ag_2CO_3 \rightarrow O_2NCF_2COOAg,$$
$$O_2NCF_2COOH + HgO[(CH_3COO)_2Hg] \rightarrow (O_2NCF_2COO)_2Hg.$$

III. The use of physicochemical methods for studying the structure and properties

1. Vibrational spectroscopy

It is infrared spectroscopy that is usually used to confirm the structure of synthesised α-halo-α-nitrocarboxylic acids and their derivatives.

An accumulation of electronegative substituents (NO_2, halogen, CN, COOR) results in a shift of the absorption bands of the nitro group to shorter wavelength. Alkyl substituents give the reverse effect (Table 1). This type of shift is also typical for absorption bands from the carbonyl group. The presence of alkyl groups on the α-carbon atom decreases the difference Δν between the absorption frequencies of asymmetric and symmetric stretching vibrations of the NO_2 group. In the IR spectrum of the mercury salt of difluoronitroacetic acid there are shifts of ν(CO) and $\nu_{as}(NO_2)$ to higher absorption frequency by ~150 and ~40 cm^{-1} respectively compared to the acid and its esters.[64,107] However, the existing data

Table 1. Wavenumbers of stretching vibrations (cm^{-1}) of α-halo-α-nitrocarboxylic acid derivatives.

Compound	NO_2, as	NO_2, s	C=O	Other functional groups	Refs.
$MeO_2C(CH_2)_2CBr(NO_2)CO_2Me$	1560	—	1740, 1725	—	[93]
$O_2NCHBr(CH_2)_2CBr(NO_2)CO_2Me$	1560	—	1740	—	[93]
$O_2NCHBrCONHBr$	1575	—	1695	3155, 3410 (NH)	[18]
$O_2NCHBr(CH_2)_2CBr(NO_2)CONH_2$	—	—	1690	3125, 3360 (NH)	[27]
$NCCBr(NO_2)(CH_2)_4CBr(NO_2)CN$	—	—	—	2220 (CN)	[26]
$(O_2N)_2CBrCN$	1608	—	—	2240 (CN)	[21]
$O_2NCHClCO_2Alk$	1592—1589	1352—1347	1774—1763	740—726 (C—Cl)	[105]
$O_2NCClCO_2R$ $R'CHOH$	~1570	~1360	~1760	3600—3300 (OH)	[106]
$O_2NCDClCO_2Me(Et)$	~1590	~1350	—	~2235 (CD)	[83, 105]
$NH_4^+[O_2N{=}CClCONH_2]$	—	—	~1620	3500—3180 (NH)	[107]
$O_2NCHClCONH_2$	~1560	—	~1680	3360—3160 (NH)	[107]
$O_2NCHClCOCl$	~1575	~1340	~1780	~3000 (CH)	[51]
$O_2NCClCOCl$ $CH(CH_3)_2$	~1570	~1360	~1780	3000—2900 (CH)	[51]
$O_2NCClCO_2Alk$ $CH(CH_3)_2$	1560—1555	1355—1350	1750—1745	2880—2870 (CH)	[51]
$O_2NCF_2CO_2Alk$	1610—1600	1313—1319	1790	~1240, 1190 (CF)	[64]

are not sufficient to make a reliable assessment of the mutual effect from the functional groups. Raevskii et al.[105] undertook such an assessment in the case of a number of chloronitroacetate esters. The absorption region of the "acidic" proton was established (C—H group, 2932—2965 cm^{-1}) from comparative data and the spectrum of the deutero analogue. The strong absorption band in the region 1774—1763 cm^{-1} corresponds to a stretching vibration of the C=O group. Polarised Raman lines correspond to the same regions. The absorption frequencies of $NO_{2,as}$ (1592—1589 cm^{-1}) and $NO_{2,s}$ (1352—1347 cm^{-1}) have been determined. The vibration frequencies of the NO_2 and CO groups differ from those of ethyl nitroacetate (1382, 1562, and 1745 cm^{-1}). The narrow intervals of three absorption bands at 740—726, 670—657, and 580—568 cm^{-1}, the constant ratio of their intensities, and the absence of other bands in these regions can be of use analytically as a spectroscopic characteristic of the chloronitro group (together with asymmetric NO_2).

2. NMR spectroscopy

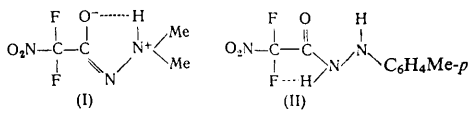
In order to investigate the possibility of self-association and association with an oxygenated solvent, ^1H NMR spectra were obtained for a number of chloronitroacetate esters in a pure form and in solution.[83,108] The signals from the α-CH protons of the pure products appear as singlets downfield (δ 6.36—6.47, HMDS). In the spectra of the same esters in oxygenated solvents—acetone-d_6 and dimethyl sulphoxide-d_6—the "acidic" protons were displaced further downfield the higher the ε value of the solvent, which is related to the formation of hydrogen bonds in which the CH proton and the oxygen atoms of the solvents participate. This is supported by the dependence of the chemical shift on the concentration of solutions. The magnitudes of the chemical shifts of the CH protons give a poor correlation with pK_a values in the series of chloronitroacetate esters.[108] The chemical shifts of the CH protons of chloronitroacetyl chloride (δ 6.67, TMS),[52] chloronitroacetamide (δ 6.56, 50% CD_3CN), and ethyl chloro- and bromo-nitroacetates (δ 6.56 and 6.66 respectively) were determined.[108] The ^{13}C NMR data of chloronitroacetyl chloride are: δ 90.33 p.p.m. (O_2NCHCl) and 161.78 p.p.m. (CO).[52] By studying the ^{13}C and ^{19}F NMR spectra of fluoronitroacetic acid, its propyl ester, and methyl chloronitroacetate, together with other halonitro and halonitroso compounds, it was demonstrated using mathematical calculations that the values of the chemical shifts give an unsatisfactory correlation with the sum of the Swain—Lupton constants (field constants) and correlate well with the charges on the carbon atom, calculated using the RMX [? Ed. of Translation] method (correlation coefficient 0.978). In the case of ^{19}F NMR spectra the paramagnetic contribution to the magnetic shielding constant is important.[109] The signal in the ^{19}F NMR spectrum of the mercury salt of difluoronitroacetic acid is displaced downfield relative to the spectra of other derivatives of this acid. This phenomenon, together with the IR spectroscopy data (see above), indicates that there is a strong donor-acceptor interaction between the Hg atom and the $O_2NCF_2COO_2$ group, with the Hg atom acting as an electron acceptor.[102]

3. Other methods

In order to confirm the structure of chloronitroacetic acid derivatives and to study their reactivity and reaction mechanism, use has been made of mass spectrometry,[52,83,107] EPR specroscopy,[83] calculation methods,[108,111] and electron-diffraction[112] and thermographic[113] methods. X-Ray diffraction analysis was used to study the structure of *aci*-ethyl chloronitroacetate[114] and *aci*-chloronitroacetamide anions.[115] The $O_2^-N{=}CClCOOC_2H_5$ anion is perfectly planar, while the $O_2^-N{=}C^1ClC^2ONH_2$ anion is almost planar. The lengths of the C—Cl bonds (1.711 and 1.713 Å respectively) have values that are intermediate between the bond lengths of C(sp^2)—Cl (1.72 Å) and C(arom)—Cl (1.70 Å).[116] Formally the N=C double bond (1.45 and 1.334 Å) is considerably longer than normal double bonds.[116] The length of the C=O bond in the ester anion is normal while in the amide anion it is extended (1.259 Å). Formally the N—C(2) single bond (1.323 Å) in the amide anion is formally shorter than an N = C double bond. The

C(1)–C(2) (1.465 Å) and N–C(2) bonds are very much shorter compared to single bonds (1.541 and 1.472 Å).[116] The distribution of bond lengths and the planarity of the anions indicate that conjugation occurs in them.

Difluoronitroacetic acid *N,N*-dimethylhydrazide has the zwitterion structure (I). In the case of aryl-substituted hydrazides, a form with a CF–HN hydrogen bond (2) occurs.[80,117]



(I) (II)

4. Acid-base properties

The introduction of chlorine atoms into molecules of nitrocarboxylic acid derivatives gives rise to a significant increase in CH-acidity (Table 2).[108,118–120] The introduction of fluorine atoms, on the other hand, reduces the acidic properties. This phenomenon is due to the destabilising effect of fluorine in the planar anion of the *aci*-form of the nitro compound, which manifests itself as "anticonjugation" (α-effect through the C=N double bond). This effect must assist the carbanion in adopting a pyramidal structure, which would lead to a partial disruption of conjugation, in other words, to destabilisation of the anion.[120] The planar configuration of the anions of ethyl chloronitroacetate and chloronitroacetamide to a certain extent confirms such a hypothesis.[114,115] An X-ray diffraction study of anions of α-fluoronitroalkanes or fluoronitroacetic acid derivatives would help to answer this question.

Table 2. CH-Acidity of α-halonitrocarboxylic acid derivatives (water, 25 °C).

Compound	pK_a	Refs.	Compound	pK_a	Refs.
$O_2NCH_2CO_2C_2H_5$	5.82	[121]	$O_2NCHClCO_2(CH_2)_2CH_3$	4.21	[108]
$O_2NCHFCO_2C_2H_5$	6.28	[118]	$O_2NCHClCO_2(CH_2)_3CH_3$	4.23	[108]
$O_2NCHClCO_2C_2H_5$	4.16	[118]	$O_2NCHClCO_2CH(CH_3)_2$	4.37	[108]
$O_2NCH_2CONH_2$	5.18	[118]	$O_2NCHClCO_2CH_2C(CH_3)_3$	4.32	[108]
$O_2NCHFCONH_2$	5.89	[118]	$O_2NCHClCO_2CH_2CH(CH_3)_2$	4.21	[108]
$O_2NCHClCONH_2$	3.60	[118]	$O_2NCHClCO_2CH(CH_3)CH_2CH_3$	4.42	[108]
$O_2NCHClCO_2CH_3$	4.02	[108]	$O_2NCHClCO_2CH_2CH_2Cl$	3.92	[108]

The nature of the alkyl substituent in the ester group has a weak effect on the change in CH-acidity in a series of chloronitroacetate esters.[108] A satisfactory relationship has been found between pK_a values and the Taft σ* constants of substituents for eight chloronitroacetate esters $O_2NCHClCOOR$ (R = Me, Et, Pr, Bu, iso-Bu, neopentyl, sec-Bu):[108] $pK_a = 3.98 - 1.94\sigma^*$; n = 8, $r = 0.98$, $s = 0.03$; $F = 143.5$. The acidic properties of α-bromo-α-nitrocarboxylic acid derivatives are not known. Determination of the dissociation constants showed that difluoronitroacetic acid is a stronger acid than trifluoroacetic acid (K_a 9.7 × 10^{-1} and 5 × 10^{-1} respectively).[62]

In terms of proton-donor properties the C–H bond of chloronitroacetate esters considerably surpasses the C–H bond in chloroform, acetylene derivatives, *o*-carborane, and it resembles the N–H bond.[105] Calorimetry was used to establish the proton-donor capacity of ethyl chloronitroacetate, which exceeds that for chloroform by a factor of 1.5. The thermodynamic constants of the hydrogen bond with trimethyl phosphate were determined and the enthalpy and autoassociation constant of this ester in CCl_4 were calculated.[122] The *P*-factor of methyl chloronitroacetate proved to be equal to the *P*-factor of *N*-methylaniline.[105] In the case of the reaction between ethyl chloronitroacetate and phenol in CCl_4 it was shown using IR spectroscopy that the electron-donor capacities of the CO and NO_2 groups were approximately equal and reduced by the mutual effect of the electronegative groups.[105]

IV. Chemical properties

1. Reactions involving the α-CH proton

As aliphatic nitro compounds that contain an active hydrogen atom at the α-position relative to the nitro group, α-halo-α-nitrocarboxylic acid derivatives react with bases to form salts of nitro compounds

$$O_2NCHXCOR \xrightarrow{:B} BH^+O_2^-N{=}CXCOR,$$

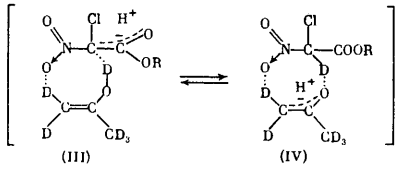
R—residues from alcohols, amines, etc.

Despite the frequent use of these salts in synthesis,[12–14,22,23,25,43,48,106,122] their stability on standing has hardly been discussed at all. Some chloronitroacetic acid derivatives, in particular the salts mentioned above,[114,115] do not decompose over a period of 1–2 months.[107] The sodium salt of benzyl chloronitroacetate[106] (5–10 g) can be stored at room temperature for 2–3 months without decomposition. Other derivatives are stable from several hours up to several days. On the whole, compounds such as salts of aliphatic nitro compounds cannot be stored for a long period because of their tendency to undergo spontaneous decomposition.

Bromo- and chloro-nitroacetate esters readily undergo the Henry reaction with aldehydes in the presence of calcium hydroxide[43] or potash.[48] The use of sodium acetate as a catalyst increased the yield of α-chloro-α-nitro-β-hydroxycarboxylic acids.[106]

$$O_2NCHXCO_2R \xrightarrow{R^1CHO} O_2NCXCO_2R,$$
$$\quad\quad\quad

suggested that deuterium exchange takes place via the highly unstable eight-membered transition states (III) and (IV).



(III) (IV)

Deuterium exchange takes place by a mechanism involving the concerted "departure" of a proton via the COOR group of (III) or the CO group of acetone in (IV) and arrival of a deuterium ion via the NO_2 group,[108] which is borne out to a certain extent by the approximately equal electron-donor capacities of the CO and NO_2 groups in chloronitroacetate esters.[105] Since a correlation exists between $T_{1/2}$ and the Taft σ^* constants of unbranched substituents, this type of deuterium exchange can serve as a method for measuring the relative mobility of protons in CH-acids.

The involvement of calculation methods for determining the charge distribution in anions that are formed by deprotonation of chloronitroacetate esters made it possible to propose an almost planar structure for the anion,[108] which was subsequently confirmed by X-ray diffraction analysis.[114]

2. Reactions involving the C—Hal bond

The presence of a nitro group at the α-position relative to a bromine atom activates the latter in a reaction with aqueous hydrazine. Diethyl bromonitromalonate is reduced more rapidly than diethyl bromomalonate.[123]

$$O_2NCBr(CO_2Et)_2 + H_2NNH_2 \rightarrow O_2NCH(CO_2Et)_2 + N_2 + HBr,$$
$$BrCH(CO_2Et)_2 + H_2NNH_2 \rightarrow CH_2(CO_2Et)_2 + N_2 + HBr.$$

The nitro group has a lesser effect on the mobility of halogen atoms in this reaction than keto or carbethoxy groups, as can be seen from the examples of the reduction of hydrazine hydrate given below.[13]

Halogen is reduced	Halogen is not reduced
$RCOCHClCO_2Et$, $RCOCRClCO_2Et$, $RCOCCl_2CO_2Et$, $CHCl(CO_2Et)_2$, $RCCl(CO_2Et)_2$, $CCl_2(CO_2Et)_2$	$O_2NCHClCO_2Et$, $O_2NCRClCO_2Et$, $O_2NCCl_2CO_2Et$

This is also confirmed by the ready reduction of ethyl bromonitroacetate, in contrast to bromonitroethane.

Bromonitrocarboxylate esters are reduced more readily than their chlorine analogues. Thus, ethyl α-chloro-α-nitropropionate and ethyl α-chloro-α-nitrobutyrate are not reduced, in contrast to their bromine analogues.

Esters of chloro-, bromochloro- and fluorochloro-nitroacetic acids when reacted with triphenylphosphine in benzene—methanol solution replace a bromine or chlorine atom with a hydrogen atom.[24] A change to a benzene medium reduced the yield of ethyl nitroacetate from ethyl chloronitroacetate from 71 to 20%.

$$O_2NCX_2COOR \xrightarrow[\text{benzene}]{Ph_3P,\ MeOH} O_2NCHXCOOR + Ph_3PO + Ph_3PO\cdot HX,\ X = H,\ Cl \text{ or } Br.$$

Hydrodechlorination of bromo- and chloro-nitroacetate esters can take place when sodium dithionite is used in aqueous alcohol.[86]

$$O_2NCHXCOOR \xrightarrow{Na_2S_2O_4} O_2NCH_2COOR.$$

3. Reactions involving the carboxyl group

Fluoronitroacetic,[50] difluoronitroacetic,[61,62] and fluorochloronitroacetic[44] acids have been obtained in a pure form. Difluoronitroacetic acid is stable in aqueous solution.[61,62] The remaining α-halo-α-nitrocarboxylic acids have only been determined as derivatives: esters, amides, acid chloride, etc. Bromo- and chloro-nitroacetic acids were determined in ether solution using IR spectroscopy.[86]

Table 3. Decarboxylation of α-halo-α-nitrocarboxylic acids and their chlorides to nitroso compounds or oximes.

Acid (chloride)	Reaction conditions	Reaction product	Yield, %	Refs.
$O_2NCHClCOCl$	conc. HCl, 20 °C	$HON{=}CCl_2$	10	[124]
$O_2NCHClCOCl$	$AlCl_3$ or AlF_3, 20–30 °C	$HON{=}CCl_2$	42 or 48	[125]
$O_2NCHClCOCl$	urea, carbonyl and other compounds, 20–35 °C	$HON{=}CCl_2$	60—75	[52]
O_2NCCl_2COCl	$AlCl_3$, 20–30 °C	$ONCCl_3$	50	[125]
$O_2NCFClCOOH$	21% aq. HCl, 100 °C	$ONCFCl_2$	60	[124]
$O_2NCFClCOOH$	KCl	$ONCFCl_2$	13	[126]
$O_2NCFClCOOH$	90% HNO_3	$O_2NCFClNO$	52	[128, 129]
$O_2NCFClCOOH$	60% HNO_3	$O_2NCFClNO$ + $+O_2NCFCl_2$	—	[128]
$O_2NCFClCOOH$	aq. HBr	$ONCFClBr$	—	[128]
$O_2NCHFCOOH$	conc. HCl, 70 °C	$HON{=}CFCl$	23	[130]
O_2NCF_2COOH	conc. HCl, 100 °C	$ONCF_2Cl$	60	[66, 131]

Table 4. Decarboxylation of α-halo-α-nitrocarboxylic acids and their chlorides to halonitroalkanes.

Acid (chloride)	Reaction conditions	Reaction product	Yield, %	Refs.
$O_2NCHClCOCl$	H_2O, 20° C	O_2NCH_2Cl	—	[132]
$O_2NCFClCOOH$	H_2O, 25—30° C	$O_2NCHFCl$	35	[44, 127]
$O_2NCFClCOOH$	KF	$O_2NCHFCl$	28	[126, 127]
$O_2NCFClCOOH$	KCl	$O_2NCHFCl$	24	[126]
$O_2NCFClCOOH$	N_2O_4	$(O_2N)_2CFCl$	—	[128]
$O_2NCFClCOOH$	Br_2+H_2O	$O_2NCFClBr$	—	[128]
$O_2NCFClCOOH$	90% HNO_3	$(O_2N)_2CFCl$	3—5	[128]
O_2NCCl_2COCl	H_2O, 20° C	O_2NCHCl_2	37	[132]
O_2NCF_2COOH	KF	O_2NCHF_2	26	[126, 127]
O_2NCF_2COOH	aq. K_2CO_3, 100 °C	O_2NCHF_2	46	[66]
$O_2NCCl(CF_2Cl)COCl$	H_2O, 45—50° C	O_2NCH_2Cl	61	[127]
$O_2NCCl(CF_3)COCl$	H_2O, 50° C	$O_2NCHClCF_3$	55	[127]

A large number of studies have been devoted to the decarboxylation of α-halo-α-nitrocarboxylic acids as a method for obtaining various halonitro-, halonitroso-, and halonitronitrosoalkanes.[44,52,66,124–132] Depending on the nature of the acid and reagents and the temperature of the medium, α-halo-α-nitrocarboxylic acids (or their acid chlorides) form halonitro, halonitroso, or halonitronitroso compounds (Tables 3 and 4). The conversion of α-nitro-α,β-dichloro-β,β-difluoropropionyl chloride to chloronitromethane when treated with water[124] is accounted for by the following reaction scheme:

$$ClCF_2CCl(NO_2)COCl \rightarrow ClCF_2CClNO_2^- \xrightarrow[-Cl^-]{} CF_2{=}CClNO_2 \xrightarrow{H_2O} \rightarrow HOCF_2CHClNO_2 \xrightarrow[-HF]{} FCOCHClNO_2 \xrightarrow[-HF]{H_2O} \rightarrow O_2NCHClCOOH \xrightarrow[-CO_2]{} O_2NCH_2Cl.$$

There is no common view on the mechanism of decarboxylation of α-nitrocarboxylic acids and their derivatives.[52,124,125] Evidently the solvating capacity and polarity of the reaction medium as well as the nature of the nitrocarboxylic acid and other reactants affect the course of the reaction and the nature of the products.

In effectively solvating polar media, *aci*-nitrocarboxylic acid is formed, undergoing decarboxylation.

$$HO_2N{=}CRCOOH \xrightarrow{-CO_2} HO_2N{=}CHR \rightarrow O_2NCH_2R.$$

Depending on the nature of the radical R, the decarboxylation product can be converted to a nitro compound or, after protonation, dehydration, and addition of an anion, to a nitroso compound (or oxime).

$$HO_2N{=}CRR' \rightleftharpoons O_2NCHRR'$$
$$\downarrow HCl$$
$$HO\diagdown \overset{+}{N}{=}CRR'Cl^- \xrightarrow{-H_2O} O{=}NCClRR'$$
$$HO\diagup$$

The course of the reaction will most likely be mainly affected by the lifetime of the *aci*-nitro compound and its concentration. The amount of *aci*-form is known[133] to vary according to the series (%): CH_3NO_2 (0.000011) < $C_2H_5NO_2$ (0.0085) < iso-$C_3H_7NO_2$ (0.275).

The presence of the electronegative substituents COOH, COOR, or halogens at the α-position of nitroalkanes evidently substantially reduces the percentage of the *aci*-form. This can explain the conversion of salts of 2-nitropropane, nitrocyclohexane,[131] and ethyl nitroacetate[134] to the corresponding chloronitroso compounds on treatment with anhydrous HCl in ether and the absence of such a reaction for diethyl nitromalonate, nitroform,[131] and ethyl chloronitroacetate.[52]

In weakly solvating nonpolar media, where the probability of a sufficiently long lasting protonated nitro group is low, an intermolecular redox decarboxylation can take place.[52,125]

$$O_2NCHClCOCl \xrightarrow[\text{base}]{\text{acid or}} \left[O{=}\overset{+}{N}{-}CHCl \;\rightleftharpoons\; O{=}\overset{+}{N}{-}CHCl \right] Cl^- \xrightarrow{-CO_2}$$
$$\longrightarrow ONCHCl_2 \longrightarrow HON{=}CCl_2.$$

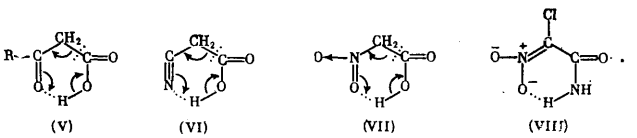
The course of the reaction is evidently also affected by the temperature, phase state, and steric and other factors. For example, difluoronitroacetic acid, as one of the strongest organic acids, can act as a base towards stronger acidic reagents.

Esters are apparently decarboxylated in the same way as acids. Thus, ethyl esters of chloro- and dichloro-nitroacetic acid,[132] and also of difluoronitroacetic acid[131] when reacted with hydrochloric acid form the corresponding halonitromethanes. Ethyl perfluoronitropropionate is converted under similar conditions to α-chloroperfluoronitrosoethane.[78]

$$O_2NCF(CF_3)CO_2C_2H_5 \xrightarrow{HCl} ONCFClCF_3 + EtOH + CO_2 + H_2O.$$

Since the values of the dissociation constants of trifluoro- and trichloro-nitroacetic acids are comparable and the stability of the former is higher, the greater stability of difluoronitroacetic acid compared to other α-nitrocarboxylic acids can be accounted for by the electron-donor properties of fluorine atoms. A series of acid stabilities has been put forward:[135] O_2NCF_2COOH > $O_2NCFClCOOH$ > $O_2NCHFCOOH$ > O_2NCH_2COOH > $O_2NCHClCOOH$.

Decarboxylation of α-substituted carboxylic acids results from the formation of six-membered transition states (V)–(VII) [136]



(V) (VI) (VII) (VIII)

The stability functions of such transition states will be mainly the planarity and solvation. In the case of fluorinated nitroacetic acids, there is evidently an affect from the same factors that determine CH-acidity, that is, repulsion beween the *p*-orbitals of the fluorine atom and the π-systems involving the central carbon atom, nitro group, and carboxyl group (covalent radii F 0.64, Cl 0.99, Br 1.14 Å). In other words, the fluorine atoms inhibit the formation of a planar six-membered transition state and thus inhibit the decarboxylation of fluoronitroacetic acids. It appears that proton solvents can form such a transition state through hydrogen bonding, as a result of which fluoro- and fluorochloro-nitroacetic acids, which are stable in a pure form, are readily decarboxylated in water. As was mentioned above, anions of chloronitroacetic acid derivatives are planar,[114,115] and evidently as a result of this, chloronitroacetic acid is readily decarboxylated. The anion of chloronitroacetamide (VIII) has a structure which resembles the hypothetical transition states (V)–(VII), which to a certain extent is an argument in favour of their possible formation.

Esterification of α-halo-α-nitrocarboxylic acid chlorides with aliphatic alcohols occurs in the normal way. However, it is better to obtain benzyl chloronitroacetate[83] by using sodium benzylate in benzyl alcohol in order to avoid decomposition of benzyl chloronitroacetate with HCl that is formed during the reaction.

$$O_2NCHClCO_2CH_2Ph \xrightarrow{HCl} O_2NCHClCOOH \xrightarrow{-CO_2} O_2NCH_2Cl.$$

By reacting chloronitroacetyl chloride with benzenediazonium chloride, the α-chloro derivative of nitroformaldehyde phenylhydrazone is formed in high yield[137]

$$O_2NCHClCOCl \xrightarrow{NaHCO_3,\ H_2O,\ PhN_2^+Cl^-} O_2NCCl{=}NNHPh.$$

However, there is no conclusive evidence in this study that benzenediazonium chloride reacts with disodium chloronitroacetate $2Na^+[O_2N{=}CClCOO]^{2-}$ rather than the sodium salt of chloronitromethane $Na^+[O_2N{=}CClH]^-$ which is formed from it by decarboxylation.

Difluoronitroacetyl fluoride and chloride form various products with trimethylsilane.[138]

$$O_2NCF_2COF + HSiMe_3 \rightarrow O_2NCF_2CO_2CH_2CF_2NO_2 + FSiMe_3,$$
$$O_2NCF_2COCl + HSiMe_3 \rightarrow O_2NCF_2CH_2OSiMe_3 + ClSiMe_3.$$

Treatment of difluoronitroacetyl fluoride with methyltrichlorosilane gives difluoronitroacetyl chloride.[138]

$$O_2NCF_2COF + MeSiCl_3 \rightarrow O_2NCF_2COCl + MeSiFCl_2.$$

An attempt to obtain the mercury salt from fluorochloronitroacetic acid and mercuric oxide gave di(fluorochloronitromethyl)-mercury.[139,140] It was suggested that the reaction takes place via the mercury salt of fluorochloronitroacetic acid, which is unstable to decarboxylation, in contrast to the mercury salt of difluoronitroacetic acid.[102,104]

Alkyl difluoronitroacetates and difluoronitroacetyl halides undergo aminolysis with ammonia and aniline without complications, giving amides and anilidies.[62,77,78] Derivatives of other α-halo-α-nitrocarboxylic acids react in more than one way. On treatment with ammonia, ethyl perfluoronitropropionate decomposes to α-hydroperfluoronitroethane and urethane.[77,78]

$$O_2NCF(CF_3)COOEt \xrightarrow{NH_3} CF_3CHFNO_2 + H_2NCOOEt.$$

Reaction of ammonia with methyl α-chloro-α-nitrotrifluoropropionate at −30 °C gives an amide which is unstable at room temperature.[141] The presence of methyl carbamate in the reaction mixture is an indication that a haloform decomposition is taking place at the same time.

$$O_2NCCl(CF_3)COOMe + NH_3 \rightarrow O_2NCCl(CF_3)CONH_2 + H_2NCOOMe.$$

At room temperature haloform decomposition is the main process.

$$O_2NCFClCOOMe + Et_2NH \rightarrow CHFClNO_2 + Et_2NCOOMe,$$
$$O_2NCCl(CF_3)COOPr\text{-}n + NH_4OH \rightarrow H_2NCOOPr\text{-}n.$$

Reaction of ethyl bromo- and chloro-nitroacetates with aqueous ammonia at 50−60 °C leads to the ammonium salts, which are acidified to give the amides. Hydrazinolysis can be achieved over a period of days at room temperature.[107]

$$O_2NCHXCOOEt + H_2NR \rightarrow H_3\overset{+}{N}R[O_2N{=}CXCONHR]^- \xrightarrow{H^+} O_2NCHXCONHR,$$
$$X = Br, Cl;\ R = H, Me, NH_2.$$

When the temperature is increased to 80−100 °C, decomposition of the initial esters occurs with formation of ammonium halides. When bromo- and chloro-nitroacetate esters are treated with aqueous solutions of sterically hindered amines and also alcohol and ether solutions of ammonia or amines, ammonium salts are also formed. This occurs because of the instability of the ammonium salts of the nitro compounds formed, as a result of their insufficient solvation, and leads to elimination of halogen and subsequent decomposition of the nitroester.[107]

Reaction of methyl difluoronitroacetate with sodium borohydride gives a mixture of difluoronitroacetaldehyde and its hemiacetal.[142]

$$O_2NCF_2COOMe + NaBH_4 \rightarrow [O_2NCF_2\overset{O^-}{\overset{|}{C}}HOMe(BH_3Na)^+] \rightarrow$$
$$\xrightarrow{H_2O} O_2NCF_2CH(OH)OMe + O_2NCF_2CHO.$$

When diethyl fluoronitromalonate is treated with alcoholic alkali and subsequently acidified, fluoronitromethane is obtained.[40] It has been suggested that the disodium salt of fluoronitromalonic acid is formed as an intermediate.

$$O_2NCF(COOEt)_2 \xrightarrow{EtOH,\ NaOH} [O_2NCF(COONa)_2] \xrightarrow[H_2O]{ClCH_2COOH} O_2NCH_2F.$$

In contrast, for example, to nitroacetic acid, difluoronitroacetic acid is not fluorinated on treatment with SF_4, which is due to a combination of the electron-acceptor effect of the fluorine atoms on fluorination and the ease of undergoing decarboxylation.[143]

$$O_2NCF_2COOH \xrightarrow[130°C]{SF_4} O_2NCF_2CF_3,$$
$$O_2NCH_2CO_2H \xrightarrow{SF_4} O_2NCH_2CF_3.$$

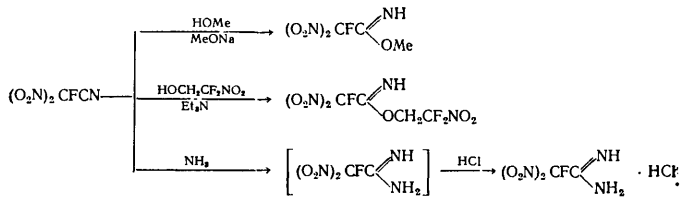
The reaction of chlorine fluorosulphate with ethyl chlorodinitroacetic acid is accompanied by displacement of the carbethoxyl group.[30]

$$(O_2N)_2CClCOOEt + ClOSO_2F \rightarrow (O_2N)_2CCl_2.$$

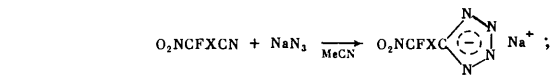
The reaction of difluoronitroacetyl fluoride with acetone and methyl ethyl ketone results in the formation of 1,1-difluoro-1-nitropentane-2,4-dione and 1,1-difluoro-1-nitro-3-methylpentane-2,4-dione.

$$O_2NCF_2COF + RCH_2COCH_3 \rightarrow O_2NCF_2COCHRCOCH_3.$$
R=H, CH_3.

The presence of two nitro groups in fluorodinitroacetonitrile increases the electrophilic nature of the nitrile group. Reaction of this compound with alcohols gives imidates,[33,145] while with ammonia an amidine is formed.[33]

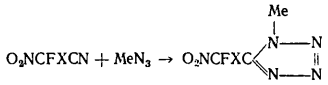


The reaction of difluoronitro- and fluorodinitro-acetonitrile with sodium azide is not so vigorous as for CF_3CN. This is because the nitro group shields the carbon atom of the nitrile group and hinders attack by azide ion.[146]



X = F, NO_2.

1,5-Disubstituted tetrazoles are synthesised by a reaction with methyl azide.[146] Reactions of trifluoroacetonitrile and chlorinated acetonitriles with MeN_3 take place with considerably greater difficulty, which is related to the strong electron-acceptor effect of the NO_2 group, which assists 1,3-cycloaddition.



By studying the kinetics of the addition of the radical $CH_3^{\cdot}$ to a number of perfluorocarbonitriles and α-nitroperfluorocarbonitriles in relation to the rate of elimination of H from iso-octane it was established that fluoronitronitriles are more reactive. Thus, O_2NCF_2CN adds on a methyl radical four times as fast, and $(O_2N)_2CFCN$ ten times as fast, as does CF_3CN. This phenomenon is due to the increased electrophilicity of the carbon atom of the nitrile group as a result of the strong electron-acceptor effect of the fluoronitro groups. The linear correlation of the ratio k_2/k_1 and σ^* indicates that the inductive effect mainly contributes to the reactivity of nitriles of this series towards a methyl radical.[147]

The mercury salt of difluoronitroacetic acid decarboxylates in the presence of strong bases.[102]

$$(O_2NCF_2COO)Hg \xrightarrow[or\ NaOH,\ H_2O]{Na_2CO_3,\ H_2O} O_2NCF_2H.$$

In ether it readily reacts with alkyl iodides and lower alkyl bromines.[102,103]

$$(O_2NCF_2COO)_2Hg + RX \xrightarrow[-HgCl_2]{ether} O_2NCF_2COOR + O_2NCF_2COOEt + ROEt,$$
$$R = Me, Et, Pr\text{-}n, Bu\text{-}n;\ X = Br, I.$$

The formation of ethyl esters as by-products, in quantities which increase as the activity of the alkyl halides decreases, occurs because

the salt undergoes reaction in solvated forms. With benzyl bromide and benzyl chloride the reaction takes place without by-products.

$$(O_2NCF_2COO)_2Hg + PhCH_2X \xrightarrow[-HgX_2]{ether} O_2NCF_2COOCH_2Ph.$$

In acetonitrile alkylation is also unaccompanied by side-reactions. The reaction in THF mainly leads to ring-opening.[103,104] The quantity of decomposition products from THF rises as the strength of the acid increases.[103]

$$(RCOO)_2Hg + MeI \xrightarrow[-HgI_2]{THF} RCOOMe + RCOO(CH_2)_4OMe,$$
$$R=O_2NCF_2,\ CF_3,\ Me,\ 2,4,6\text{-}Cl_3C_6H_2OCH_2.$$

The explanation that side-reactions occur because of solvation is not entirely convincing. The overall logic of these studies[102–104] indicates that two independent processes are taking place under these conditions — alkylation of the salts with alkyl halides and decomposition of ether or THF by difluoronitroacetic acid derivatives formed during reaction.

4. Reaction of α-halo-α-nitrocarboxylic esters with trivalent phosphorus compounds

The reaction of α-halonitrocarboxylic acids with trivalent phosphorus compounds, as a special case of the reaction of aliphatic and alicyclic α-halo-α-nitro compounds with phosphines and phosphites, is the most characteristic feature of these compounds.[23,24,148–154] The reaction has been studied in the case of α-bromo- and α-chloro-nitro compounds. The products of the reaction between α-halonitro compounds and triphenylphosphine and triphenyl phosphite, as a rule, are of differing types.

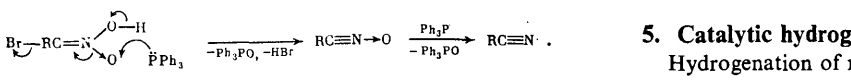
In a study of the reaction of triphenylphosphine with a number of α-bromonitro compounds it was found[148,149] that bromonitromethane and 1-bromo-1-nitroethane form quaternary salts which do not react with a further portion of triphenylphosphine.

$$Ph_3P + BrCRHNO_2 \rightarrow Ph_3\overset{+}{P}\text{—}CR{=}NO_2H\ Br^-.$$

At the same time, 1-bromo-1-nitropropane, ethyl bromonitroacetate, 1-bromo-1-nitro-octane, and bromonitrophenylmethane with twice the amount of triphenylphosphine give nitriles with yields of 63, 50, 72, and 75% respectively.

$$2Ph_3P + BrCRHNO_2 \rightarrow RC{\equiv}N.$$

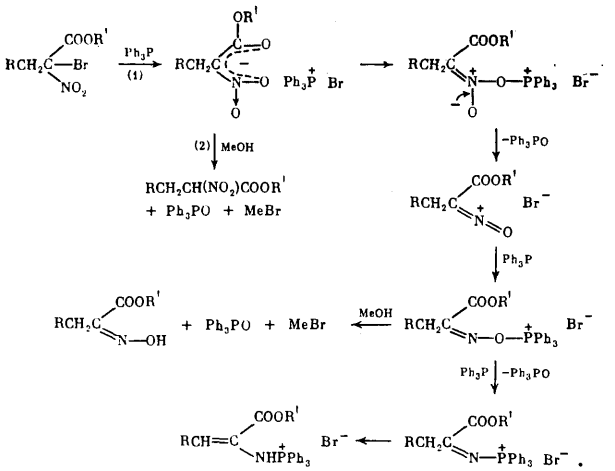
In the opinion of Trippet and Walker,[149] in the latter cases attack by Ph_3P occurs on the oxygen atom of the nitrile group.



Subsequently, reaction of 1-bromo-1-nitroalkanes with twice the amount of Ph_3P gave salts of phosphonium-substituted oximes, whose structure was confirmed by elemental analysis and IR and ^1H NMR spectroscopy.[150]

$$2\,Ph_3P + BrCRHNO_2 \rightarrow Ph_3\overset{+}{P}CR{=}NOH\ Br^- + Ph_3PO,$$
$$R=H,\ Me,\ Et..$$

The various stages were studied in the case of the reaction of a number of α-bromo-α-nitrocarboxylate esters with triphenylphosphine, with determination of the intermediate and final products, which to a considerable extent clarified the reaction route.[23]



Chloro-, fluorochloro-, and dichloro-nitroacetate esters react with triphenylphosphine in a similar manner according to reactions (1) and (2).[24]

The reaction of bromo-, chloro- and fluorochloro-nitroacetic acids and α-chloro-α-nitrotrifluoropropionic acid with triethyl phosphite gives phosphorylated oximes.[151,153]

$$O_2NCRXCOOR' + (EtO)_3P \rightarrow (EtO)_2\overset{O}{\overset{\|}{P}}\text{—}O\text{—}N{=}CRCOOR'.$$

The same products are obtained by counter synthesis from the ammonium salts of *aci*-nitrocarboxylate esters and diethyl phosphorochloridite.[152]

$$(EtO)_2PCl + NH_4^+[O_2N{=}CXCOOR]^- \rightarrow (EtO)_2\overset{O}{\overset{\|}{P}}\text{—}O\text{—}N{=}CXCOOR,$$
$$X=H,\ Cl,\ Br.$$

Phosphoryloximes were obtained for the first time by Allen[154] in the reaction of triethyl phosphite with 2-chloro-2-nitropropane and 2-chloro-2-nitrosopropane.

Methyl diphenylphosphinite also reacts to form a phosphorylated oxime.[23] This reaction, in principle, is a link that connects the reactions of α-halo-α-nitro compounds with triphenylphosphine and trialkyl phosphites into a single whole.

5. Catalytic hydrogenation

Hydrogenation of methyl and ethyl chloronitroacetates over palladium catalysts gives glycine ester hydrochlorides.[86,113]

$$O_2NCHClCOOR + H_2 \xrightarrow[EtOH]{Pd} HCl \cdot H_2NCH_2COOR.$$

A study of the kinetics of the process using thermography showed[113] that the main quantity of hydrogen is absorbed at the initial stage. It is possible to conclude from the decrease in reaction heat effect and small absorption of hydrogen at high degrees of conversion that at 40–50 °C decarboxylation starts to play a significant role. This conclusion is also supported by the fact that carbon dioxide has been detected in excess hydrogen removed from the reaction. Decarboxylation may take place because of the accumulation of water and hydrogen chloride during reduction, which increases the probability of hydrolysis of the initial ester to chloronitroacetic acid. This is one of the possible reasons for the low yields of final products (up to 65%).

V. Physiological activity

Bromine- and chlorine-containing α-halonitroacetate esters acquire a yellow colour and sharp odour on standing as a result of partial decomposition. Methyl bromonitroacetate has an irritating effect on the eyes and cause irritation on skin contact.[10] According to the WHO classification, chloronitroacetate esters are classed as compounds with moderate and low hazards. For peroral administration to mice, the acute toxicity amounted to 830 to 2300 mg kg^{-1} (2.3–9.1 mmol kg^{-1}) and for skin application it was 6000–8100 mg kg^{-1}.[85,155] Introduction of additional halogen atoms into the different parts of the molecules of these compounds increases the toxicity by a factor of 3–10.[85] The toxicity of fluorochloronitroacetate esters is higher than for esters of chloro-, dichloro-, and bromochloro-nitroacetic acids.[156] In working with difluoronitroacetic acid and its derivatives it is recommended to use care because of the known toxicity of these compounds.[62,66]

Chloronitroacetate esters at concentrations of 0.5–3 μM increase the ionic permeability of mitochondria, in other words, they act as decouplers of oxidative phosphorylation. Their effective concentrations are 10–15 times higher than for the traditional decoupler—2,4-dinitrophenol.[155] At minimum concentrations they inhibit the activity of mitochondrial succinate oxidase.[155]

Propyl and butyl chloronitroacetates have insecticidal activity.[85] Various esters of the same acid have suppressed the growth of bacteria of fungal mycelia and also the development of plant diseases.[85] Growth-regulating activity has been found in them, according to the results of initial experiments.[85]

Fluorochloronitroacetate esters have an anti-choline esterase action.[84,156–158] The most active is the butyl ester. The bimolecular constants for irreversible inhibition (k_2) of acetyl- and butyryl-choline esterase are $(3 \pm 0.7) \times 10^{-4}$ and $(5.1 \pm 0.5) \times 10^{-5}$ litres mol^{-1} min^{-1} respectively.

The effect of chlorine- and fluorine-containing nitroacetate esters on the morphology of mouse liver has been studied.[159] α-Fluoro-nitrocarboxylic acid hydrazides inhibit monoamine oxidase and have hypotensive properties.[160]

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During preparation of the manuscript for printing, a number of publications whose contents considerably complement the present review have appeared.

The bromination of nitroacetonitrile with bromine has been carried out without using bases.[161] Dinitroacetonitrile anion is almost quantitatively chlorinated on platinum, graphite, and ruthenium oxide-titanium anodes.[162] α-Fluoro-α-nitrocarboxylate esters can serve as initial reactants for the synthesis of various fluorine-containing synthons.[163] Nitration of symmetric difluoro-dichloroethylene and fluoro-1,2-dichloroethylene with a nitration mixture containing added SO_3 gives fluorochloro- and chloro-nitroacetyl fluorides respectively.[164] 1,1-Dichlorodifluoro-1,2-dinitroethane, in addition to difluoronitroacetyl chloride, is found amongst the products from the gas-phase nitration of 1,1-difluorodichloroethylene.[165] The conversions of alkyl fluoronitroacetates have been studied in Henry and bromination reactions.[166] Treatment of diethyl 2,5-dinitroadipate with excess aqueous KOBr gives diethyl 2,5-dibromo-2,5-dinitroadipate.[167] When treated with xenon difluoride, difluoro- and fluorochloro-nitroacetic acids can undergo halo- and nitro-decarboxylation.[168,169] The same system can be used for the halonitromethylation of benzene derivatives.[170–172] Primary and secondary amines can aminolyse methyl difluoro- and fluorochloro-nitroacetates.[173,174] Chloronitroacetic acid derivatives readily undergo sulphonation and dehalogenation with sodium sulphite, hydrosulphite, and dithionite.[175–178] Replacement of the chlorine atom is accompanied by oxidation of S(IV) to S(VI). Treatment of anhydrous ammonium salts of halonitroacetic acid derivatives with thionyl chloride gives the corresponding halo-oximinoacetic acid derivatives.[178,179] Chloronitroacetic acid derivatives coordinate with Cu(II) and Ni(II) ions.[180,181] The minimum negative charge on the chlorine atom in chloronitroacetic acid derivatives has been established using ^{35}Cl NQR and quantum-chemical calculations. The composition and molecular structures of chloronitroacetanilide,[183] dichloronitroacetamide,[184] bis(chloronitro-acetamidato)tetra-amminecopper(II),[185] and the hydrazine salt of 1-difluoronitroacetyl-2-acetylhydrazide[186] have been studied using X-ray diffraction analysis. On changing from esters to thioesters of fluorochloronitroacetic acid, their anti-choline esterase activity is markedly reduced.[187] Chloronitroacetamide has a retardant effect on wheat plants.[188] Detailed information on the synthesis and relationship between the hypotensive and anti-monoamine oxidase activities of difluoronitroacetic acid hydrazides has been published.[189–191] The synthesis of chiral α-substituted fluoronitro-acetates has been carried out and the racemates have been separated.[192–194] The absolute configuration of their optical isomers has been established by X-ray diffraction analysis.[195] The formation of isoxazoline-*N*-oxide from dibromonitroacetonitrile and tetramethylethylene has been reported.[196]

References

1. *Methoden der Organischen Chemie* (Methods of Organic Chemistry) Part 10(1), Georg Thieme Verlag, Stuttgart, pp 32, 34, 68, 138, 139
2. H M Feuer (Editor) *The Chemistry of Nitro and Nitroso Groups* (Translated into Russian), Vol. 1, Izd. Mir, Moscow, 1972, p. 241
3. R Kh Freidlina, F K Velichko, E Ts Chukovskaya, et al. *Khlor. Alifaticheskie Soedineniya. Metody Elementoorganicheskoi Khimii* (Chlorine. Aliphatic Compounds in Methods of Organoelemental Chemistry), Izd. Nauka, Moscow, 1973, p. 567
4. S S Novikov, G A Shvekhgeimer, V V Sevostyanova, V A Shlyapochnikov *Khimiya Alifaticheskikh i Alitsiklicheskikh Nitrosoedinenii* (The Chemistry of Aliphatic and Alicyclic Nitro Compounds), Izd. Khimiya, Moscow, 1974, pp 175, 178, 184, 195
5. M T Shiphandler *Synthesis*, 1979, 676
6. A V Fokin, A I Rapkin, V A Komarov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1785
7. E R Bissell *Fluorine Chem. Rev.*, 1969, **4** 119–188
8. A L Fridman, V D Surkov, S S Novikov *Usp. Khim.*, 1980, **49**(11) 2159 [English translation in *Russ. Chem. Rev.*, 1980(11)]
9. L Schischkoff *Liebigs Ann. Chem.*, 1861, **119** 247
10. H Wieland *Liebigs Ann. Chem.*, 1903, **328** 154
11. H Willstätter, V Hottenroth *Ber. Bunsenges. Phys. Chem.*, 1904, **37** 177
12. W Steinkopf, L Bohrmann *Ber. Bunsenges. Phys. Chem.*, 1908, **41** 1044
13. A K Macbeth, D Traill *J. Chem. Soc.*, 1925, 892
14. W Steinkopf *Ber. Bunsenges. Phys. Chem.*, 1909, **42** 617

15. W Steinkopf *J. Prakt. Chem.*, 1910, **81**(2) 97–149, 193–253
16. W Steinkopf, A Supan *Ber. Bunsenges. Phys. Chem.*, 1910, **43** 3239
17. F Ratz *Monatsh. Chem.*, 1904, **25** 687
18. S K Brownstein *J. Org. Chem.*, 1958, **23** 113
19. W Steinkopf *Ber. Bunsenges. Phys. Chem.*, 1908, **41** 3571
20. A K Macbeth, D Traill *J. Chem. Soc.*, 1925, 1118
21. C O Parker, M Emmons, H Rolewicz, K McCallum *Tetrahedron*, 1962, **17** 79
22. H G Adolph, R E Osterling, M Sitzmann *J. Org. Chem.*, 1968, **33** 4296
23. D Leguern, G Morel, A Foucard *Bull. Soc. Chim. Fr.*, 1975, 252
24. I V Martynov, L V Postnova, R Kh Bikkineev, A I Yurtanov *Zh. Org. Khim.*, 1984, **20** 1724
25. L A Bocharova, A S Polyanskaya *Tr. Pedvuzov Dal'nego Vostoka, Ser. Khim.*, 1966, 66
26. H Feuer, C Savides *J. Am. Chem. Soc.*, 1959, **81** 5826
27. H Feuer, C Savides *J. Am. Chem. Soc.*, 1959, **81** 5830
28. H Feuer, B Vincent *J. Org. Chem.*, 1964, **29** 939
29. R Scholl, B Nyberg *Ber. Bunsenges. Phys. Chem.*, 1906, **39** 1956
30. A V Fokin, Yu N Studnev, A I Rapkin, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 489
31. A Amrollah-Macjabari, R Bengelmans, A Lechevallier *Synthesis*, 1986, 828
32. A V Fokin, V S Komarov, V P Radchenko *Zh. Obshch. Khim.*, 1969, **39** 1345
33. A V Fokin, V S Galakhov, A T Uzun, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 456
34. R A Wiesboeck, J K Ruff *J. Org. Chem.*, 1968, **33** 1257
35. M J Kamlet, H G Adolph *J. Org. Chem.*, 1968, **33** 3073
36. J P Freeman *J. Am. Chem. Soc.*, 1960, **85** 3869
37. L V Okhlobystina, V M Khutoretskii, A A Fainzil'berg *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, 476
38. V M Khutoretskii, L V Okhlobystina, A A Fainzil'berg *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1970, 387
39. Y Takeuchi, A Muraiama, T Hagi, T Koizumi *J. Chem. Soc. Jpn., Chem. Ind. Chem.*, 1985, 2029
40. J P Lorand, J Urban, J Overs, Q A Ahmed *J. Org. Chem.*, 1969, **34** 4176
41. I V Martynov, Yu L Kruglyak *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1963, **8** 237
42. I V Martynov, Yu L Kruglyak *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1963, **8** 237
43. I V Martynov, Yu L Kruglyak, S P Markarov *Zh. Obshch. Khim.*, 1963, **33** 3382
44. I V Martynov, Yu L Kruglyak, S P Makarov *Zh. Obshch. Khim.*, 1963, **33** 3384
45. I V Martynov, Yu L Kruglyak, S P Makarov, V G Tkachev *Zh. Obshch. Khim.*, 1963, **33** 3388
46. I V Martynov, Yu L Kruglyak, S P Makarov *Zh. Obshch. Khim.*, 1963, **33** 3386
47. I V Martynov, Yu L Kruglyak *Zh. Obshch. Khim.*, 1965, **35** 967
48. I V Martynov, Yu L Kruglyak *Problemy Organicheskogo Sinteza* (Problems in Organic Synthesis), Izd. Nauka, Moscow–Leningrad, 1965, p. 57
49. I V Martynov, Z I Khromova, Yu L Kruglyak *Problemy Organicheskogo Sinteza* (Problems in Organic Synthesis), Izd. Nauka, Moscow–Leningrad, 1965, p. 60
50. I V Martynov, Yu L Kruglyak, N F Privezentseva *Zh. Org. Khim.*, 1969, **5** 432
51. A I Yurtanov, S V Kovalenko, I V Martynov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2814
52. A I Yurtanov, A N Pushchin, S V Vitt, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 934
53. Z L Ovsyannikova, M K Baranaev, V K Kurochkin, et al. *Zh. Org. Khim.*, 1968, **4** 1209
54. J Chedin *C. R. Seances Acad. Sci.*, 1936, **202** 220, 1067
55. N C Marziano, P G Traverso, A De Santis, M Sampoli *J. Chem. Soc., Chem. Commun.*, 1978, 873
56. D S Ross, K E Kuhlmann, R Malhorta *J. Am. Chem. Soc.*, 1983, **105** 4299
57. A I Titov *Zh. Obshch. Khim.*, 1948, **18** 190
58. A N Baryshnikov, A I Titov *Dokl. Akad. Nauk SSSR*, 1953, **91** 1099
59. A I Titov *Usp. Khim.*, 1958, **27** 845
60. M I Boeseken *Recl. Trav. Chim. Pays-Bas*, 1913, **32** 17
61. I L Knunyants, A V Fokin *Dokl. Akad. Nauk SSSR*, 1956, **111** 1035
62. I L Knunyants, A V Fokin *Dokl. Akad. Nauk SSSR*, 1957, **112** 67
63. I L Knunyants, A V Fokin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1957, 1439
64. E R Bissell *J. Org. Chem.*, 1961, **26** 5100
65. I L Knunyants, A V Fokin, V A Komarov *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1962, **7** 709
66. A V Fokin, A T Uzun, Yu M Kosyrev *Zh. Obshch. Khim.*, 1966, **36** 540
67. I L Knunyants, A V Fokin, Yu M Kosyrev *Zh. Obshch. Khim.*, 1967, **37** 2011
68. A V Fokin, V A Komarov, A A Skladnev, S M Davydova *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1964, **9** 710
69. A V Fokin, V A Komarov, A A Skladnev, S M Davydova *Zh. Obshch. Khim.*, 1965, **35** 1662
70. A V Fokin, V A Komarov, A A Skladnev, S M Davydova *Zh. Obshch. Khim.*, 1965, **35** 1664
71. A V Fokin, A T Uzun, A I Bol'shakova, USSR P. 168 677; *Ref. Zh. Khim.*, 1966, 17H93
72. A V Fokin, A T Uzun *Zh. Obshch. Khim.*, 1966, **36** 117
73. I L Knunyants, Yu A Sizov, O V Ukharov *Usp. Khim.*, 1983, **52**(6) 976 [English translation in *Russ. Chem. Rev.*, 1983(6)]
74. A V Fokin, Yu M Kosyrev, A T Uzun *Zh. Obshch. Khim.*, 1966, **36** 119
75. I L Knunyants, A V Fokin, Yu M Kosyrev *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1963, 1772
76. A V Fokin, Yu M Kosyrev, I N Sorochkin, V P Radchenko *Zh. Obshch. Khim.*, 1967, **37** 633
77. R A Bekker, B L Dyatkin, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1966, 194
78. B L Dyatkin, R A Bekker, I L Knunyants *Dokl. Akad. Nauk SSSR*, 1966, **168** 1319
79. A V Fokin, K V Frosina, V A Komarov *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1967, **12** 357
80. I V Martynov, V K Brel', A N Chekhlov *Tezisy Dokladov V Vsesoyuznoi Konferentsii po Khimii Ftororganicheskikh Soedinenii* (Abstracts of Reports at the Vth All-Union Conference on the Chemistry of Organofluorine Compounds), Moscow, 1986, p. 80
81. L W Kissinger, H E Ungnade *J. Org. Chem.*, 1959, **24** 1244

82. W Steinkopf, M Kuhnel *Ber. Bunsenges Phys. Chem.*, 1942, **75** 1323
83. I V Martynov, V O Zavel'skii, S V Kovalenko, A I Yurtanov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1029
84. Yu Ya Ivanov, V K Brel', L V Postnova, I V Martynov *Khim.-Farm. Zh.*, 1985, 968
85. I V Martynov, A I Yurtanov, Yu Ya Ivanov, et al. *Dokl. Akad. Nauk SSSR*, 1986, **289** 109
86. A I Yurtanov, E V Kulish, I V Martynov *Tezisy Dokladov VI Mezhdunarodnoi Konferentsii po Organicheskomu Sintezu* (Abstracts of Reports at the VIth International Conference on Organic Synthesis), Moscow, 1986, p. 73
87. H Britzinger, I Jancke *Ber. Bunsenges Phys. Chem.*, 1950, **83** 103
88. L W Kissinger, H E Ungnade *J. Org. Chem.*, 1958, **23** 1517
89. V V Perekalin, A S Sopova, E S Lipina *Nepredel'nye Nitrosoedineniya* (Unsaturated Nitro Compounds), Izd. Khimiya, Leningrad, 1982, p. 211
90. V A Buevich, N Zh Nakova *Zh. Org. Khim.*, 1977, **13** 2619
91. V A Buevich, N Zh Nakova, V V Perekhalin *Zh. Org. Khim.*, 1979, **15** 1473
92. V A Buevich, N Zh Nakova, G Kempter, V V Perekalin *Zh. Org. Khim.*, 1977, **13** 2618
93. H Feuer, J W Shepherd, C Savides *J. Am. Chem. Soc.*, 1957, **59** 5768
94. A A Skladnev, A F Kolomiets, Z N Kvasha, Yu N Studnev, USSR P. 143 387; *Ref. Zh. Khim.*, 1963, 3H77
95. A A Skladnev, A F Kolomiets, Z N Kvasha, Yu N Studnev, USSR P. 140 057; *Byull. Izobret.*, 1961, (15)
96. A V Fokin, A A Skladnev, V A Komarov *Zh. Obshch. Khim.*, 1963, **33** 3271
97. A V Fokin, V A Komarov, K V Frosina, USSR P. 124 428; *Byull. Izobret.*, 1959, (23)
98. A V Fokin, V P Stolyarov, A N Voronkov, S S Il'in *Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Khimii Ftororganicheskikh Soedinenii* (Abstracts of Reports at the IVth All-Union Conference on the Chemistry of Organofluorine Compounds), Tashkent, 1982, p. 192
99. E R Bissell *J. Org. Chem.* 1963, **28** 1717
100. V A Ginsburg, N F Privezentseva, N P Rodionova, et al. *Zh. Obshch. Khim.*, 1960, **30** 2406
101. E R Bissell, US P. 3 267 134 (1966)
102. A V Fokin, V A Komarov, A F Kolomiets, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 707
103. A V Fokin, A I Rapkin, T M Potarina, et al. *Tezisy Dokladov III Vsesoyuznoi Konferentsii po Khimii Ftororganicheskikh Soedinenii* (Abstracts of Reports at the IIrd All-Union Conference on the Chemistry of Organofluorine Compounds), Odessa, 1978, p. 97
104. A V Fokin, A I Rapkin, V A Komarov, T M Potarina *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 2400
105. O A Raevskii, T B Chenskaya, A I Yurtanov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 885
106. I V Martynov, E V Stoyankova, A I Yurtanov *Zh. Org. Khim.*, 1982, **18** 1849
107. A I Yurtanov, I V Martynov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1572
108. I V Martynov, V O Zavel'skii, S V Kovalenko, et al. *Dokl. Akad. Nauk SSSR*, 1983, **269** 152
109. V I Shestov, V O Zavel'skii, V K Brel', et al. *Tezisy Dokladov V Vsesoyuznoi Konferentsii po Khimii Ftororganicheskikh Soedinenii* (Abstracts of Reports at the Vth All-Union Conference on the Chemistry of Organofluorine Compounds), Moscow, 1986, p. 124
110. V I Shestov, I V Martynov, V O Zavel'skii, et al. *Zh. Obshch. Khim.*, 1986, **56** 1393
111. I V Martynov *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1985, **30** 227
112. V P Novikov, A V Yarkov, A V Golubinskii, et al. *Tezisy Dokladov III Vsesoyuznogo Soveshchaniya "Stroenie i Svoistva Polimetallicheskikh Metalloorganicheskikh Soedinenii"* (Abstracts of Reports at the IIIrd All-Union Conference "The Structure and Properties of Polymetallic Organometallic Compounds"), Gor'kii, Chernogolovka, 1981, p. 40
113. A A Butakov, I V Martynov, V M Pichkasov, A I Yurtanov *Material II Vsesoyuznoi Konferentsii "Nestatsionarnye Protsessy v Katalize"* (Data from the IInd All-Union Conference "Nonstationary Processes in Catalysis"), Novosibirsk, 1983, p. 21
114. A N Chekhlov, A I Yurtanov, I V Martynov *Dokl. Akad. Nauk SSSR, Ser. Khim.*, 1985, **282** 323
115. A N Chekhlov, A I Yurtanov, I V Martynov *Kristallografiya*, 1986, **31** 270
116. *International Tables for X-Ray Crystallography, Vol. 3*, Kynoch Press, Birmingham, 1968, pp 270, 275, 276
117. A I Chekhlov, V K Brel', I V Martynov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2446
118. H G Adolph, M J Kamlet *J. Am. Chem. Soc.*, 1966, **88** 4761
119. A I Tal'vik *Reaktsionnaya Sposobnost' Org. Soedin.*, 1972, **9** 233
120. O A Reutov, I P Beletskaya, K P Butin *CH-Kisloty* (CH-Acids), Izd. Nauka, Moscow, 1980, p. 83
121. R G Pearson, R L Dillon *J. Am. Chem. Soc.*, 1953, **75** 2439
122. I V Martynov, V P Solov'ev, L V Govorkova, et al. *Zh. Obshch. Khim.*, 1986, **56** 2516
123. E L Hirst, A K Macbeth *J. Chem. Soc.*, 1922, 904
124. I V Martynov, Yu L Kruglyak *Zh. Obshch. Khim.*, 1965, **35** 248
125. I V Martynov, A N Degtyarev *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 650
126. I V Martynov, Yu L Kruglyak *Problemy Organicheskogo Sinteza* (Problems in Organic Synthesis), Izd. Nauka, Moscow–Leningrad, 1965, p. 56
127. I V Martynov, Yu L Kruglyak, A V Fokin, I L Knunyants, USSR P. 159 821; *Byull. Izobret.*, 1964, (2)
128. I V Martynov, V K Brel', L V Uvarova, V I Uvarov *Tezisy Dokladov V Vsesoyuznoi Konferentsii po Khimii Ftororganicheskikh Soedinenii* (Abstracts of Reports at the Vth All-Union Conference on the Chemistry of Organofluorine Compounds), Moscow, 1986, p. 97
129. I V Martynov, V K Brel', L V Uvarova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 952
130. I V Martynov, V K Brel', V I Uvarov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 1420
131. I L Knunyants, A V Fokin, V S Blagoveshchenskii, Yu M Kosyrev, *Dokl. Akad. Nauk SSSR*, 1962, **146** 1088
132. I V Martynov, R Kh Bikkineev, V I Uvarova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 941

133. *Kratkaya Khimicheskaya Entsiklopediya* (A Short Chemical Encyclopaedia), Sovetskaya Entsiklopediya, Moscow, 1964, Vol. 3, p. 530
134. W Steinkopf, B Jurgens *J. Prakt. Chem.*, 1911, **83** 453
135. I V Martynov, Yu L Kruglyak *Zh. Obshch. Khim.*, 1967, **37** 1221
136. *Kratkaya Khimicheskaya Entsiklopediya* (A Short Chemical Encyclopaedia), Sovetskaya Entsiklopediya, Moscow, 1961, Vol. 1, p. 1056
137. V A Buevich, N N Lazareva *Zh. Org. Khim.*, 1983, **19** 885
138. A N Voronkov, A V Fokin *Tezisy Dokladov III Vsesoyuznoi Konferentsii po Ftororganicheskikh Soedinenii* (Abstracts of Reports at the IIIrd All-Union Conference on the Chemistry of Organofluorine Compounds), Odessa, 1978, p. 99
139. I V Martynov, V K Brel', L V Postnova, B I Martynov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 2832
140. I V Martynov, V K Brel', L V Uvarova, V I Uvarov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2790
141. I V Martynov, Yu L Kruglyak *Zh. Obshch. Khim.*, 1967, **37** 1221
142. M E Hill, L O Ross *J. Org. Chem.*, 1967, **32** 2595
143. E R Bissell, D B Fields *Tetrahedron*, 1970, **26** 5737
144. A V Fokin, A T Uzun *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 2350
145. A V Fokin, Yu N Studnev, V P Stolyarov, N N Baranov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 937
146. A V Fokin, Yu N Studnev, A I Rapkin, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1592
147. V P Sass, A N Voronkov, T A Nadervel', et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 2353
148. S Trippet, D M Walker *J. Chem. Soc.*, 1959, 3874
149. S Trippet, D M Walker *J. Chem. Soc.*, 1960, 2976
150. S Trippet, D M Walker *J. Chem. Soc.*, 1965, 7140
151. I V Martynov, Yu L Kruglyak *Zh. Obshch. Khim.*, 1967, **37** 1132
152. Yu L Kruglyak, G A Leibovskaya, I V Martynov *Zh. Obshch. Khim.*, 1969, **39** 1263
153. I V Martynov, Yu L Kruglyak, N F Privezentseva *Khimiya i Primenenie Fosfororganicheskikh Soedinenii* (The Chemistry and Use of Organophosphorus Compounds), Izd. Nauka, Moscow, 1972, p. 273
154. J F Allen *J. Am. Chem. Soc.*, 1957, **79** 3071
155. M V Tsybul'skaya, Yu Ya Ivanov, A I Yurtanov, I V Martynov, Manuscript Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 22.5.85, No. 3529-85; *Ref. Zh. Toksikol.*, 1985, (8) 75
156. Yu Ya Ivanov, V K Brel', I V Martynov *Dokl. Akad. Nauk SSSR*, 1984, **279** 506
157. Yu Ya Ivanov, V K Brel', L V Postnova, I V Martynov, Manuscript Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 12.3.85, No. 3481-85
158. Yu Ya Ivanov, N L Rezaeva, V K Brel', I V Martynov *Fiziologiya i Biokhimiya Mediatornykh Protsessov. Tezisy Dokladov IV Vsesoyuznoi Konferentsii* (Abstracts of Reports at the IVth All-Union Conference on the Physiology and Biochemistry of Mediator Processes), Vol. 1, Moscow, 1985, p. 133
159. E F Volkova, Yu Ya Ivanov, A I Yurtanov, et al. *Biol. Eksperim. Biologii i Meditsiny*, 1986, (3) 384
160. S O Bachurin, B K Beznosko, V K Brel', et al. *Tezisy Dokladov V Vsesoyuznogo Simpoziuma "Poluchenie i Primenenie Biokatalizatorov v Narodnom Khozyaistve i Meditsine"* (Abstracts of Reports at the Vth All-Union Symposium "The Preparation and Use of Biocatalysts in the National Economy and in Medicine"), Vol. 1, Kobuleti, 1985, p. 136
161. V Yu Shadrin, A S Polyanskaya, V V Perekalin *Sintez i Issledovanie Nitrosoedinenii i Aminokislot* (Synthesis and Study of Nitro Compounds and Amino Acids), Leningrad, 1986, p. 31
162. V A Petrosyan, M E Niyazymbetov, B V Lyalin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 306
163. Y Takeuchi, K Nagata, T Koizumi *J. Org. Chem.*, 1987, **52** 5061
164. I V Martynov, V I Anufriev, V I Uvarov, V K Brel' *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 700
165. J Czarnowski *J. Fluorine Chem.*, 1987, **37** 41
166. I V Martynov, V I Uvarov, V K Brel', G I Tsyganova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1406
167. H Feuer, H S Bevinakatti, X-G Luo *J. Heterocycl. Chem.*, 1987, **24** 9
168. I V Martynov, V K Brel', V I Uvarov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 466
169. I V Martynov, V K Brel', V I Uvarov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2639
170. V K Brel', V I Uvarov, I V Martynov, et al. *Tezisy Dokladov V Vsesoyuznogo Simpoziuma po Organicheskomu Sintezu "Novye Metody i Reagenty v Tonkom Organicheskom Sinteze"* (Abstracts of Reports at the Vth All-Union Symposium on Organic Synthesis, "New Methods and Reagents in Fine Oragnic Synthesis"), Izd. Nauka, Moscow, 1988, p. 45
171. V I Uvarov, V K Brel', I V Martynov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2650
172. V I Uvarov, Abstract of Candidate's Thesis, Institute of Physiologically Active Compounds, USSR Academy of Sciences, Chernogolovka, 1988
173. V K Brel', M V Dodonov, A N Chekhlov, I V Martynov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 890
174. I V Martynov, V I Uvarov, V K Brel', et al. *Zh. Obshch. Khim.*, 1988, **58** 1538
175. A I Yurtanov, E S Naidovskii, Yu P Belov, I V Martynov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1162
176. A I Yurtanov, A N Chekhlov, I V Martynov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1430
177. A I Yurtanov, A V Yarkov, T I Ignat'eva, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2549
178. A I Yurtanov *Tezisy Dokladov V Vsesoyunogo Simpoziuma po Organicheskomu Sintezu "Novye Metody i Reagenty v Tonkom Organicheskom Sinteze"* (Abstracts of Reports at the Vth All-Union Symposium on Organic Synthesis, "New Methods and Reagents in Fine Organic Synthesis"), Izd. Nauka, Moscow, 1988, p. 69
179. A I Yurtanov, A N Chekhlov, I V Martynov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2431
180. A I Yurtanov *Tezisy Dokladov VI Vsesoyuznogo Soveshchaniya po Khimii Nevodnykh Rastvorov Neorganicheskikh i Kompleksnykh Soedinenii* (Abstracts of Reports at the VIth All-Union Conference on the Chemistry of Nonaqueous Solutions of Inorganic and Complex Compounds), Izd. Nauka, Rostov-on-Don – Moscow, 1987, p. 77
181. A I Yurtanov, A N Chekhlov, I V Martynov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 214

182. V I Shestov, I V Martynov, A I Yurtanov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1998
183. A N Chekhlov, A I Yurtanov, I V Martynov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1300
184. A N Chekhlov, V I Anufriev, I V Martynov *Dokl. Akad. Nauk SSSR*, 1988, **303** 1420
185. A N Chekhlov, A I Yurtanov, I V Martynov *Koord. Khim.*, 1987, **13** 1541
186. A N Chekhlov, I V Martynov, V K Brel' *Dokl. Akad. Nauk SSSR*, 1987, **292** 149
187. Yu Ya Ivanov, V I Uvarov, V K Brel', I V Martynov *Khim.-Farm. Zh.*, 1988, 538
188. A I Yurtanov, I V Martynov *Pestocydy* , 1988, (3) 62
189. I V Martynov, S O Bachurin, B K Beznosko, et al., USSR P. 1 432 052; *Byull. Izobret.*, 1988, (39) 76
190. I V Martynov, S O Bachurin, V K Brel', et al. *Khim.-Farm. Zh.*, 1988, **22** 1339
191. B K Beznosko, S O Bachurin, V K Brel', et al. *Dokl. Akad. Nauk SSSR*, 1989, **304** 461
192. Y Takeuchi, M Asahina *J. Org. Chem.*, 1986, **51** 955
193. Y Takeuchi, M Asahina, K Nagata, T Koizumi *J. Chem. Soc., Perkin Trans. I*, 1987, 2203
194. Y Takeuchi, M Asahina, K Nagata *J. Liq. Chromatogr.*, 1987, **10** 3279
195. Y Takeuchi, M Nojiri, T Koizumi, Y Iitaka *Tetrahedron Lett.*, 1988, **29** 4727
196. J H Boyer, T Manimaran *Heterocycles*, 1988, **55** 2059

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Extraction with thio and dithio phosphorus acids

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ABSTRACT. The main physicochemical characteristics of thio and dithio phosphorus acids—acid and redox properties, stability in solution, tautomerism, association and solubility in nonaqueous media, distribution in water–organic solvent systems—are reviewed. The effect of the structure of the reagents on their properties is analysed. The optimum conditions and chemical nature of extraction, the effect of substituents and diluents on the extract of metal dialkyldithiophosphates is discussed. Examples are given of the effective use of thio and dithio phosphorus acids for the separation of elements and the isolation of Cu, Hg(II), Tl(I), Sn(II), As(III), and Bi from other elements. The potential application of the extraction of elements with thio and dithio phosphorus acids is examined.

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I. Introduction

There is no standard nomenclature for dithio phosphorus acids. In the English literature dithio phosphorus acids are more frequently called dialkyldithiophosphoric acids or dialkyl dithiophosphates. The term "dialkyl dithiophosphates" emphasises that they are classed as partial esters of dithiophosphoric acid. Correspondingly for thio acids, the terms dialkylthiophosphoric acids and dialkyl thiophosphates are more widely used. In the German literature these reagents are called dithiophosphate esters. In the Russian literature the terms dialkyl- and diaryl-dithiophosphoric acids have become established, *O*,*O*-dialkyl- and *O*,*O*-diaryl-dithiophosphoric acids are to be found less often. In the Russian literature the term dialkyldithiophosphates relates to complex compounds such as nickel diethyldithiophosphate, etc. In this review we have used the terms dialkyl- and diaryl-dithiophosphoric acids and dialkyl- and diaryl-thiophosphoric acids respectively. Complex compounds of elements with these reagents are to be known as dialkyldithiophosphates.

The ability of complex compounds of metals with organic thio and dithio phosphorus acids to be extracted into various solvents was established back in 1949,[1,2] and in 1965 a review on the extraction of these complexes was published.[3] A large amount of material on the extraction of thiophosphates and dithiophosphates has been collected up to the present time and it requires classification. The range of extractants has been extended, the mechanism of extraction has been studied, and schemes for the separation of elements have been developed. In particular, the optimum conditions for extracting many elements with diethyldithiophosphoric acid (DEDTPA),[3–9] di-n-butyldithiophosphoric acid (DBDTPA),[5,6] diphenyldithiophosphoric acid (DPDTPA),[10] and di-2-ethylhexyldithiophosphoric acid (D2EHDTPA)[5,7] have been found. For the extraction of heavy metals, salts of dialkyldithiophosphoric acids have also been used; these contain alkali metals,[9,11] zinc,[12] and nickel.[12,13] Metal dialkyldithiophosphates are more stable than the corresponding acids both in aqueous solution and in organic solvents, and they are also more selective, so their future use is promising.

In addition, the possible use of full esters of dialkyldithiophosphoric acids—*O*,*O*,*S*-trialkyl dithiophosphates,[14–17]—amides,[28,29] bis(dialkyldithiophosphoryl) disulphide,[30] and other derivatives as extractants has been examined.

The use of the extraction of dithiophosphates in a large group of combined methods is of interest.

Almost all dialkyldithiophosphates do not absorb light in the visible or near UV region of the spectrum. This is the reason why extraction spectrophotometry has not been widely developed. Only the determinations carried out on different compounds of copper,[31,32] bismuth,[33,34] and palladium,[35,36] which are based on the ability of Cu(II), Bi(III), and Pd(II) dialkyldithiophosphates to absorb in the visible region of the spectrum, constitute an exception.

The extraction of dithiophosphates is used on a large scale in extraction polarography. By combining extraction with polarography it is possible to determine metals that are present together without initially separating them. Thus, for example, Zn, Co(II), and Ni dithiophosphates are co-extracted, but they can be determined separately by polarography in a benzene–ethanol mixture with 0.2 M $LiClO_4$ as the supporting electrolyte.[37] The polarographic properties of the diethyldithiophosphates of Zn, Cd, Sb(III), Bi(III), Cr(III), U(VI), Mn(II), Fe(II), Ni,[38] Cu(II)[39,40] Pb(II), ^{12}Fe(II)[41], and Pd[42] have been studied. Complexes of elements with full d^{10} shells give reversible polarographic waves in the solvent mixture benzene–ethanol.

The electrolytic oxidation of heteroligand complexes of Cu, Co(II), and Ni with diethyldithiophosphoric acid and bases—2,2′-dipyridyl, 1,10-phenanthroline, and aminopyridine[43,44]—has been studied. Extraction polarography has been widely applied; the main theoretical conclusions and practical recommendations for its use are covered in a review.[45]

The trends towards the use of dialkyldithiophosphoric acids in extraction atomic absorption analysis have been outlined. Elements are determined after their initial extractive or adsorptive concentration (on active carbon) as dialkyldithiophosphates.

Diethyldithiophosphoric acid has been used for extractive concentration of As, Sb, and Bi from industrial nickel electrolytes,[46] for concentration of Cd, Pb, and Bi from sea-water on active carbon,[47] and of Cu, Cd, In, Tl, and Bi in the analysis of metallic aluminium and gallium.[48] Dibutyldithiophosphoric acid is a good reagent for the combined extraction and adsorptive concentration from sea-water of Cu, Zn, Cd, Pb, and Bi, which are then determined by atomic absorption spectroscopy.[49,50]

The first studies on the use of dialkyldithiophosphates in high-performance liquid chromatography indicate that it is possible to use the most stable of them, for example, silver dialkyldithiophosphates,[51] for concentration and separation from associated ions.

The aim of the present review is to correlate the data on the extraction of dithio- and thio-dithiophosphates and to identify the most important aspects of using them in analytical chemistry and the ways of developing them further.

II. Properties of thio and dithio phosphorus acids

1. Acid properties

Thio and dithio phosphorus acids are quite strong acids.[11,52–57] Aqueous solutions of recrystallised dialkyldithiophosphates of alkali and alkaline earth metals have a pH of 7, and as salts of strong acids, they are virtually unhydrolysed.[54] An aqueous 0.109 M solution of DEDTPA has a pH of 1, $K_a = 2.4 \times 10^{-2}$. The potentiometric titration curve of an aqueous solution of DEDTPA against a solution of NaOH is characteristic of strong monobasic acids. The centre of rapid change in potential corresponds exactly to pH 7. Potentiometric titration curves of aqueous solutions of DEDTPA and H_2SO_4 with the same molarity against a solution of NaOH virtually coincide in form and magnitude of sudden change at the equivalence point.[11]

Substituents on the phosphorus atom have little effect on the pK_a values of dialkyldithiophosphoric acids.[56–58] It was found by pH titration of dithio acids in aqueous ethanol solutions containing 40 vol. % ethanol with a constant ionic strength of 0.3 (KNO_3) and at a temperature of 25 ± 0.1 °C that the pK_a values of dithio acids have virtually no dependence on the nature of the substituents, and they are equal to 2.00–2.25.[58] The lack of dependence of the acid strength on the structure of alkyl and alkoxyl groups has been confirmed by a determination of pK_a in aqueous isopropanol solutions containing 90 vol. % isopropanol (pK_a values vary from 2.75 to 2.85).[59] According to other results the pK_a values of acids that have different substituents do not remain constant. Thus, an increase in the length of carbon chain of the substituents leads to a reduction in the acid strength: for DEDTPA $pK_a = -1.10$, while for DBDTPA $pK_a = 0.22$.[62] In absolute ethanol and aqueous ethanol mixtures the solvation conditions are not the same, causing a variation in acid strength by a factor of almost $10^{2.5}$ [53,60] (Table 1). Moreover, the difference in acid strengths may partly be due to a change in function of the glass electrode in absolute ethanol. The pK_a values of some dithio acids have also been determined in other solvents—for aliphatic dithio phosphorus acids they range from 3.60 to 4.40 in benzene and from 2.30 to 2.90 in anisole.[63] Acids with cyclic substituents on the phosphorus atom in benzene ($pK_a = 1.90–3.23$) or anisole ($pK_a = 0.62$-1.65) are stronger than acids that contain aliphatic groups.[63,64]

The dissociation constants of some acids in the presence of different salts ($NaClO_4$, NaCl) were determined spectrophotometrically. It was recorded[65] that compounds containing $P(S)S^-$ have a maximum absorption at 225 nm. A study of the absorption spectra of potassium dibutyldithiophosphate in perchloric and hydrochloric acid in relation to the acidity of the aqueous solution showed that the intensity of light absorption at 225 nm decreases as the concentration of mineral acid increases; this is due to the equilibrium being shifted towards formation of the undissociated form (HA) of the acid. The undissociated form (HA) and the conjugated form—dibutyldithiophosphate ion (A^-)—have different molar absorption coefficients ($\varepsilon_{HA} = 3.9 \times 10^3$ and $\varepsilon_{A^-} = 4.15 \times 10^3$). The average molar absorption coefficients of DBDTPA at 225 nm in solutions of different acidity ($\mu = 1.0$; $NaClO_4$) are given below:[65]

c_{H^+}, M	1.03	0.72	0.31	0.185	0.103
$\bar{\varepsilon}$	4039	4062	4097	4116	4130 .

Table 1. Dissociation constants of dithio and thio phosphorus acids in aqueous ethanol solutions and in anhydrous ethanol.

Acid	pK_a values for ethanol content (vol.%)				Refs.
	7	40 (μ=0,3)	80	100	
$HS(S)P(OC_2H_5)_2$	1.64		2.65	2.84	[60]
		2.00			[55]
$HO(S)P(OC_2H_5)_2$		1.83			[55]
$HS(S)P(C_2H_5)_2$	1.74		2.62	5.06	[60]
		2.62			[55]
$HO(S)P(C_2H_5)_2$		3.60			[55]
$HS(S)P(OC_2H_5)(CH_3)$				3.46	[60]
$HS(S)P(n\text{-}C_3H_7)_2$		2.55			[61]
$HS(S)P(iso\text{-}C_3H_7)_2$	1.85		2.74	2.83	[60]
$HO(S)P(n\text{-}C_3H_7)_2$		2.61			[61]
$HS(S)P(C_2H_5)(n\text{-}OC_3H_7)$		2.82			[61]
$HS(S)P(C_2H_5)(n\text{-}OC_4H_9)$		2.89			[61]
$HS(S)P(OC_6H_5)_2$	1.84		2.75	2.41	[60]
$HS(S)P(C_6H_5)_2$	1.77		2.69	3.48	[60]
$HS(S)P(n\text{-}C_6H_4CH_3)_2$	1.84		2.74	3.93	[60]

In $HClO_4$ the dissociation constant of DBDTPA is equal to −0.24 and in HCl it is equal to −0.09 (in pK_a units) (spectrophotometric determination).[65] These values are not in agreement with those found by the distribution method: 0.28 and 0.22 in $HClO_4$ and HCl respectively.[65,66] For dimethyldithiophosphoric acid (DMDTPA), $pK_a = -0.33$.[67]

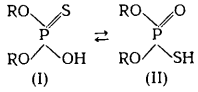
2. Stability in solution

Dialkyldithiophosphoric acids can decompose in aqueous solution with elimination of H_2S and alcohol, but they are more stable than diethyldithiocarbamic acid and xanthic acid.[11] It is assumed that thio phosphorus acids in aqueous solution are hydrolysed on the thiol group. The salts of these acids in aqueous solution are more stable. Thus, the concentration of the sodium salt of DEDTPA remains constant (120 μg ml^{-1}) for a month, while there is 9% decomposition of DEDTPA during this time. In 1 M HCl the decomposition half-life of DEDTPA is 250 h[11] while in 10 M HCl it is 4.8 h. For comparison, diethyldithiocarbamic acid has a decomposition half-life of 1–2 h. DEDTPA decomposes

more slowly in sulphuric acid than in hydrochloric acid of the same concentration.[11,68] Diphenyldithiophosphoric acid does not decompose in neutral or acidic solutions over a period of two months.[69] The decomposition of dialkyldithiophosphoric acids is a first-order reaction. Dialkyldithiophosphoric acids are stable in organic solvents.[11]

3. Tautomerism

A tautomeric conversion of the thione form (I) ⇄ thiol form (II) is characteristic of thio phosphoric acids:[53]



(I) (II)

In aqueous solution the equilibrium is shifted towards the thiol form; in ethanol the thione form predominates.

4. Distribution in the system water–organic solvent

The behaviour of dithio acids in water–organic solvent systems has not been studied in sufficient detail and is only known for acids that are used as extractants. In particular, the extraction of diethyl–, diisopropyl-, di-n-butyl-, diisobutyl- and di-2-ethylhexyl-dithiophosphoric acids has been studied.[52,70] The acid distribution constants and the acidic dissociation constants have been determined in the system HCl–CCl_4 (Table 2). An increase in the length of the hydrocarbon group leads to some reduction in acidic properties, which is in agreement with other results;[62] this applies particularly to DEDTPA and D2EHDTPA (Table 2).

Table 2. Distribution constants and dissociation constants (in pK_a units) of some dialkyldithiophosphoric acids when $\mu = 1$ at 25 °C.[52,70]

Alkyl group	Solvent	$pH_{1/2}$*	$\lg K_D$	pK_a**
Ethyl-	Carbon tetrachloride	0.35	0.45	−0.10
Isopropyl-	"	1.89	1.90	0.00
n-Butyl-	"	2.70	2.52	−0.22
	Methyl isobutyl ketone	2.77	2.54	−0.25
	n-Amyl acetate	2.40	2.23	−0.18
Isobutyl-	Carbon tetrachloride	2.74	2.63	−0.10
2-Ethylhexyl-	"	4.17	5.42	−1.25
	n-Heptane	—	5.43	—
	Benzene	—	5.39	—

*$pH_{1/2} = pK_a + \log K_D$, where K_D is the distribution constant of dialkyldithiophosphoric acid (organic phase saturated with the aqueous phase and aqueous phase saturated with the organic phase); **K_a is acid dissociation constant in water saturated with the organic solvent.

The extraction of DBDTPA into CCl_4 decreases at an acid concentration of 6 M regardless of the nature of the mineral acid (HCl, HBr, H_2SO_4, $HClO_4$, HNO_3).[52] The effect of ionic strength on the distribution of dithio acids is complex in nature. For example, in the extraction of DBDTPA from solutions with a constant HCl content, the addition of NaCl initially leads to a reduction and then to a marked increase in distribution coefficient of the reagent.[52] Dithio acids are not extracted from weakly alkaline and neutral solutions; this is due to the formation of dithiophosphate anions. The extraction of DPDTPA from solutions of HCl, HNO_3, and H_2SO_4 has been studied. It is at a maximum when 2–7 M solutions are used. However, the distribution constants and dissociation constants have not been determined.[10] These values are generally difficult to determine separately for dialkyldithiophosphoric acids, therefore the ratio K_D/K_a, that is, the two-phase stability constant, is frequently determined (Tables 3 and 4).

Table 3. Logarithms of two-phase stability constants $\log(K_{D,HA}/K_{a,HA})$ of dithio phosphorus acids $(RO)_2P(S)SH$ in the system water–nonpolar organic solvent[71,72]

R	$\lg(K_{D,HA}/K_{a,HA})$ in		
	heptane	CCl_4	toluene
C_3H_7-	—	1.71	1.88
iso-C_3H_7-	—	1.99	2.12
C_4H_9-	2.10	2.98	3.12
iso-C_4H_9-	2.00	2.93	3.01
sec-C_4H_9-	2.48	3.36	3.44
C_5H_{11}-	3.36	4.23	4.38
iso-C_5H_{11}-	3.10	4.02	4.11
sec-C_5H_{11}-	3.80	4.64	4.71

Table 4. Logarithms of two-phase stability constants $\log(K_{D,HA}/K_{a,HA})$ of DBDTPA and MHDTPA in the system 1 M $HClO_4$–organic solvent.[72]

Solvent	$\lg(K_{D,HA}/K_{a,HA})$	
	DBDTPA	MHDTPA
Toluene	3.12	3.05
Carbon tetrachloride	2.98	2.89
	3.05*	2.88*
Cyclohexane	2.40	—
Heptane	2.10	1.97
Dodecane	1.94	—

*$\log(K_{D,HA}/K_{a,HA})$ values determined in the system CCl_4–1 M NaCl.

5. Polymerisation and solubility in nonaqueous media

Dialkyldithiophosphoric acids, in contrast to phosphoric acids, have no tendency to polymerise in nonaqueous media.[73] However, the association of dithio and thio phosphorus acids in nonaqueous solvents has not been studied in sufficient detail. It is known that DBDTPA does not form dimers or polymers in CCl_4, methyl isobutyl ketone, and amyl acetate.[52] It was also established by cryoscopy that there were no dimers or more complex associated forms of DEDTPA in benzene.[74] D2EHDTPA also does not polymerise in nonaqueous media.[74] An analysis of the IR spectra of DMDTPA and DEDTPA showed that in dilute solutions in CCl_4 these acids were present to a considerable extent as

monomers.[75]

On the basis of the results of a two-phase titration of DBDTPA and methylheptyldithiophosphoric acid (MHDTPA) in cyclohexane and dodecane, a solubility parameter was calculated, which can be applied to all acids with unbranched groups when the number of carbon atoms does not exceed eight.[76] Compounds with a P(S)SH group are characterised by a lower intermolecular interaction energy than the corresponding oxygen-containing compounds. Thus, dithio phosphorus acids have a lower tendency to dimerise through formation of intermolecular hydrogen bonds than, for example, dibutylphosphoric acid.[73] However, the high polarisability of the sulphur atoms assists the interaction of dithio acids with a polar solvent. Therefore, it may be assumed that it is possible to determine solubility parameters more accurately in a nonpolar solvent than in a polar one which is subject to the inductive effect.[76]

6. Redox properties

Dialkyldithiophosphoric acids exhibit reducing properties and are readily oxidised with mild oxidising agents such as iodine to form bis(dialkyldithiophosphoryl) disulphides $[(RO)_2P(S)S]_2$, which are solid, low-melting compounds that are slightly soluble in water.[77] For example, the solubility of bis(dimethyldithiophosphoryl) disulphide in water at 25 °C is 4×10^{-5} M.[78] When dithio acids are treated with chlorine, the following reaction occurs[79]

$$2\,(RO)_2P\begin{matrix}\diagup S\\ \diagdown SH\end{matrix} + 3\,Cl_2 \rightarrow 2\,(RO)_2P\begin{matrix}\diagup S\\ \diagdown Cl\end{matrix} + S_2Cl_2 + 2\,HCl.$$

Anions of dialkyldithiophosphoric acids are oxidised on dropping mercury and platinum electrodes. The half-wave potential for diethyldithiophosphate ion (10^{-3} M) is -0.062 V on a dropping mercury electrode (relative to a saturated calomel electrode) and $+0.696$ V on a rotating platinum microelectrode.[80]

Dialkyldithiophosphate ions and their oxidation products form reversible redox systems for which the Nernst equation is valid.[78] Their reduction takes place in accordance with the following equation:

$$(RO)_2P(S)S{-}{-}S(S)P(OR)_2 + 2e \rightleftarrows 2\,(RO)_2P(S)S^-.$$

The potential of a system containing dialkyldithiophosphate ions and their insoluble oxidation products is given by the following equation:

$$E = E_0 - 0.058 \lg a_{(RO)_2P(S)S^-}.$$

As bis(dialkyldithiophosphoryl) disulphides are only slightly soluble in water, their saturated solution can be readily obtained by the addition of small quantities of iodine or previously synthesised bis(dialkyldithiophosphoryl) disulphide to a solution of dithiophosphate ions. In practice there is no need to introduce the oxidation product of dialkyldithiophosphate since the platinum electrode maintains a constant potential even in freshly prepared solutions of dialkyldithiophosphates; this is probably due to the presence of traces of reagent oxidation products in them. The measurement of redox potentials by a balancing method in the circuit

$$Pt\,|\,KS(S)P(OR)_2\ (m)\ |\,[(RO)_2P(S)S]_2\ (s),\ 0.1M\ KCl\,\|\,0.1\ M\ KCl,\ Hg_2Cl_2\,|\,Hg$$

gave the following results:[78]

R	E_0, V	R	E_0, V
CH_3	+0.315	C_6H_{13}	−0.015
C_2H_5	+0.255	iso-C_3H_7	+0.196
C_3H_7	+0.187	iso-C_4H_9	+0.158
C_4H_9	+0.122	iso-C_5H_{11}	+0.086
C_5H_{11}	+0.050		

As the length of the carbon chain of the RO group increases, the redox potential of the acid decreases. Dithio acids with branched substituents and also with a long unbranched chain are oxidised with somewhat greater difficulty than dithiophosphates with a small unbranched carbon chain.

The redox potentials found from potentiometric titration of aqueous ethanol solutions of dithiophosphinic acids against a 0.1 M solution of I_2 in 40% ethanol at pH 6.5 (phosphate buffer solution) have been determined.[61]

III. Extraction with thio and dithio phosphorus acids

1. Reagents used and optimum extraction conditions

The use of DMDTPA as an extractant has been studied less than the others. It is the most soluble in water and passes into the organic phase less effectively than the other acids. Moreover, DMDTPA complexes with metal ions are the least stable and are fairly readily soluble. This is likely to account for the limited use of DMDTPA in extraction chemistry.

A study of the extraction of nickel dimethyldithiophosphate $Ni[S_2P(OCH_3)_2]_2$ with toluene from a 1 M solution of a mixture of $Na[S_2P(OCH_3)_2]$ and $NaClO_4$ showed that the distribution coefficients of the complexes were low and varied from -2 to $+1$ (in $\log K_D$ units).[67] In the system water–toluene the equilibrium stops after 30 min. In the opinion of Wingefors[67] the extraction of nickel dimethyldithiophosphate from weakly acidic solutions is effected because of the large value of the distribution constant of the complex ($\log K_{D,2} > 2$). The complex is not associated in the organic phase even when there is a large concentration of nickel in the initial aqueous solution.

DMDTPA forms a complex with palladium that is insoluble in water but soluble in CCl_4, diethyl ether, and chloroform[35] and which is suitable for the extraction and photometric determination of palladium. The same acid can be used to extract uranyl ions from 0.005–0.01 M $HClO_4$ into benzene, but the distribution coefficients of the complex are very low.[81]

The extraction of diethyldithiophosphates of copper,[13,82,83] silver and gold,[9,82,84,85] bismuth,[86] iron(III),[83] noble metals,[9] ruthenium and osmium,[9,87] and palladium[42,88] has been extensively studied. The extraction conditions using DEDTPA from 0.1–10 M solutions of HCl and 0.05–7.5 M H_2SO_4 into CCl_4 for many elements have been described.[9]

Elements of Groups I–III as well as Zn, V(III), V(V), Nb, Ta, Sn(II), Cr(III), and rare earth elements do not form sparingly soluble compounds with DEDTPA and are not extracted.

Copper(II) is quantitatively extracted from 0.1–5 M solutions of HCl or 0.05–6 M solutions of H_2SO_4,[9] as well as from weakly acidic and neutral solutions.[13] At pH 9 it remains almost completely in aqueous solution. This was used as a basis for the successive extraction of copper and silver with a solution of DEDTPA into CCl_4.[2] Copper diethyldithiophosphate was used for a photometric determination of copper.[83] Silver was completely extracted with DEDTPA from a 0.1–3 M solution of HCl into CCl_4.[9] In a more recent study[82] it was shown that it can also be extracted from less acid solutions up to pH 11. Depending on the ratio of the component concentrations, gold(III) forms different products with DEDTPA. Gold(I) is completely extracted from acid

and neutral media, so DEDTPA has been used in an extraction-atomic absorption determination of gold (and silver) in natural water.[85]

Alkaline earth elements and zinc do not form complexes that can be extracted with DEDTPA. Cadmium is incompletely extracted from 0.1 – 10 M solutions of HCl or 0.05 – 5 M solutions of H_2SO_4, but is completely extracted from media with pH 3.0 – 7.0, and in the presence of 2,2′-dipyridyl it is extracted at pH 6.5 – 8.5.[41] Mercury(II) is quantitatively extracted from 0.1 – 5 M solutions of HCl or 0.1 – 7.5 M H_2SO_4, while mercury(I) is reduced to the metal.[9] A more recent study[89] showed that mercury(II) is extracted from media containing 5 M HCl (or 8 M H_2SO_4) up to pH 7. In this case the complex exists in the organic phase in monomeric form.

Indium is not completely extracted with DEDTPA from a 0.1 M solution of HCl, and thallium(I) is only extracted to the extent of 5%. Thallium(I) is readily extracted from weakly acidic solutions,[9] and in the presence of 2,2′-dipyridyl it is extracted at pH 6.5 – 7.0.[45] Thallium(III) is reduced to thallium(I) by the reagent (sometimes the reduction takes place over several hours).[9]

Germanium(IV) is not extracted from 3 M solutions of HCl, while from solutions with a lower HCl concentration the extraction is not quantitative.[9] Tin(II) and tin(IV) are also incompletely extracted from 0.1 – 10 M HCl or 0.05 – 5 M H_2SO_4.[9] Lead(II) is extracted with DEDTPA from acid, neutral, and alkaline solutions.[9]

Arsenic(III) is quantitatively extracted with DEDTPA from weakly acidic and strongly acidic solutions while arsenic(V) is not extracted under these conditions. Antimony(III) is effectively extracted from 0.1 – 12 M solutions of HCl or 0.05 – 2.5 M H_2SO_4; antimony(V) in this case is first reduced and then extracted as the diethyldithiophosphate.[4,9] Bismuth diethyldithiophosphate is extracted over an acidity range from 5 M HCl (2.5 M H_2SO_4) to pH 2.5.[9,34,86]

Selenium(IV) and tellurium(IV) are extracted with DEDTPA from weakly acidic and strongly acidic solutions. Selenium(VI) is only extracted from strongly acidic solutions, probably being reduced initially to selenium(IV). Tellurium(VI) is only 60% extracted even from a 10 M solution of HCl.[9] Uranyl ions are extracted from 0.0005 – 0.01 M solutions of $HClO_4$ into benzene in the form of uranyl diethyldithiophosphate with very low distribution coefficients.[81]

Rhenium(VII) is extracted as its diethyldithiophosphate to the extent of 20% from a 0.1 M solution of HCl to which has been added a 15% solution of $TiCl_3$, whereas it is not extracted at all from 6 M HCl. From a mixture of potassium perrhenate – sodium diethyldithiophosphate — $SnCl_2$ containing 1 – 3 M HCl, rhenium is extracted with benzene, chloroform, diethyl ether, ethyl acetate, isoamyl acetate, and isobutanol.[9]

Iron(III) is quantitatively extracted at pH 2 – 3 while at lower pH values it is reduced to iron(II).[9] In order to prevent the reduction of iron(III) the extraction is carried out in the presence of H_2O_2. The distribution constant of iron(III) diethyldithiophosphate for passage of the latter into hexane is equal to 51.9.[83] At low concentrations cobalt(II) does not react with sodium diethyldithiophosphate in aqueous solution, but on extraction from solutions with a high cobalt concentration the extract changes to a green colour[4] which is characteristic of a complex of cobalt(III) with DEDTPA. Cobalt(II) diethyldithiophosphate in the extract is oxidised with atmospheric oxygen after several hours.[9] In the presence of 2,2′-dipyridyl, cobalt(II) is extracted with DEDTPA at pH 5.5 – 10.0.[45] Nickel(II) is incompletely extracted from 50% CH_3COOH with sodium diethyldithiophosphate.[4] The extraction becomes quantitative when the operation is repeated four times. In the presence of 2,2′-dipyridyl, Ni(II) is extracted at pH 0.5 – 2.0.[41]

Ruthenium(III) is extracted with carbon tetrachloride at room temperature in the presence of diethyldithiophosphate ions from a 0.1 – 10 M solution of HCl or a 0.05 – 7.5 M solution of H_2SO_4.[9] Osmium(IV) is not quantitatively extracted with DEDTPA from a 0.1 – 8 M solution of HCl or a 0.05 – 6 M solution of H_2SO_4 into carbon tetrachloride. Iridium(III) and rhodium(III) are not extracted from media containing HCl or H_2SO_4.[9] Iridium(IV) is reduced by the reagent to iridium(III), but iridium(III) diethyldithiophosphate precipitates out incompletely. The precipitate is extracted with chloroform and carbon tetrachloride.[4]

Platinum(II) is effectively extracted from acid solutions.[4] If platinum(IV) is reduced to platinum(II) in the presence of diethyldithiophosphate ions using $SnCl_2$, it is rapidly extracted from 1 – 10 M solutions of HCl into CCl_4 as a complex with the ratio $Pt:A^- = 1:2$.[90] Palladium is extracted from neutral and weakly alkaline solutions.[4,9] The reagent has been used to determine palladium in ore.[88]

Diethyldithiophosphates form the following series of extractability: As(III) > Bi > Pb > Zn > Ni > Co > Cd.[9,61,73] However, this series, which corresponds to the optimum extraction conditions, needs to be adjusted (this concerns, for instance, the positions of Cd and Zn) and requires a quantitative characterisation.

Diisopropyldithiophosphoric acid (DIPDTPA), like the other acids, forms coloured compounds with Cu(II), Bi, Pd(II), and Pt(II) ion.[35] The extraction of copper with zinc diisopropyldithiophosphate into CCl_4 is quantitative from 0.1 – 5 M HCl, 0.05 – 2.5 M H_2SO_4, 0.1 – 5 M $HClO_4$, 0.1 – 1.5 M H_3PO_4, or 0.1 – 2 M HNO_3.[91] The extraction of copper from less acid solutions has not been studied. Bismuth diisopropyldithiophosphate is also extracted from acid solutions. The extracts are characterised by a maximum absorption of light at 350 nm. It is possible to determine photometrically 5 – 70 μg of bismuth in 5 ml of chloroform.[92] Uranyl ions are extracted with DIPDTPA from 0.0005 – 0.01 M solutions of $HClO_4$ into benzene but the distribution coefficients are very low.[81]

Dibutyldithiophosphoric acid (DBDTPA) has been studied as an extractant fairly comprehensively.[5] Out of 42 elements studied, 22 have been satisfactorily extracted from media containing 0.03 – 9 M HCl or 0.1 – 18 M H_2SO_4. The extraction only requires a few minutes and is carried out in a single operation. The concentrations of metal can vary over a wide range from submicrogram to milligram quantities per ml of solution.[5] Ag and Bi(III) ions are quantitatively extracted with DBDTPA even from 1×10^{-7} M solutions of their salts. The maximum extractable quantity of metal depends on the initial concentration of DBDTPA in the organic phase, the ratio of volumes of the phases, and the solubility of the complex formed in the organic solvent.

According to the results of Handley and Dean,[5] Ag and Hg(II) are extracted with DBDTPA from an acid medium up to pH 10. Copper(II) and palladium are extracted from ammonia solutions with pH 8. The extraction of silver and palladium cannot solely be attributed to an exchange reaction with DBDTPA and its salts.[6,8] Evidently a coordination and ionic interaction is also occurring in this case. The passage of zinc dibutyldithiophosphate into CCl_4 and heptane from perchloric acid[93] and hydrochloric acid[94] has been characterised in considerable detail (Table 5). For comparison, in the extraction of a complex of cadmium with DBDTPA using carbon tetrachloride from a 1 M solution of HCl with an ionic

strength of 1, $\log K_{ex} = 5.3$; $\log \beta_2 = 9.7$; $\log K_D = 0.9$; $\log(K_{D,2}\beta_2) = 10.6$ [here, $\log(K_{D,2}\beta_2)$ is the two-phase stability constant].[95]

Table 5. The distribution of zinc dialkyldithiophosphate in different systems.

Alkyl	lg K_{ex}	lg β_2	lg K_D	lg $(K_{D,2}\beta_2)$
	CCl_4–1 M HCl (Ref.94)			
Ethyl-	—10			—9.3
Butyl-	1.22	3.81	2.77	6.57
Isobutyl-	1.29	4.00	2.70	5.77
sec-Butyl-	1.37		2.77	
2-Ethylhexyl-	1.40		2.86	
	CCl_4–$HClO_4$ (Ref.93)			
Butyl-	1.67	2.27	5.37	6.05
	Heptane–$HClO_4$ (Ref.93)			
Butyl-	1.85	2.27	3.78	

Zinc dibutyldithiophosphate was used as an extractant for the extraction of mercury(II), which was then determined in the extract by polarography.[12] Nickel dibutyldithiophosphate is extracted into heptane with very high distribution coefficients ($\log D > 3$), but the extraction takes place slowly and re-extraction is not quantitative.[67] Uranyl ions can be extracted from perchloric acid solutions into benzene using DBDTPA.[81]

Dibutyldithiophosphate form the following series of extractability:[5,73]

$$\text{Pd(II)} > \text{Au(III)} > \text{Cu(I)} > \text{Hg(II)} > \text{Ag} > \text{Cu(II)} > \text{Sb(III)} > \\ > \text{Bi(III)} > \text{Pb} > \text{Cd} > \text{Ni} > \text{Zn}.$$

The use of zinc isobutyl-2-ethylhexyldithiophosphate in the form of a 50% solution in a mineral oil (industrial name DF-II) as an extractant for copper has been proposed. This compound is used as an oil additive.[96] The availability of the reagent, its high copper capacity, low viscosity, and good compatibility with kerosine have determined its use in hydrometallurgy.[96] In a single extraction the distribution coefficients of copper are higher by 3–5 orders than for associated elements.

The extraction metals with di-2-ethylhexyldithiophosphoric acid has been studied in the greatest detail. A considerable amount of attention has been given not only to the conditions but also the extraction mechanism, a determination of the extraction constants and distribution constants of the complexes, and the effect of diluents. The extraction of Cu(II),[97–101] Ag,[102] Au(III),[103] Ca,[104] In,[105,106] Tl(I),[107,109] As(III),[110,111] and Bi[112,113] has been studied.

Other dialkyldithiophosphoric acids with large alkyl groups—n-hexyl-, n-octyl-, dodecyl-, and isododecyl-dithiophosphoric acids, and other acids with unbranched C_9–C_{18} groups—have also been tested as extractants. These acids are virtually insoluble in water and in acid and alkali solutions. For example, the solubility of D2EHDTPA in water is 0.0088 g litre^{-1}, in 1 M H_2SO_4 it is 0.022 g litre^{-1}, and in 2 M NaOH 0.114 g litre^{-1}. Out of the acids listed it is best to use D2EHDTPA, since the extraction of metals with its solutions in organic solvents occurs with sufficient rapidity.[114] In contrast to acids synthesised from C_8–C_{18} alcohols, D2EHDTPA does not form stable emulsions. These extractants are not decomposed by solutions of 7–9 M HNO_3, H_2O_2 (in the presence of HCl or H_2SO_4), Br_2, Tl(III), and other oxidising agents.[114] In the absence of oxidising agents, solutions of D2EHDTPA are stable and their extractive capacity does not change with time.[114] The reagent D2EHDTPA forms such stable complexes with metal ions that even compounds of alkali and alkaline earth metals can be extracted. The extraction constants of ammonium and sodium ions into heptane ($\mu = 1$) are equal to -3.50 ± 0.06 and -3.70 ± 0.01 (in $\log K$ units) respectively.[115] The use of the polar solvent 2-ethylhexanol markedly improves the extraction of ammonium ions; in this case $\log K_{ex} = -1.55 \pm 0.10$. Systems with sodium ions separate into phases slowly (20–24 h) while with ammonium ions they separate after a few minutes. Sodium ions are evidently strongly hydrated in the organic phase. The solubility of D2EHDTPA in ammonia solutions is low. After mixing equal volumes of a 1 M solution of NH_3 and $(NH_4)_2CO_3$ with a 0.22 M solution of D2EHDTPA in heptane, 0.05 g litre^{-1} of D2EHDTPA and its anion is extracted into the aqueous phase.

Copper(II) is quantitatively extracted with solutions of D2EHDTPA in saturated hydrocarbons from media containing 0.05–11 M H_2SO_4, 0.1–8.7 M $HClO_4$, 0.1–12 M CH_3COOH, 0.1–12 M HCl, or 0.1–7 M HBr.[97,98] The extraction is virtually complete after 2 min. The extraction of copper with solutions of D2EHDTPA in the presence of diethylenetriaminepentaacetic acid has been studied.[9]

The extraction of copper(II) is made difficult by its partial reduction to copper(I).[100,116] This process has received very little study and is sometimes completely ignored. In dilute solutions reduction takes place quite slowly and after brief contact (30 s) of a solution of D2EHDTPA in toluene with a 1–2 M solution of $CuSO_4$, CuA_2 passes into the organic phase (pH of solution not specified). The electronic spectra of CuA_2 and CuA differ considerably. It is assumed that a dynamic equilibrium is established during extraction

$$2CuA_2 \rightleftarrows 2CuA + A_2.$$

The CuA complex is associated in solution (degree of association 4–5) when the concentration of Cu(I) is 1 mg ml^{-1}.

In the extraction of large quantities of Cu(II) the process can also be complicated by polymerisation of the CuA_2 complex in the organic phase.[97,117] Copper is not re-extracted with a 2.5 M solution of H_2SO_4 or with solutions of $Na_2S_2O_3$, $H_2C_2O_4$, and phosphoric acid salts.[101] Re-extraction can be carried out using 5 M NH_3 or 10 M HNO_3. NaOH solutions are unsuitable for re-extraction, 7–10% solutions of thiourea in 1–3 M solutions of a mineral acid are used for this purpose.[97]

Silver is completely extracted with a 0.01 M solution of D2EHDTPA in octane from media containing 0.1–8.7 M $HClO_4$, 0.05–9 M H_2SO_4 ($D > 2 \times 10^3$), 0.1–8 M HCl, or 0.1–3 M HBr.[102]

The extraction of gold(III) with the reagent D2EHDTPA from solutions of mineral acids has been studied. During extraction from HNO_3 solutions there is a sharply defined minimum when the concentration of acid is 9 M. Gold is extracted from solutions of mineral acids regardless of its form in the initial solution. The distribution coefficients of gold during extraction from HCl solutions are higher than from HBr solutions. They attain a maximum value when the concentration of mineral acids ranges from 0.1 to 10 M. The extractant is decomposed by the mixture

$HCl + H_2O_2$ (9:1); gold is not extracted from this mixture. Another good re-extraction agent is a 0.5 M solution of thiourea in 0.1 N HCl, HBr, or H_2SO_4.[103]

The extraction of calcium with solutions of ammonium di-2-ethylhexyldithiophosphate in heptane, octanol, TBP, and hexadecane has been studied.[104] The equilibrium stops after 2–3 minutes. In the extraction of calcium with this reagent from 0.5–4 M solutions of its salts, $\log K_{ex} = 0.73 \pm 0.05$. Calcium ions are extracted even more effectively with the sodium salt of the acid. The Ca–Na exchange constant is higher than the Ca–NH_4 exchange constant: $\log K_{Ca-Na} = 1.05 \pm 0.04$; $\log K_{Ca-NH_4} = 0.64 \pm 0.06$. D2EHDTPA appears to extract the ammonium ion more effectively than the sodium ion. A solution of D2EHDTPA in n-decane (0.1 M) extracts Mg, Ca, Sr, and Ba. The degree of extraction depends on the pH of the aqueous phase; at pH > 4 extraction is quantitative.[118]

The distribution coefficients of indium are sufficiently high to ensure its almost quantitative extraction with 0.3–0.5 M solutions of D2EHDTPA in saturated hydrocarbons (heptane, toluene, octane) from solutions of $HClO_4$ and H_2SO_4 of any concentration and from solutions of hydrohalic acids up to 3 M HCl, 4 M HBr, and 5 M HI. Extraction decreases in the series HCl > HBr > HI.[106] The extraction constant of indium ($\log K_{ex} = 10.3$) is very high. The distribution coefficients of indium remain high even for extraction with dilute solutions of D2EHDTPA (0.02 M) from solutions of oxoacids. Extraction decreases in the series $HClO_4$ > H_2SO_4 > H_3PO_4 > $H_2C_2O_4$. Indium is also extracted from alkaline and ammonia solutions. For media containing 0.5–5 M NH_3 or NaOH, the distribution coefficients of indium are constant, and they are much higher for the former than for the latter.

A solution of D2EHDTPA in decane (0.1 M) effectively extracts Tl(I) from solutions of oxoacids and from solutions of hydrohalic acids of low concentration. In extraction from isomolar solutions the distribution coefficients increase in the series $HClO_4$ > H_3PO_4 > H_2SO_4 > HNO_3 > HCl. The largest reduction in distribution coefficients occurs in the presence of chlorides; sulphates and phosphates have virtually no effect on this property. Thallium(I) can be re-extracted with an 8–9 M solution of HNO_3. High concentrations of oxalic and citric acids have comparatively little effect on the extraction of Tl(I). Thallium(I) is extracted with high distribution coefficients not only from buffer solutions with pH 5–10 but also from highly concentrated solutions of NH_3 and alkalis; $\log D$ has a constant value up to a concentration of 5 M NH_3 or NaOH.[107] Thallium(I) is quantitatively extracted with a 1 M solution of D2EHDTPA in 2-ethylhexanol from 0.05–2.5 M H_2SO_4.[108]

The extraction of tin(II) with solutions of D2EHDTPA has been studied in detail.[119,120] It occurs quantitatively over a wide concentration range of H_2SO_4 and from HCl solutions up to an acidity corresponding to 3 M HCl. Tin is quantitatively re-extracted with an 8–9 M solution of HCl. It was shown by saturation of the organic phase that the ratio of metal to reagent in the extract was 1:2. The distribution coefficient of tin when it is extracted from sulphuric and hydrochloric acid solutions and HBr solutions with a solution of D2EHDTPA in octane, decane, cyclohexane, benzene, toluene, CCl_4, and chloroform is directly proportional to the square of the concentration of extractant in the organic phase and inversely proportional to the square of the hydrogen ion concentration in the aqueous phase.

A solution of D2EHDTPA in octane (0.05 M) can quantitatively extract bismuth from a 0.1–8.7 M solution of $HClO_4$ and a 0.05–15 M solution of H_2SO_4; with a concentration of bismuth of 5×10^{-3} M, $\log D > 3$.[113] It is extracted in a more acidic medium from solutions of HCl or HBr. As the concentration of hydrohalic acid in the aqueous phase increases, the distribution coefficients are reduced, the decrease being more substantial in extraction from HBr solutions, which is due to the differing stabilities of halide complexes of bismuth.[113] From among cation-exchange extractants — dialkyldithiophosphoric, dialkylthiophosphoric, alkylphosphoric, and naphthenic acids, and alkyl mercaptans — the most effective for bismuth are D2EHDTPA and dioctylthiophosphoric acid. Bismuth is quantitatively extracted with a 0.05 M solution of D2EHDTPA in octane from media containing 0.1–6 M HNO_3 ($\log D > 3$).[112]

The extraction of arsenic(III) from solutions of HNO_3, $HClO_4$, H_2SO_4, HCl, and HBr over a wide concentration range with a solution of D2EHDTPA in decane has been studied.[110] Extraction from strongly acidic media ($\leqslant 5$ M H^+) is complete, while arsenic is not extracted from solutions with pH 6–7. Acetates, tartrates, fluorides, iodides, and EDPTA do not inhibit extraction.[110,121] The highest distribution coefficients are attained in extraction from media containing 8 M H_2SO_4 (up to pH 2) and from a 1–10M solution of HCl. A feature of the extraction of arsenic(III) is the increase in the distribution coefficient as the concentration of the acid in the aqueous phase increases. Levin et al[111] attribute this to the increase in concentration of the extractable species:

$$AsO_3^{3-} + 6H^+ = As^{3+} + 3H_2O.$$

The extraction of nickel and cobalt with solutions of D2EHDTPA in decane has been studied.[122] Nickel extracts have a green colour. The highest distribution coefficients occur in the extraction of nickel from solutions in the region of pH 2 to 0.5 M H_2SO_4 or 1 M HCl. Cobalt has lower distribution coefficients, its maximum extraction is reached at pH 1.6–1.2. The extraction constants of nickel and cobalt are equal to 1.4×10^3 and 0.9 respectively when $\mu = 4.8$; $\log K_{ex} = 2.29 \pm 0.07$. The elements are quantitatively re-extracted with 6-10 M HCl.

Solutions of D2EHDTPA have also been used for extraction of platinum metals. Palladium(II) forms a complex with D2EHDTPA in 2–3 M HCl without heating in the presence of acetone; the complex is quantitatively extracted into the organic solvent. Silver and gold are extracted under the same conditions, but platinum and rhodium are not extracted. After addition of 0.01 M $SnCl_2$ to an aqueous solution of this type, platinum and rhodium are extracted on standing for 2 h, but iridium is not extracted.[123] By using a 0.01 M solution of extractant in toluene it is possible to extract palladium almost completely from a 0.1–10 M solution of NH_3 or a 0.1–5.3 M solution of NH_4Cl. Toluene, CCl_4, and saturated hydrocarbons can be used as diluents. With a ratio of $V_{org}:V_{aq} = 1:50$ and a palladium concentration of 0.02 μg ml^{-1}, more than 98% of palladium was extracted from 1 M NH_3 and NH_4Cl.[124] The extraction constant of palladium with D2EHDTPA is very high ($\sim 10^{20}$). The inhibiting effect of Cu, Pb, Mn, and Co is eliminated by the addition of excess EDTA.[124]

Iridium(III) is quantitatively extracted into the organic phase from an aqueous solution containing 1–4 M HCl when a 100-fold excess of D2EHDTPA is used (when the concentration of iridium is 1×10^{-3} M) in the presence of acetone, heating being required in this case. The optimum extraction conditions are: 2–3 M HCl, 0.1 M solution of extractant in acetone, acetone content 50 vol. %, heating at 100 °C for 30–40 min. The extraction constant of the complex using chloroform is quite high ($\log K_{ex} = 4.41 \pm 0.1$).[123]

Iridium is not re-extracted with 6 M NaOH, 1 M EDTA, or hydrochloric or sulphuric acid solutions of thiourea because of the formation of kinetically inert iridium complexes. Under the optimum conditions the extraction of iridium is not inhibited by the presence of the following metals (in excess quantities): Fe(III) 20; Cu 3×10^3; Ni 1×10^4; Co 3×10^4. The extraction of iridium becomes complicated in the presence of tin(II), which under these conditions evidently forms tin chloride-containing complexes of iridium of different compositions.

The elements can be arranged in the following series in relation to their ability to be extracted with D2EHDTPA from HCl solutions:[125]

$$Bi > Cu(II) > Pb \geqslant As > Cd \geqslant In > Fe > Ni > Zn.$$

A more complete series based on extraction constants is given in another study[126]

$$Au(I) > Ag(I) > Hg(II) > Pt(II) > Pd(II) > Cu(II) > Ir(III) > > Bi(III) > As(III) > Ru(III) > In(III) > Pb(II) > Sn(II) > > Cd(II) > Fe(III) > Tl(I) > Ni(II) > Zn(II) > Co(II).$$

Table 6. Exchange constants and extraction from perchloric acid solutions.[125]

System M_1-M_2	$\log K_{exch}$	System M−H	$\log K_{ex}$
Zn^{2+}—In^{3+}	11.0±0.3	Zn^{2+}—H	2.25±0.03
Zn^{2+}—Ni^{2+}	0.75±0.03	Ni^{2+}—H	3.14
As^{3+}—Pb^{2+}	−0.67±0.05	Fe^{3+}—H	8.62±0.08
In^{3+}—As^{3+}	1.7±0.1	In^{3+}—H	10.22±0.3
Cd^{2+}—As^{3+}	2.82±0.07	Cr^{2+}—H	7.01±0.07
Fe^{3+}—In^{3+}	1.6±0.08	Pb^{2+}—H	8.09±0.05
As^{3+}—Cu^{2+}	12.94	As^{3+}—H	11.93
		Cu^{2+}—H	12.3
		Bi^{3+}—H	20.1±0.06

There is considerable interest in the exchange reactions of metal di-2-ethylhexyldithiophosphates in the presence of anions that have a tendency towards complex formation with exchangable cations. The extraction constants of metals that form complexes with anions of mineral acids and other complex-forming ligands are equal to $K/(1 + \beta_i c^i)$, where K is the extraction constant in the absence of complex-forming ligand, β_i is the stability constant of the ith complex, c is the concentration of ligand. Depending on the conditions, the exchange constants can vary over a wide range, as a result of which many metals alter their position in the exchange-extraction series. Table 6 lists the exchange constants and extraction constants of certain metals from perchloric acid solutions. In hydrochloric acid solutions these constants have different values.

The exchange constants of the pairs Bi−As and As−Cu when $\mu = 5$ (LiCl) and at an H^+ concentration of 1 M are 0.78 and 5.32 respectively, while the $\log K_{ex}$ values for bismuth and copper complexes are 11.5 and 10.01.[125] As arsenic does not form acido-complexes, the value of K_{ex} at a constant acidity of 1 M H^+ remains unchanged ($\log K_{As-H} = 11.9$) if the extraction is carried out from either perchloric acid or hydrochloric acid solutions.

The extraction of metals with diphenyldithiophosphoric acid (DPDTPA) has been well studied.[127] The latter can be used to extract Cu(II), Pd,[35] Bi,[92] and Pt(II).[128] For example, platinum(II) is quantitatively extracted from a 2.5 M solution of HCl or 1.25 M solution of H_2SO_4.[128] Selenium(IV) is extracted with DPDTPA in chloroform from solutions in the region pH 1 to 10 M HCl.[129] The extraction of cadmium from a 0.05 M solution of H_2SO_4 was used for a subsequent titrimetric determination of cadmium in the presence of Zn, Al, Cr, Co, Mn, and Fe(III).[130]

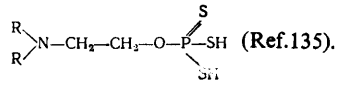
Amongst cyclic alkylidenedithiophosphoric acids, 1,3- and 2,3-butylenedithiophosphoric acids have been studied as extractants for the selective isolation of copper.[13] Solutions of these in chloroform (0.3 M) completely extract copper from acidic media ranging from 2.5 M H_2SO_4 to pH 5. The extraction time in the presence of extraneous elements is 30 min. Using these acids at pH 2, the following may be extracted (in %): Fe(III) 0.3−0.4; Co, Mn, Zn 0.1−0.2. These acids are more selective than isobutylethylhexyldithiophosphoric acid, a 0.15 M solution of which in chloroform at pH 2 extracts 46% iron(III) and 90% nickel. A 0.25 M solution of H_2SO_4 containing 0.5−11.0 M thiourea or a 0.025−0.1 M solution of EDTA in 5% ammonia are suitable for re-extraction of copper. In the presence of Na_2SO_3 copper(I) is quantitatively extracted while there is 1% extraction of iron(II). A 2.5 M solution of H_2SO_4 can be used to re-extract copper(I). The distribution coefficients of 1,3- and 2,3-butylidenedithiophosphoric acids in the system water−$CHCl_3$ at pH > 2 are very small and do not change as the pH increases, which is due to anions of the acids being present in aqueous solution.

Dibutylthiophosphoric acid has been studied from amongst thiophosphoric acids. The extraction of 30 elements using a 0.2 M solution of this acid in CCl_4 from sulphuric acid, hydrochloric acid,[132] and nitric acid[133] solutions has been studied. Ag, Au(I), Pb(II), Hg(II), Bi, and Pd(II) are effectively extracted from solutions of 0.005−5 M H_2SO_4 and 0.01−10 M HCl. Cadmium and zinc are completely extracted from solutions of sulphuric or hydrochloric acid with a concentration of less than 0.05 M. The extraction of As(III), In, Ga, Tl(I), Se(IV), Sn(II), and Fe(III) is characterised by high distribution coefficients. Y, La, Sb(III), Nb, and Mo(VI) are only slightly extracted and Cr(III), Mn(II), Fe(II), Co(II), Ni, alkali metals, and alkaline earth metals are not extracted at all.[132]

Extraction from nitric acid solutions is complicated by oxidation of the reagent, which is marked when the concentration of HNO_3 is more than 6 M. The extractant can be used to separate different groups of elements: Cu, Sc, Se(IV), Pd, Cd, Bi, Sb(V), Zn, In, Te(IV), Tl(I) are extracted from a 1 M HNO_3 solution; Cu, Sc, Se(IV), Pd, Cd, Sb(V), and Bi are extracted from a 3 M solution; and Pd, Bi, and Sb(V) are extracted from a 5 M solution.[133]

Cyclic pinacolinethiophosphoric acid in $CHCl_3$ quantitatively extracts palladium from 0.5−1.0 M HCl. On boiling the extract for 10−15 minutes, the complex decomposes to give PdS.[134]

There has been a qualitative study[135] of the extraction of heavy and platinum metals with dithiophosphoric acids $(RO)_2P(S)SH$, where R are unsaturated groups (allyl, β-methylallyl, propargyl) and also trithiophosphoric acid derivatives such as dimethyl-aminomethyl- and diethylaminoethyl-trithiophosphoric acids with the general formula



(Ref.135).

2. Chemical nature of extraction

Dialkyldithiophosphoric acids extract elements from acidic aqueous solutions by a cation-exchange mechanism, which has been studied in the greatest detail in the case of D2EHDTPA.[136–140] The absence of anions of mineral acids in the extract whatever the type of acid is typical for the extraction of Cu(II),[99] Ag,[102] Ca,[118] In,[105] Tl(I),[109] As,[111] Be,[113] U(VI),[81] Ni,[122] and Pd.[123,124] It has been established using a saturation method that compounds with the composition MA_n which are not solvated with molecules of free acid[99,105,113,122,124] and not hydrated[122,136] are extracted into the organic phase. However, in certain cases the complexes can add on molecules of free acid. For example, complexes of magnesium and alkaline earth elements are solvated with a single D2EHDTPA molecule.[118] The results of elemental analysis of complexes between iridium(III) and D2EHDTPA isolated using thin layer chromatography indicate that they have the composition $Ir_2A_3 \cdot HA$.[123]

The electronic spectra of the organic phases obtained by extraction of metals from solutions of different mineral acids ($HClO_4$, H_2SO_4, HCl, etc.) are identical whatever the nature of the diluent and the concentration of the acid.[105,109,111,113,119,124] The reduction in distribution coefficients as the concentration of acid in the aqueous phase increases [with the exception of As(III)[137]] suggests that there is a cation-exchange mechanism for extraction.

A detailed study of the IR spectra of metal-containing extracts obtained when D2EHDTPA and DPDTPA are used in saturated hydrocarbons also points to a cation-exchange mechanism for extraction. In the IR spectrum of pure D2EHDTPA there is a band with a maximum at 2460 cm^{-1} and two bands with maxima at 2560 and 2595 cm^{-1}. In nonpolar solvents the intensity of the latter two bands increases while the intensity of the band at 2460 cm^{-1} decreases. The bands at 2560 and 2595 cm^{-1} are attributed to (P)–S–H stretching vibrations of the monomeric acid molecules. In the spectrum of the deuterated extractant the $O_2P(S)SD$ maxima at 2560 and 2595 cm^{-1} are shifted to lower frequency. It is assumed that the band at 2460 cm^{-1} is an indication of the presence of dimeric acid molecules.[114] The presence of an asymmetric band with a maximum at 675 cm^{-1} is due to vibrations of the P=S group. Bands in the region 700–400 cm^{-1} are attributed to P–S vibrations, but their interpretation is ambiguous because these bands can correspond to the vibrations of a hydrocarbon group.[114]

In the IR spectrum of the pure acid there is a broad band at 2460 cm^{-1} and two sharp maxima at 2560 and 2595 cm^{-1} due to vibrations of the S–H group; these disappear if the extract contains Ag,[102] In,[105] Tl(I),[109] Sn(II),[119] As(III),[111] Bi,[113] and Pd.[114,124] This phenomenon indicates that the hydrogen ion of the S–H group is replaced by a metal ion, namely, that there is a cation-exchange mechanism for extraction.

The occurrence of an interaction between the sulphur atom of the P=S group and metal ions is supported by the change in position and shape of this band in the spectra of extracts containing complexes compared to its position and shape in the IR spectra of the pure acids. Instead of an intense band at 675 cm^{-1} due to asymmetric vibrations of the P=S group,[114] in the spectrum of an extract that contains bismuth a new band of medium intensity with two clearly defined maxima at 627 and 640 cm^{-1} appears.[113] In the spectrum of an extract of silver complex a band with a maximum at 635 cm^{-1} and a weak shoulder at 645–650 cm^{-1} appears.[124] Similar changes in the vibration bands of the P=S and (P)–S–H groups also occur in the IR spectra of extracts of other metals: In,[105] Tl(I),[109] Sn(II),[114,119] and As(III).[111]

A comparison of the IR spectra of solutions of the reagent in heptane and in TBP with the spectra of extracts saturated with calcium showed that the position of the absorption band due to the P=S group (681 cm^{-1}) did not change. Some broadening of the bands was an indication of a weak interaction between the thione sulphur of the P=S group and the metal.[104] The vibrational bands of the P–S bond (400–700 cm^{-1}) change considerably. The weak maxima at 600, 580, and 535 cm^{-1} and the shoulder at 490 cm^{-1} in the spectrum of the extract of free reagent are shifted to shorter wavelength at 610, 590, and 550 cm^{-1} respectively in the spectrum of the extract of bismuth while the shoulder maintains its position at 490 cm^{-1}.[113] The position of the bands from the P–S bond also change in the spectra of extracts of complexes of Ag,[102] Sn(II),[114,119] As(III),[111] and U(VI),[66] but an interpretation of these shifts is ambiguous.

An asymmetric band with a maximum at 1015 cm^{-1} and poorly defined shoulders at 985 and 1035 cm^{-1} is attributed to vibrations of the (P)–O–C bonds.[114] This band undergoes considerable changes in the spectra of extracts of complexes of Sn(II),[119] As(III),[111] Bi,[113] and other metals[66,114] compared to its position in the spectrum of the free acid. The nature of the changes depends on the degree of ionic character of the P–S–M bond.

The band due to asymmetric vibrations of Pd–S in the Raman spectrum of a complex of palladium with D2EHDTPA is situated at 330 cm^{-1} while in the spectrum of palladium diethyldithiophosphate it occurs at 317 cm^{-1}.[124]

The IR spectra of extracts of bismuth[111] and tin(IV)[119] after they have been diluted with free reagent have also been studied.

The IR spectra of complexes of iridium, rhodium, platinum, and palladium with D2EHDTPA are similar to the spectra of other dithiophosphates. The absorption bands due to vibrations from S–H groups (2560 and 2595 cm^{-1}) disappear, while the band from the P=S group at 673 cm^{-1} in the free reagent is shifted in complexes of these metals to lower frequency by 41, 42, 39, and 40 cm^{-1} respectively.[138] The band from the coordinate P=S group has a doublet structure for all dithiophosphates; this is due to the existence of two rotational isomers.[138] D2EHDTPA evidently acts as a bidentate ligand. However, it is thought that complexes that are solvated with molecules of free D2EHDTPA can also be extracted in small quantities. Such complexes are less mobile and are separated from the main component on silica gel.[123]

In the IR spectrum of free DPDTPA there is an absorption band from the P=S group at 665 cm^{-1}; in the case of the potassium salt of DPDTPA the absorption band from this group appears at 690 cm^{-1}. The absorption bands from the P=S group in diphenyldithiophosphates of Ag(I), Cd, Hg(II), Bi, Pb, and Ni, are shifted to longer wavelength by 5–15 cm^{-1} compared to the frequency of vibrations from this group in the free acid and by 15–60 cm^{-1} compared to the potassium salt. The vibration frequency of the P–O–C group at 1160 and 1025 cm^{-1} remains unchanged.[139] Shishkov and Busev[139] attribute this to the formation of a chelate with a four-membered ring.

Dialkyldithiophosphates are mainly extracted as monomeric compounds, but some of them are associated in the organic phase. The degree of association of gold when it is extracted with solutions of D2EHDTPA in heptane is 3, while mercury(II) dibutyldithiophosphate is extracted from sulphuric acid solutions into carbon tetrachloride as its tetramer.[89] Association also occurs

in the organic phase when large quantities of copper(II) are extracted with D2EHDTPA solution.[97] Ammonium dialkyldithiophosphate is highly associated in an inert solvent.[104] As a rule, unsaturated coordinate complexes are associated in the organic phase.[89,97,102]

Extraction from acidic aqueous solution that takes into account association is given by the following equation

$$mM^{n+} + \frac{m}{x}(n+s)(HR)_x + my\,H_2O \rightleftarrows (MR_n \cdot s\,HR \cdot y\,H_2O)_m + mn\,H^+.$$

The extraction constants are given in Table 6.

For some metals the extraction constants are very large and they cannot be calculated by the standard method based on the functions $\log D - \log[HA]_{org}$ or $\log D - \log[H^+]_{aq}$ because of the impossibility of determining very low concentrations of metal ($10^{-8}-10^{-7}$ M) in the aqueous phase after distribution.[140] Although dialkyldithiophosphoric acids are classed as strong acids and extract metals from acid media, there are results that indicate that dithiophosphates can also be extracted from weakly alkaline media. This relates to those that are most soluble in water (DMDTPA, DEDTPA, DPrDTPA, DBDTPA). Thus, DMDTPA extracts nickel from aqueous solution in the region of pH > 4:[66,81]

$$Ni^{2+}_{(aq)} + 2A^-_{(aq)} \rightleftarrows NiA_{2(org)}.$$

Uranyl ions are extracted with these acids in a similar manner. Extraction from alkaline media is particularly characteristic of metals that do not form very stable dithiophosphates (Zn, Co, Ni). Extraction of metal dithiophosphates in the presence of amines or donor-active added components is confirmation of the formation of complexes in aqueous solution in an alkaline medium.

Dithiophosphates of the transition metals Mn(II), Fe(II), and Co(II) in the presence of 2,2′-dipyridyl (Dipy) or 1,10-phenanthroline (Phen) are extracted in weakly alkaline media as mixed ligand complexes. The maximum degree of extraction of Mn(II), Fe(II), and Co(II) complexes is reached at pH 6–7 while for Ni(II) the maximum occurs at pH < 2. The pH region for extraction is very narrow as at pH 1–3 ligand exchange can occur because of the low stability of the dithiophosphates. At pH < 7 all of the amine is in the aqueous phase and at pH < 2.5 it is completely protonated. On the other hand, dialkyldithiophosphate ions are protonated at H < 2.7 and the acid concentration in the organic phase increases sharply. In the pH region 6–7 dialkyldithiophosphoric acids (HA) and the amine exist completely in the aqueous phase and the ratio of Dipy : HA that is conducive to extraction of Fe(II) is 3 : 2. The formation of complexes with HA and amine occurs in the aqueous phase and can be represented by the following scheme:

$$Fe(Dipy)^{2+}_3 + 2A^- \rightleftarrows [Fe(Dipy)_3A_2]_{(org)}.$$

In the absence of amine or dithiophosphate ion there is no extraction of Fe(II) complexes. Only the combined presence of both ligands leads to a considerable synergistic effect.[41]

3. Effect of substituents on the extraction of dialkyldithiophosphates

Interesting observations have been made in comparing the extractive capacity of different dialkyldithiophosphoric acids. It should be noted first of all that replacement of oxygen atoms by sulphur increases the extractive capacity of dialkyldithiophosphoric acids compared to dialkylphosphoric acids. Thus, for example, the extraction constant of bismuth with a solution of D2EHDTPA is 10^{16} times higher than the extraction constant of bismuth with di-2-ethylhexylphosphoric acid (D2EHPA);[113] the extraction constant of silver with D2EHDTPA is 2.1×10^{41}, while its extraction constant with D2EHPA is 1.4×10^{-2}. A similar phenomenon occurs in the extraction of indium.[105]

Bode and Arnswald,[9,11] who had studied the extraction of metals with only DEDTPA, proposed that the RO group on the phosphorus atom has little effect on the properties of the extractant. However, it was shown[5] that replacement of ethyl groups by n-butyl groups leads to an increase in the degree of extraction of elements. Moreover, the use of acids with a larger number of carbon atoms in the alkyl group of the acid increases the range of extractable elements. Thus, in contrast to DEDTPA, the dibutyl analogue completely extracts Zn, Tl(III), and Ni, and partially extracts Co(II) and Cr(III); Au(III) is extracted without reduction to elemental gold. Mercury and zinc are extracted more effectively with D2EHDTPA than with DBDTPA. Out of those studied, D2EHDTPA is the most effective extractant.[5] The effect of subsituents on the extractive capacity of dithio acids is noticeable in the case of the extraction of uranyl ions;[81] on increasing the carbon chain in dialkyldithiophosphoric acids the distribution coefficients of the complexes decrease in the series $2\text{-}(C_2H_5)C_6H_{12} > n\text{-}C_4H_9 > C_3H_7 \gg C_2H_5$.

It is interesting to monitor the effect of substituents on the phosphorus atom in the case of the extraction of certain dialkyldithiophosphates.[71,141] Extraction can be quantitatively characterised by the two-phase stability constant of extracted complex ($K_{D,2}\beta_n$). A variation in substituents substantially changes the two-phase stability constant of dialkyldithiophosphate. As the number of carbon atoms in the substituents increases, there is a trend towards an increase in $K_{D,2}\beta_n$ (Table 7),[141] which may be due to the effect of substituents on the distribution constants of the complexes and their stability constants.[142]

Table 7. Characteristics of the extraction of dialkyldithiophosphates with different solvents.[141]

Alkyl	Nickel in		Zinc in C_7H_{16}	Calcium in $C_6H_5CH_3$	Lead in CCl_4
	$CHCl_3$	C_6H_6			
Ethyl-	4.45	4.06	2.70	5.22	8.84
Propyl-	7.11 (2.3)	6.87 (2.9)	5.13 (1.7)	7.55 (3.8)	11.62 (7.6)
Isopropyl-	7.98 (2.6)	7.43 (3.0)	5.44 (1.5)	7.95 (3.7)	11.78 (6.9)
Butyl-	9.97 (2.7)	9.41 (3.0)	7.72 (1.8)	10.32 (4.1)	14.37 (7.4)
Isobutyl-	9.32 (2.2)	9.07 (2.8)	7.49 (1.6)	10.03 (4.0)	13.83 (6.9)
sec-Butyl-	10.89 (2.9)	10.52 (3.4)	8.29 (1.6)	11.78 (3.5)	14.52 (6.8)
t-Butyl-	11.99 (2.5)	11.49 (3.1)		12.83 (4.1)	16.36 (7.2)
Amyl-	12.59 (2.8)	12.02 (3.0)	10.37 (1.9)	12.48 (4.3)	17.17 (7.4)
Isoamyl-	12.01 (2.7)	11.69 (3.3)	10.04 (2.0)	12.48 (4.3)	16.69 (7.9)
Hexyl-	15.07 (2.7)	14.63 (3.2)		15.58 (4.3)	

Note. $\log(K_{D,2}\beta_2)$ values are listed (those in brackets are $\log K_{ex}$ values).

The stability of the complexes increases with the introduction of a more electron-donating group into the ligand molecule, so complexes with dithiophosphinic acid derivatives are the most stable.[143] But an increase in stability of dialkyldithiophosphates is also due to the steric effects of substituents on phosphorus. A

linear correlation exists between the logarithms of the stability constants of the complexes and the sum of the steric constants of substituents on the phosphorus atom (E_s^0). However, in order to derive correlation equations it is also necessary to take into account the hydrophobic effects of the substituents, which affect the distribution constants of the complexes. In order to determine the two-phase stability constants of dialkyldithiophosphates, two-parameter equations that include the steric and hydrophobic effects of the substituents on the phosphorus atom have been propounded. Taft constants E_s^0 are used to determine the steric effect and the number of carbon atoms are used to determine the hydrophobic effect. Correlation equations for the determination of two-phase stability constants of nickel have been derived for the systems water–toluene, water–heptane, and water–carbon tetrachloride.[71]

The two-phase stability constants of the dithiophosphates of Zn, Cd, Pb, and Ni also rise with the increase in steric and hydrophobic effects of substituents on the phosphorus atom (Table 7).[71,141]

4. Effect of diluents on the extraction of dialkyldithiophosphates

This effect can be closely followed in the case of complexes of metals with D2EHDTPA. In the majority of studies unreactive organic diluents are used (Table 8).

Table 8. Extraction constants of bivalent elements ($\log K_{ex}$) with D2EHDTPA solutions in different diluents (μ = 5).[144]

Element	Octane	CCl_4	$CHCl_3$	MIBK	Octanol
Hg	40.18	39.02	38.62	39.62	35.12
Pt	24.11	33.00	22.60	20.85	19.05
Pd	20.10	18.94	18.54	16.54	15.04
Cu	12.06 (12.30)	11.50 (11.40)	10.50	8.80 (8.80)	7.00
Pb	8.55 (8.09)	7.39	6.99	5.29	3.49
Sn	7.55 (7.79)	6.39	5.99	4.29	2.49
Cd	7.55 (7.04)	6.39	5.99	4.29	2.49
Ni	3.09 (3.14)	1.87	1.37	−0.23	−2.03
Zn	2.02 (2.25)	0.86	0.46	−1.24	−3.04
Co	0.02	−1.14	−1.54	−3.24	−5.04
Fe	−3.00	−4.10	−4.56	−6.26	−8.06
Mn	−6.02	−7.17	−7.57	−9.27	−11.07

Note. Calculated values of $\log K_{ex}$ are listed (those in brackets are the experimental figures).

The extraction constants of tin(II) from solutions of HCl and HBr differ almost by a factor of 10, which is attributed[119] to a discrepancy in the data on the stability of chloride and bromide complexes of tin. The extraction constants from sulphuric acid solutions are less than from solutions of HCl and HBr. It was not possible to make a comparative determination of the extraction constants of tin with D2EHDTPA from perchloric acid solution because of the instability of tin(II) solutions in perchloric acid.

The extraction constants of bivalent metals with D2EHDTPA in different diluents as determined by calculation are in good agreement with the exeperimental values (Table 8).[144] By using the principle of strong and mild acids and bases (SMAB) as a basis for determining K_{ex} it is possible to calculate these values from three experimental quantities.

A comparison of the extraction constants of the di-2-ethylhexyldithiophosphates of silver,[102] tin(II),[119] and bismuth[113] in different diluents shows that inert diluents have little effect on the extraction of dialkylphosphorodithioates. Oxygenated solvents, such as tributyl phosphate (TBP) and trioctylphosphine oxide (TOPO), have a marked effect on extraction. Decane, benzene, CCl_4, and chloroform have little effect on the extraction constant of arsenic(III) with D2EHDTPA ($\log K_{ex}$ = 10.8), but methyl hexyl ketone, dibutyl ether, and dichloroethane decrease it by a factor of 100–1000.[111] On dilution with kerosene, the phases separate out slowly when these elements are re-extracted.[121]

Diluents affect the extraction of zinc and mercury(II) in quite different ways. The most complete extraction of zinc occurs when the extractant DBDTPA is diluted with n-heptane or carbon tetrachloride; amyl alcohol and amyl acetate cause extraction to be reduced. On the other hand, the distribution coefficients of mercury(II) when using oxygentaed solvents such as ethyl acetate and isopropyl ether are higher than when n-heptane, xylene, and toluene are used, particularly at a low acidity of the aqueous solution (0.1 M HCl).[5]

Table 9. Extraction constants of indium ($\log K_{ex}$) with D2EHDTPA solutions in different diluents (μ = 5).[105]

Diluent	$HClO_4$	H_2SO_4
Decane	(10.6)	(10.3)
CCl_4	9.6 (9.8)	9.3
Benzene	9.4 (9.5)	9.1
Chloroform	8.6 (8.2)	8.5 (8.3)
Dibutyl ether	7.1 (6.7)	6.8 (6.3)
Methyl hexyl ketone	6.6 (8.7)	6.3
TBP	5.1 (10.1)	4.8 (7.4)
Octanol	4.9	4.6 (7.4)

Note. Calculated values of $\log K_{ex}$ are listed (those in brackets are the experimental figures).

The experimental and calculated extraction constants of indium only coincide for solvents with low polarity (Table 9).[105] TBP can exert both an antagonistic effect and a synergistic effect depending on the concentration. The distribution coefficient of indium in extraction with a solution of D2EHDTPA in TBP initially decreases as the proportion of the latter increases and then, when the concentration of TBP is above 0.5 M, increases sharply, in all probability because a TBP molecule is being incorporated into the extracted compound.[105]

Diluents have a substantial effect on the distribution coefficients of thallium(I)[109] and relative to this factor are arranged in the series: alcohols > aromatic hydrocarbons > halogen derivatives > ethers > saturated hydrocarbons and cyclic hydrocarbons. The distribution coefficients are at a maximum when TBP is used as the diluent, but the solution of extractant changes its properties substantially on standing in this diluent. Thus, a freshly prepared 0.1 M solution of D2EHDTPA in TBP extracts thallium(I) from 0.1 M H_2SO_4 with a distribution coefficient of about 190, but on standing for two weeks this value decreases to 3. Such phenomena do not occur when other diluents are used.[107]

Oxygenated solvents have the strongest but an unequal effect on the extraction of low-stability complexes of cobalt and nickel (Table 10).[121] When TBP or 2-ethylhexanol are used, the distribution coefficients of cobalt are higher, while the distribution coefficients of nickel are lower, than when saturated hydrocarbons are used. For example, TBP and TOPO reduce the rate of extraction of nickel by a factor of 20.[145] According to the results of one study,[117] added quantities of 2-ethylhexanol and TBP increase the rate of extraction of nickel with a 1 M solution of D2EHDTPA in hexane from solutions of H_3PO_4, and instead of 12 h required for extracting nickel without donor-active components (DAC), in the presence of 20 vol. % 2-ethylhexanol nickel is completely extracted in 2 min. It has been proposed that the extraction of nickel is limited by surface reactions with a single rate-limiting stage. The kinetic functions in the extraction system nickel-D2EHDTPA are determined by the limiting role of chelate formation in the adsorbed layer on the phase interface. This process is represented hypothetically by the equations

$$[Ni(H_2O)_6^{2+}]_{(aq)} + R^-_{(s)} \rightleftarrows [Ni(H_2O)_{6-n}R]^+_{(s)} + nH_2O,$$
$$[Ni(H_2O)_{6-n}R]^+_{(s)} + R^-_{(s)} \rightarrow [NiR_2]_{(s)} + (6-n)H_2O,$$
$$[NiR_2]_{(s)} \rightleftarrows [NiR_2]_{(org)},$$

where the index s corresponds to the state of sorption at the phase interface.[146]

Table 10. Effect of diluents on the distribution coefficients of complexes of cobalt and nickel with D2EHDTPA.[121]

Diluent	Cobalt (0.25 M HA, 0.25 M $HClO_4$)	Nickel (0.1 M HA, 2.0 M $HClO_4$)
2-Ethylhexanol	12.0	0.81
Tributyl phosphate	8.7	1.72
Cyclohexane	4.3	2.12
Decane	3.5	14.2
Dibutyl ether	3.4	0.28
Carbon tetrachloride	1.5	3.66
Benzene	1.4	0.427
Chlorobenzene	0.96	0.56
Chloroform	0.4	0.66

Cobalt is oxidised during extraction with solutions of D2EHDTPA. The compound of cobalt(II) with D2EHDTPA that is extracted into the organic phase changes colour from blue at the start of extraction to dark brown on prolonged agitation. The Co(II) compound is rapidly extracted and then Co(II) in the organic phase is slowly oxidised to Co(III). This process is determined by an equilibrium that is slowly reached.[147] The time taken to establish equilibrium in the extraction of cobalt with a solution of D2EHDTPA in decane depends on the concentration of cobalt in the organic phase. At relatively high concentrations the equilibrium is established after 10 h. At a low concentration (less than 3×10^{-4} M), agitation is required for 45 h. If the concentration of cobalt(II) in the organic phase exceeds 1×10^{-3} M it is almost completely oxidised.[148] Added quantities of TBP and TOPO increase the rate of extraction of Co(II) and considerably reduce its rate of oxidation.[145] The latter phenomenon is due to formation of a mixed ligand complex Co–DAC–HA which is not oxidised in the organic phase.[145]

In general the effect of DAC on the extraction of cobalt and nickel is very complex and it depends on their concentration and nature (some added components inhibit extraction while others accelerate it) and also on the nature of the extracted complex. A reduction in time of phase contact, the introduction of DAC, and a lowering of the partial pressure enable cobalt and nickel to be separated.[145,149,150]

In the extraction of uranyl ions with solutions of diethyl-, di-n-propyl-, and di-n-butyl-dithiophosphoric acids in n-butanol, the distribution coefficients are higher than in benzene. It is thought[151] that n-butanol is incorporated into the extracted compound. The extraction constants of uranyl ions with solutions of 2DEHDTPA in different diluents are also dissimilar.[81] The values of $\log K_{ex}$ for different diluents are: benzene 0.37; chloroform 0.79; carbon tetrachloride 0.92; and cyclohexanol 0.28.[152]

IV. The use of dithio phosphorus acids for the separation of elements

There is virtually no information about the use of thio phosphorus acids for the separation of elements. It is only known that a solution of DBTPA in CCl_4 has been used for the extractive separation of the following element pairs in nitric acid solutions: Te(IV)–Se(IV), Au(III)–Tl(I), Pt(IV)–Pd(II), As(V)–In(III), As(V)–Sb(V), In(III)–Ga(III), and Bi(III)–As(V).[133] Apart from that, Te, Se, Bi, In, Zn, and Cu ions have been isolated from 0.3 M HNO_3 using a 0.3 M solution of DBTPA for their determination in pure silver.[153]

We will therefore examine below the separation of elements with dithio phosphorus acids, amongst which the main position is occupied by D2EHDTPA. In studying the extractive properties of this reagent, three groups of metal cations can be distinguished. The first is made up by elements that are effectively extracted from strongly acidic solutions—Ag(I), Au(I), Cu(I) and Cu(II), Hg(I) and Hg(II), Bi(III), Sb(III), As(III), Sn(II) and Sn(IV), Pb(II), and platinum metals. In the second group are elements that can only be slightly extracted (extracted at low concentrations of HCl or H_2SO_4)—Tl(I), Cd(II), In(III), Fe(III), Zn(II), Ni(II), and Co(II). The third group consists of unextractable elements: alkali metals, alkaline earth metals, Al, Ti(IV), Ga, Ga, Mn(II), Fe(II), Zr(IV), and Cr(III) and Cr(VI).[114,126] Different schemes for the separation of complex systems and methods for isolating elements using D2EHDTPA have been put forward.

1. Isolation of copper

Copper is isolated from unextractable elements and those of low extractability using D2EHDTPA solutions in inert diluents from solutions with a high concentration of H_2SO_4.[114] Ag, Au, Hg(II), In, Sb(III), and Bi are extracted together with copper. In, Sb(III) and Bi ions are re-extracted with conc. HCl[97] (copper is not re-extracted with solutions of acids, alkalis, or ammonia). Copper is slowly re-extracted only with solutions of oxidising agents that decompose the extractant[114] [in the re-extraction of copper(II) with an 85% solution of thiourea in 0.5 M H_2SO_4, 20–40% of D2EHDTPA is oxidised depending on the time of agitation[97]]. Because of the slow re-extraction of copper, it is possible to separate it from bismuth at this stage.

A number of ions remain in the aqueous phase when a metal dialkyldithiophosphate is used as the extractant, having an

extraction constant which is less than for copper but higher than for the remaining metals. Cadmium di-2-ethylhexyldithiophosphate is suitable for such a purpose (log K_{ex} = 10.67). In the extraction of copper(II) with a saturated solution of this extractant in a saturated hydrocarbon, Zn, Tl(I), Tl(III), Co, Ni, Sn(II) and (partly) In remain in aqueous solution.[97] Copper(II) is extracted almost completely from 1–6 M solutions of HCl with 0.05 M D2EHDTPA in heptane over a period of 2 min.[98] Under these conditions Pd(II), Sn(II), and Sn(IV) have very low distribution coefficients (D < 0.1). The small quantities of palladium which pass into the organic phase in the extraction of copper(II) do not interfere with a photometric determination of copper at 420 nm as the molar absorption coefficient of the palladium complex at this wavelength is a hundred times lower in magnitude. A 0.05 M solution of D2EHDTPA completely extracts palladium ($D > 5 \times 10^3$) from ammonium chloride solutions with a concentration of 0.5–6 M NH_3. In the presence of EDTA the distribution coefficient of copper is markedly reduced. In extraction from a 0.5–1 M solution of NH_3 containing 0.05 M EDTA, the partition coefficient of the Pd–Cu pair is 10^5, in other words, by adding EDTA to the ammonia solution it is possible to re-extract copper selectively.[98]

2. Isolation of mercury(II)

The use of a 0.05 M solution of D2EHDTPA in octane for extraction permits the complete extraction of 5×10^{-3} M Hg(II) from solutions containing 0.1–8.7 M $HClO_4$, 0.5–9 M H_2SO_4, 0.1–7 M HCl, or 0.1–2 M HBr ($D > 500$).[154] An increase in the concentration of hydrohalic acids sharply reduces the distribution coefficient of mercury, the reduction being more significant in extraction from HBr solutions than from HCl solutions. Mercury is effectively re-extracted with concentrated acid solutions of thiourea and NH_4SCN and concentrated solutions of HCl or HBr. The presence of a more than tenfold excess of tin(II) in the aqueous phase inhibits the extraction of mercury. The negative effect from the presence of tin can be eliminated by the addition of 1–2 ml of a 1% solution of NH_4F. Mercury is separated during extraction from elements of low extractability—Al, Ga, Ti(IV), Zr, Cr(III), Mn(II). In order to isolate it from the co-extracted elements—Zn, Cd, Sn, Pb, Tl(I), Ni, and As(III)—it is possible to use bismuth di-2-ethylhexyldithiophosphate. Mercury(II) is extracted with a 0.006–0.01 M solution of bismuth di-2-ethylhexyldithiophosphate in octane from 0.1–3 N mineral acids. Mercury is isolated from zinc and cadmium by extraction with a solution of DEDTPA in heptane; 2 M HCl or H_2SO_4 must be present in the medium. Cadmium is then separated from Hg(II) by re-extraction with a 1 M solution of HCl or it is directly determined with 1-(2-pyridylazo)-2-naphthol in the extract.[155]

3. Isolation of thallium(I)

Thallium(I) is separated from elements of low extractability by extraction with a solution of 1 M D2EHDTPA in 2-ethylhexanol from 1.5–2 M solutions of H_2SO_4.[108] Cu, Ag, Zn, As(III), Hg, Fe, Ni, and Sb(III) are extracted together with Tl(I). It is isolated from these elements by washing the organic phase with different complexing agents. Washing the extract with a 40% solution of diethylamine in 30% $(NH_4)_2SO_4$ leads to the re-extraction of Zn and Ni. A second component—pyro-2-ethylhexylphosphoric acid—is added to the organic phase in order to isolate Tl(I) from Sb and Fe. On shaking the mixed organic phase with an oxidising agent (8 M HNO_3), D2EHDTPA is decomposed and Tl(I) passes into the aqueous phase while Sb and Fe remain in the organic phase as the second component is not oxidised.

Ag and Hg(II) ions are not separated from Tl(I) on washing the organic phase with solutions of acids and bases or amines. But the oxidation product of D2EHDTPA—most probably bis(alkyldithiophosphoryl) disulphide—extracts silver and mercury with high distribution coefficients. Therefore, when D2EHDTPA is decomposed with a solution of HNO_3, Tl(I) passes into the aqueous phase while Ag and Hg remain in the organic phase.

Since the distribution coefficients of copper when it is extracted with D2EHDTPA are substantially higher than for Tl(I), copper readily displaces thallium from the organic phase.[108]

4. Isolation of tin(II)

Tin(II) is isolated from co-extracted metals by re-extraction with 3–5 M H_2SO_4 or 1–2 M HCl.[120] However, it is not possible to remove all the co-extracted elements in this manner but only Zn, Ni, Co, Fe(III), Sb(III), Mo(VI), and Tl(I). Cu, Ag, As, Bi, and Hg(II) are not separated even when the organic phase is washed with conc. H_2SO_4 or $HClO_4$, but Sn(II) is readily isolated by re-extraction with an 8 M solution of HCl. Bi and Sb(III) ions are re-extracted with HCl solutions of higher concentration, but As(III), Cu, and Hg are not re-extracted even with conc. HCl.[120]

5. Isolation of arsenic(III)

It is possible to separate As(III) from elements of low extractability—Mg, Mn, Cr, Ti, Zr, Al, rare earth elements—during extraction from acid solutions.[110] The separation of arsenic from metals that form anionic chloride complexes occurs when it is extracted from solutions with a high HCl content or after washing the extract with HCl. Solutions of the oxidising agents HNO_3, H_2O_2 + HCl, Tl(III), and Br_2, the most suitable of which is bromine,[156] can be used for the re-extraction of arsenic.

Arsenic can be extracted from sulphuric acid and hydrochloric acid solutions with nickel diethyldithiophosphate by means of exchange reactions. The exchange process between arsenic and nickel

$$3NiA_{2(org)} + 2As^{3+}_{(aq)} \rightleftarrows 2AsA_{3(org)} + 3Ni^{2+}_{(aq)}$$

is quite slow (about 2 h) and is very dependent on the pH of the solution. By using nickel diethyldithiophosphate it is possible to remove arsenic from a nickel electrolyte to a sufficient degree in two stages.[121]

6. Isolation of bismuth

In order to separate bismuth from elements of low extractability, it is extracted with a 0.01 M solution of D2EHDTPA in octane from 0.1–4 M $HClO_4$, H_2SO_4, HCl, or HBr and the organic phase is washed once with a 1.5–3 M solution of H_2SO_4.[157] Cu(II), Zn, Cd, In, Tl(I), Sn(II), Pb, As(III), Sb(III), Fe(III), Co, and Ni are extracted together with bismuth.[114] Bismuth is extracted almost quantitatively at any concentration of these elements and in addition it displaces them on extraction. Bismuth is separated from cobalt by extraction from 2.5 M H_2SO_4. Bismuth can be determined in the presence of the following elements (their admissible excess quantity relative to Bi is given in brackets): Zn, Cd (600); Ni (60); Sn(II) (8); Sb(III) (3). The adverse effect of Sn(II) is eliminated by washing the organic phase with 3–4 M HCl, since Sn(II) is re-extracted considerably less with concentrated HCl solutions than is bismuth.

Ag, Au, Hg, and Bi ions form strong thiourea complexes, but the latter do not interfere with the extraction of bismuth, so it can

be isolated from these elements. The product from oxidation of D2EHDTPA with nitric acid extracts Ag, Au, and Hg, but not Bi, with high distribution coefficients. Therefore, when the extract is washed with 6 M HNO_3, Ag, Au, and Hg ions remain in the organic phase while bismuth passes into the aqueous phase, where it can be determined using KI. Determination of bismuth is possible in the presence of a 20-fold excess of Ag and Au, and 10-fold excess of Hg.[157]

7. Separation of platinum metals

The scheme for separation of the platinum metals, Au, and Ag is based on a difference in the conditions for forming extractable di-2-ethylhexyldithiophosphates.[123,126] Ag, Au, and Pd and some of the class *a* metals are extracted under normal conditions without heating the aqueous solution in the presence of the reagent and acetone. After addition of 0.1 M $SnCl_2$ to the aqueous solution and allowing it to stand for 1 h, platinum and rhodium are extracted, the aqueous solution is then heated and iridium is extracted. Thus, D2EHDTPA can be used for the group concentration of platinum metals and for separations of the pairs palladium–platinum and rhodium–iridium.[123] Cu(I), Hg(I), As(III), Bi(III), and Sb(III) are extracted together with iridium. All of the metals apart from Cu(I) can be separated from iridium by re-extraction with a 10 M solution of HCl.

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It should be pointed out in conclusion that there are no quantitative characteristics for determining the efficiency of the extraction processes involving dialkyldithiophosphates. A possible exception to this is D2EHDTPA, for which the extraction constants of metal cations are known. Nevertheless even for this the stability constants of the complexes are still unknown. In fact, a determination of extraction, stability, and distribution constants of complexes and also the two-phase stability constants provides material that serves as a basis for using dithio acids in analytical chemistry and therefore it is worthy of close attention.

References

1. A I Busev *Dokl. Akad. Nauk SSSR*, 1949, **66**(6) 1093
2. A I Busev *Zh. Anal. Khim.*, 1949, **4**(4) 234
3. T H Handley *Talanta*, 1965, **12**(10) 893
4. A I Busev, M I Ivanyutin *Tr. Komis. po Anal. Khim. Akad. Nauk SSSR*, 1960, **11** 172
5. T H Handley, J A Dean *Anal. Chem.*, 1962, **34**(10) 1312
6. T H Handley *Nucl. Sci. Eng.*, 1963, **16** 440
7. T H Handley, R H Zucal, J A Dean *Anal. Chem.*, 1963, **35**(9) 1163
8. T H Handley *Anal. Chem.*, 1965, **37**(2) 311
9. H Bode, W Arnswald *Fresenius' Z. Anal. Chem.*, 1962, **185**(3) 179
10. U Khudaibergenov, A G Ganiev *Aktivatsionnyi Analiz Blagorodnykh Metallov* (Activation Analysis of Noble Metals), Izd. Filial Akad. Nauk, Tashkent, 1970, p. 73
11. H Bode, W Arnswald *Fresenius' Z. Anal. Chem.*, 1962, **185**(2) 99
12. N A Ulakhovich, G K Budnikov, N K Shakurova *Zh. Anal. Khim.*, 1980, **35**(6) 1081
13. A I Busev, M I Ivanyutin, E M Feigina *Zavod. Lab.*, 1958, **24**(3) 265
14. A I Busev, T V Rodionova *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1968, (5) 63
15. A I Busev, T V Rodionova *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1969, (5) 77
16. A I Busev, T V Rodionova *Zh. Neorg. Khim.*, 1969, **14**(5) 1283 [English translation in *Russ. J. Inorg. Chem.*, 1969(5)]
17. A I Busev, T V Rodionova *Anal. Lett.*, 1969, **2**(1) 9
18. A I Busev, T V Rodionova, A Alvarez-Escartin *Zh. Neorg. Khim.*, 1970, **15**(6) 1624 [English translation in *Russ. J. Inorg. Chem.*, 1970(6)]
19. A I Busev, T V Rodionova, A Alvarez-Escartin, A N Shishkov *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1971, **12**(5) 590
20. A I Busev, T V Rodionova, A Alvarez-Escartin, Y A Albitsky *Anal. Lett.*, 1971, **4**(4) 231
21. A I Busev, T V Rodionova, A Alvarez-Escartin *Zh. Anal. Khim.*, 1972, **27**(8) 1508
22. A I Busev, T V Rodionova, A N Batalin, N J Verbitskaya *Anal. Lett.*, 1970, **3**(5) 243
23. A I Busev, T V Rodionova, N I Verbitskaya *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1972, **13**(5) 556
24. A I Busev, T V Rodionova, N J Verbitskaya *Anal. Lett.*, 1972, **5**(4) 237
25. A I Busev, T V Rodionova, P Nenning *Wiss. Z. Karl-Marx Univ. Leipzig. Math-Naturwiss. R.*, 1975, **24**(4) 439
26. V M Ivanov, T V Rodionova, G F Bel'skaya, S V Makarova *Zh. Neorg. Khim.*, 1986, **31**(9) 2330 [English translation in *Russ. J. Inorg. Chem.*, 1986(9)]
27. T V Rodionova, V M Ivanov *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1986, **27**(5) 493
28. T H Handley *Anal. Chem.*, 1964, **36**(3) 2467
29. I V Seryakova, G A Vorob'eva, G F Bebikh, Yu A Zolotov *Zh. Anal. Khim.*, 1976, **31**(5) 845
30. A I Busev, A N Shishkov, N K Nikolov *Zh. Anal. Khim.*, 1975, **30**(1) 136
31. A I Busev, M I Ivanyutin *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1957, (5) 157
32. A I Busev, A N Shishkov *Zh. Anal. Khim.*, 1968, **23**(2) 181
33. L K Kobanova, S V Usova, P M Solozhenkin *Izv. Akad. Nauk Tadzh. SSR, Otd. Fiz-Mat. i Geol-Khim. Nauk*, 1971, (1) 47
34. M I Ivanyutin, A I Busev *Nauchn. Dokl. Vyssh. Shkol. Khimiya i Khim. Tekhnol.*, 1958, (1) 73
35. A I Busev, M I Ivanyutin *Zh. Anal. Khim.*, 1958, **13**(1) 18
36. A I Busev, A N Shishkov *Zh. Anal. Khim.*, 1968, **23**(11) 1675
37. V F Toropova, G K Budnikov, N A Ulakhovich *Talanta*, 1978, **25** 263
38. G K Budnikov, N K Shakurova, N A Ulakhovich, et al. *Zh. Anal. Khim.*, 1977, **32**(7) 1326
39. V F Toropova, M G Gabdullin, A R Garifzyanov, R A Cherkasov *Zh. Anal. Khim.*, 1984, **39**(2) 267
40. N A Ulakhovich, G K Budnikov, L G Fomina, T N Kolesnikova *Izv. Vuzov: Khimiya i Khim. Tekhnol.*, 1979, **22**(12) 1449
41. N A Ulakhovich, I V Postnova, G K Budnikov *Zh. Anal. Khim.*, 1985, **40**(8) 1502
42. N A Ulakhovich, G K Budnikov, N K Shakurova *Zavod. Lab.*, 1978, **44**(3) 270

43. N A Ulakhovich, I V Postnova, G K Budnikov *Zh. Obshch. Khim.*, 1983, **53**(4) 736
44. N A Ulakhovich, I V Postnova, G K Budnikov *Zh. Obshch. Khim.*, 1985, **55**(12) 2696
45. G K Budnikov, N A Ulakhovich *Usp. Khim.*, 1980, **49**(1) 147 [English translation in *Russ. Chem. Rev.*, 1980(1)]
46. A D Beloglazova, V K Krupnov *Zavod. Lab.*, 1969, **35**(4) 451
47. T V Rodionova, V M Ivanov, M S Sheikh, G V Kozyreva *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1985, **26**(4) 398
48. H Berndt, J Messerschmidt *Fresenius' Z. Anal. Chem.*, 1981, **308**(2) 104
49. T V Rodionova, V M Ivanov *Zh. Anal. Khim.*, 1986, **41**(12) 2181
50. T V Rodionova, L N Simonova, M S Sheikh *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1985, **26**(1) 70
51. T A Bol'shova, E N Shapovalova, G A Okuneva, et al. *Zh. Anal. Khim.*, 1989, **44**(2) 284
52. R H Zucal, J A Dean, T H Handley *Anal. Chem.*, 1963, **35**(8) 988
53. M I Kabachnik, S T Ioffe, T A Mastryukova *Zh. Obshch. Khim.*, 1955, **25**(4) 684
54. A I Busev, M I Ivanyutin, M F Turchinskii *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1957, (2) 177
55. V F Toropova, M K Saikina, R Sh. Aleshov *Zh. Obshch. Khim.*, 1967, **37**(3) 725
56. J P Chupp, P E Nevallis *J. Org. Chem.*, 1962, **27**(11) 3832
57. M I Kabachnik, T A Mastrukova, A E Shipov, T A Melentjeva *Tetrahedron*, 1960, **9**(1) 10
58. V F Toropova, R A Cherkasov, N I Savel'eva, A N Pudovik *Zh. Obshch. Khim.*, 1970, **40**(5) 1043
59. M G Gabdullin, A R Garifzyanov, V F Toropova *Zh. Neorg. Khim.*, 1984, **29**(9) 2420 [English translation in *Russ. J. Inorg. Chem.*, 1984(9)]
60. T A Mastryukova, L L Spivak, A A Grigor'eva, et al. *Zh. Obshch. Khim.*, 1971, **41**(9) 1938
61. V F Toropova, M K Saikina, N I Guseva, et al. *Zh. Obshch. Khim.*, 1968, **38**(9) 2088
62. A K De, S M Khopkar, R A Chalmers *Solvent Extraction of Metals*, Van Nostrand–Reinhold, New York, 1970, p. 19
63. R A Cherkasov, F M Batyrshina, E M Petrova, N V Kashina *XII Nauchnaya Sessiya po Khimii i Khimicheskoi Tekhnologii Organicheskikh Soedinenii Sery i Sernistykh Neftei: Tezisy Dokladov* (Abstracts of Reports at the XIIth Scientific Session on the Chemistry and Chemical Technology of Organic Sulphur Compounds and Sulphur-containing Oils), Riga, 1971, p. 19
64. V F Toropova, R A Cherkasov, N I Savel'eva, E I Petrova *Zh. Obshch. Khim.*, 1974, **44**(3) 531
65. S Wingefors *Acta Chem. Scand., Ser. A*, 1980, **34**(4) 301
66. M Curtui, G Marcu, I Haiduc *Stud. Univ. Babes-Bolyai, Chem.*, 1976, **21** 74
67. S Wingefors *Acta Chem. Scand., Ser. A*, 1980, **34**(4) 327
68. H Bode *Fresenius' Z. Anal. Chem.*, 1954, **142** 414
69. A N Shishkov *Nauchn. Tr. Ped. Inst. Plovdiv*, 1971, **9**(1) 101
70. T F Rodina, V I Varentsova, A N Kolyshev, I S Levin *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1973, (6) No. 14 14
71. V F Toropova, A R Garifzyanov, I E Panfilova, et al. *Zh. Obshch. Khim.*, 1984, **54**(10) 2200
72. S Wingefors *Acta Chem. Scand., Ser. A*, 1980, **34**(4) 289
73. J Stary, Ed. *The Solvent Extraction of Metal Chelates*, Pergamon Press, New York, 1964 (Translated into Russian), Izd. Mir, Moscow, 1966, p. 252
74. E M Popov, M I Kabachnik, L S Mayants *Usp. Khim.*, 1961, **30**(7) 846 [English translation in *Russ. Chem. Rev.*, 1961(7)]
75. A Menefee, D Alford, C B Scott *J. Chem. Phys.*, 1956, **25**(2) 370
76. S Wingefors *Acta Chem. Scand., Ser. A*, 1980, **34**(4) 297
77. M I Kabachnik, T A Mastryukova *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1953, (1) 121
78. I A Kakovskii, B A Stepanov, O F Ryazantseva, N V Serebryakova *Zh. Fiz. Khim.*, 1959, **33**(8) 1830 [English translation in *Russ. J. Phys. Chem.*, 1959(8)]
79. J H Fletcher, J C Hamilton, I Hechenbleikner, E I Hoegberg, et al. *J. Am. Chem. Soc.*, 1961, **72**(12) 2461
80. R F Makens, H-H Vaughan, R R Chelberg *Anal. Chem.*, 1955, **27**(7) 1062
81. M Curtui, I Haiduc, G Marcu *J. Radioanal. Chem.*, 1978, **44**(1) 109
82. N Abdusalyamov, A Ganiev, P Kh Nishanov, A I Busev *Zh. Anal. Khim.*, 1969, **24**(1) 69
83. K Hayashi, Y Sasaki, S Tagashira, et al. *Bunseki Kagaku*, 1984, **33**(5) 247
84. N Abdusalyamov, A G Ganiev, K Yuldasheva *Uzb. Khim. Zh.*, 1968, **12**(1) 20
85. U Khudaibergenov, K T Yuldasheva, A G Ganiev *Dokl. Akad. Nauk Uzb. SSR*, 1978, (11) 28
86. N Abdusalyamov, O G Murtazin, M M Usmanova *Radioaktivatsionnye Metody Analiza Ob"ektov Prirodnogo Proiskhozhdeniya* (Radioactivation Methods for the Analysis of Samples of Natural Origin), Izd. Filial Akad. Nauk Tashkent, 1980, p. 79
87. A G Ganiev, K T Yuldasheva, R N Gafurova, Kh R Rakhimov *Dokl. Akad. Nauk Uzb. SSR*, 1983, (2) 21
88. N Abdusalyamov, K T Yuldasheva, A G Ganiev, A I Busev *Zh. Anal. Khim.*, 1968, **23**(5) 716
89. T V Rodionova, V M Ivanov, L V Karavaeva, N A Chernova *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1988, **29**(2) 199
90. V I Severin, E E Rakovskii, Tr. TsNIGRI, 1973, (107) 135
91. W A Forster, P Brazenall, J Bridge *Analyst (London)*, 1961, 86(1023) 407
92. A Shishkov, D Atanosova *Nauchn. Tr. Vyssh. Ped. Inst. Plovdiv.*, 1975, **13**(3) 209
93. S Wingefors, J Rydberg *Acta Chem. Scand., Ser. A*, 1980, **34**(5) 313
94. T H Handley, R H Zucal, J A Dean *Anal. Chem.*, 1962, **34**(10) 1312
95. T V Rodionova, V M Ivanov, Dada Assefa *Vestn. Mosk. Univ., Ser. 2: Khim.*, 1986, **27**(2) 205
96. Yu A Zolotov, G E Vlasova, E V Rybakova, et al. *Tsvet. Metally*, 1978, (1) 14
97. I S Levin, N A Balakireva, L A Novosel'tseva, V G Ponomareva *Zh. Anal. Khim.*, 1975, **30**(7) 1296
98. T A Udalova, Yu M Yukhin, O V Tarasova *Zavod. Lab.*, 1984, **50**(12) 1
99. I S Levin, N A Balakireva *Zh. Neorg. Khim.*, 1978, **23**(7) 1888 [English translation in *Russ. J. Inorg. Chem.*, 1978(7)]
100. V I Kuz'min, O A Logutenko, A I Khol'kin, A Yu Erastov *Zh. Neorg. Khim.*, 1986, **31**(10) 2613 [English translation in *Russ. J. Inorg. Chem.*, 1986(10)]

101. Yu A Zolotov, G E Vlasov, E V Rybakova *Zh. Prikl. Khim. (Leningrad)*, 1976, **49**(8) 1703
102. Yu M Yukhin, N E Kozlova, L A Novosel'tseva, I S Levin *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1974(3) No. 7 64
103. N A Balakireva, L A Novosel'tseva, I S Levin *Zh. Anal. Khim.*, 1975, **30**(4) 684
104. Yu M Samoilov, Yu M Yukhin, S S Shatskaya *Zh. Neorg. Khim.*, 1985, **30**(8) 2053 [English translation in *Russ. J. Inorg. Chem.*, 1985(8)]
105. I S Levin, O M Frid, T F Rodina *Zh. Neorg. Khim.*, 1977, **22**(10) 2816 [English translation in *Russ. J. Inorg. Chem.*, 1977(10)]
106. O M Talapova, I S Levin *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1981(2) No. 4 60
107. I S Levin, V I Varentsova, T F Rodina *Izv. Sib. Otd. Akad. SSSR, Ser. Khim. Nauk*, 1973,(3), No. 7 132
108. V I Varentsova, T F Rodina, I S Levin *Zh. Anal. Khim.*, 1973, **28**(6) 1086
109. V I Varentsova, T F Rodina, I S Levin, et al. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1974(4) No. 9 147
110. I S Levin, V V Sergeeva, L I Tishchenko *Zh. Anal. Khim.*, 1973, **28**(5) 962
111. I S Levin, V V Sergeeva, I A Vorsina *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1975(2) No. 4 107
112. Yu M Yukhin, I S Levin, G A Marinkina, A P Korzhov *Zh. Anal. Khim.*, 1979, **34**(1) 142
113. I S Levin, Yu M Yukhin, I A Bykhovskaya, et al. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1973(5), No. 12 83
114. I S Levin, V V Sergeeva, V A Tarasova, et al. *Zh. Neorg. Khim.*, 1973, **18**(6) 1643 [English translation in *Russ. J. Inorg. Chem.*, 1973(6)]
115. Yu M Samoilov, I S Levin *Zh. Neorg. Khim.*, 1979, **24**(9) 1993 [English translation in *Russ. J. Inorg. Chem.*, 1979(9)]
116. L Ya Shubov, I B Zalesnik, S I Mitrofanov, et al. *Tsvet. Metally*, 1975, (11) 84
117. A I Potapova, M K Zhekeev, A I Dzhurumbaev *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.*, 1986, (3) 10
118. A N Turanov, I N Kremenskaya *Zh. Neorg. Khim.*, 1978, **23**(9) 2481 [English translation in *Russ. J. Inorg. Chem.*, 1978(9)]
119. V A Tarasova, I S Levin *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1974(3), No. 7 59
120. I S Levin, V A Tarasova *Zh. Anal. Khim.*, 1973, **28**(7) 1341
121. I S Levin, V L Kheifets, L M Gindin *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk*, 1973(5), No. 12 117
122. L M Gindin, L M Kuznetsova, A I Khol'kin *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk*, 1972(6), No. 14 126
123. N A Borshch, O M Petrukhin, Yu A Zolotov *Zh. Anal. Khim.*, 1978, **33**(6) 1120
124. T A Udalova, Yu M Yukhin, S S Shatskaya *Zh. Anal. Khim.*, 1984, **39**(4) 659
125. I S Levin, V V Sergeeva *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk*, 1974(3), No. 7 53
126. O M Petrukhin, G I Malofeeva *Teoriya i Praktika Ekstraktsionnykh Metodov* (The Theory and Practice of Extraction Methods), Izd. Nauka, Moscow, 1985, p.246
127. A N Shishkov *Nauchn. Tr. Vyssh. Ped. Inst. Plovdiv*, 1969, **7**(1) 129
128. A I Busev, A N Shishkov *Nature (Plovdiv)* 1970, **3**(1) 71
129. A N Shishkov, D Atanasova, A Georgieva *Nauchn. Tr. Vyssh. Ped. Inst. Plovdiv*, 1975(1976), **13**(3) 199
130. A I Busev, A N Shishkov, N K Nikolov *Nature (Plovdiv)*, 1968, **2**(1) 55
131. G E Vlasova, E V Rybakova, A R Garifzyanov, et al. *Zh. Neorg. Khim.*, 1981, **26**(8) 2204 [English translation in *Russ. J. Inorg. Chem.*, 1981(8)]
132. T H Handley *Anal. Chem.*, 1963, **35**(8) 991
133. P I Artyukhin, E A Startseva, I L Kotlyarevskii, Z M Bobrova *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk*, 1971(4), No. 9 131
134. USSR P. 699 804; *Byull. Izobret.*, 1980(37), 316
135. A G Pilipenko, A L Rozenfel'd *Ukr. Khim. Zh (Russ. Ed.)*, 1970, **36**(11) 1151
136. L M Kuznetsova, L M Gindin, A I Khol'kin *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk*, 1973(1), No. 2 42
137. L M Kuznetsova, L M Gindin, A I Khol'kin, et al. *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk*, 1973(6), No. 14 29
138. C K Jörgensen *Inorganic Complexes*, Acad. Press, New York–London, 1963, p. 133
139. A N Shishkov, A I Busev *Nature (Plovdiv)*, 1970, **3**(1) 77
140. I S Levin, V V Sergeeva, T F Rodina, et al. *Gidrometallurgiya. Avtoklavnoe Vyshchelachivanie, Sorbtsiya, Ekstraktsiya* (Hydrometallurgy: Autoclave Leaching, Sorption, and Extraction), Izd. Nauka, Moscow, 1976, p. 211
141. V F Toropova, A R Garifzyanov, I E Panfilova, R A Cherkasov *Zh. Obshch. Khim.*, 1985, **55**(11) 2547
142. V F Toropova, A R Garifzyanov, V V Ovchinnikov *XIV Vsesoyuznoe Chugaevskoe Soveshchanie po Khimii Kompleksnykh Soedinenii: Tezisy Dokladov* (Abstracts of Reports at the XIVth All-Union Chugaev Conference on the Chemistry of Complex Compounds), Ivanovo, 1981, Part 2, p. 474
143. V F Toropova, R A Cherkasov, N I Savel'eva, et al. *Zh. Obshch. Khim.*, 1971, **41**(8) 1673
144. O M Petrukhin, N A Borshch *Koord. Khim.*, 1982, **81**(1) 22
145. Yu B Kletenik, S A Sedova *Zh. Prikl. Khim. (Leningrad)*, 1983, **56**(7) 1510
146. S A Sedova, Yu B Kletenik *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk*, 1976(5), No. 12 73
147. G N Dolenko, A I Khol'kin, A S Chernobrov, et al. *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk*, 1979(1), No. 2 32
148. A I Khol'kin, A S Chernobrov, L M Gindin, et al. *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk*, 1976(5), No. 12 68
149. USSR P. 699 806; *Byull. Izobret.*, 1980(37)
150. S A Sedova, V A Navrotskaya, Yu B Kletenik *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk*, 1984(6), No. 17 98
151. G Marcu, M Curtui, I Haiduc *J. Inorg. Nucl. Chem.*, 1977, **39**(8) 1415
152. M Curtui, I Haiduc *J. Radioanal. Nucl. Chem. Lett.*, 1984, **16**(5) 281
153. V P Khrapai, E A Startseva, L E Zhuravleva, N M Popova *Zh. Anal. Khim.*, 1974, **29**(11) 2137
154. Yu M Yukhin, I S Levin, B Sh Litvinova *Zh. Anal. Khim.*, 1975, **30**(6) 1091
155. T V Rodionova, V M Ivanov, L V Karavaeva, I P Efimov *Zh. Anal. Khim.*, 1989, **44**(6)
156. V V Sergeeva, I S Levin, L I Tishchenko, V S Dan'kova *Zh. Anal. Khim.*, 1973, **28**(11) 2188
157. Yu M Yukhin, I S Levin, N M Meshkova *Zh. Anal. Khim.*, 1975, **30**(1) 99

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Polycyclotrimerisation of cyanamides

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ABSTRACT. The results of studies in the field of the synthesis of polymers with a network structure by the polycyclotrimerisation of cyanamides and oligomers containing cyanamide groups are surveyed and analysed. The prospects for the use of polymers based on compounds containing cyanamide groups in the preparation of various thermostable materials are discussed.

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I. Introduction

The synthesis of structured polymers containing *sym*-triazine groups at the network nodes has recently attracted special attention since it is one of the promising ways of creating new polymeric materials.[1–17] The increase in thermal stability and the improvement of physicomechanical characteristics of such polymers are achieved as a result of the development of the highly selective polycyclotrimerisation and the elucidation of the influence of the heterounit structure of network systems on their properties. As a result of this, the polycyclotrimerisation reactions of monomers and oligomers containing the N ≡ C–NH and N ≡ C–NR functional groups are of great interest. They make it possible to obtain cross-linked polymers having a regular chemical structure with a definite specified size of the internodal fragments and stable *sym*-triazine rings at the network nodes. An advantage of this reaction, leading to the synthesis of network polymers, is that it proceeds without the evolution of low-molecular-weight products. Because of this, articles can be made from such polymers by polymerising monomers or oligomers prepared beforehand (which are as a rule low melting and are readily soluble in organic solvents), i.e. by the usual methods for the processing of thermoreactive polymers.

Numerous studies devoted to the characteristics of the cyclotrimerisation of cyanamides and related compounds, which merit a special survey in combination with earlier information,[1–4,8,10,11,13,15,16,18–21] have been published recently. Therefore the consideration of the advances in the synthesis, investigation, and applications of network polymers based on cyanamides and oligomers containing cyanamide groups has become the subject of the present review. Attention has been concentrated on the latest studies which have not been described in reviews published previously.[1–4,8,11,13,15,16,19–21]

II. The synthesis of N-substituted cyanamides

The commonest method of synthesis of cyanamides involves the interaction of the corresponding amines with halogenocyanogens (ClCN, BrCN):[8,11,19,21–30]

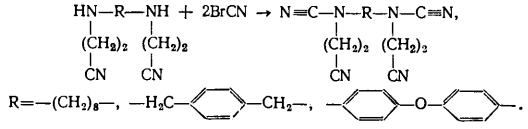
$$2\,R{-}NH_2 + HalCN \rightarrow R{-}NH{-}C{\equiv}N + R{-}NH_2 \cdot HHal,$$

R = alkyl or aryl.

It has also been suggested that cyanamides be synthesised in amide solvents, which play the role not only of solvents but also of acceptors of the hydrogen halides evolved, which makes it possible to increase by a factor of two the yield of cyanamides.[29] This method is convenient for the synthesis of cyanamides from primary amines.[11,28,29,31] In the synthesis of N-substituted cyanamides from secondary amines,[11,28,29] $NaHCO_3$ can be used as the acceptor.

Certain other methods of synthesis of substituted cyanamides are also known.[32–34] The preparation of lower aliphatic cyanamides by the interaction of calcium hypochlorite with amine salts followed by the treatment of the resulting alkyl-disubstituted chloroamines with a solution of KCN or NaCN has been described.[32]

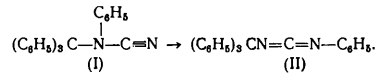
Cyanoethylated bis(cyanamides) have been obtained[35] by the interaction of cyanoethylated diamines with bromocyanogen in accordance with the scheme



The introduction of the cyanoethynyl group; as a substituent at the nitrogen atom lowers the melting point of the cyanoethylated bis(cyanamides) compared with the corresponding unsubstituted bis(cyanamides), which is especially important in the practical use of these compounds.

A specific property of cyanamides is the tendency towards tautomerisation,[36–40] which has a significant influence both on the chemical properties of cyanamides and on the mode of their cyclotrimerisation (on the structure of the products formed). Spectroscopic studies on cyanamide[41,42] have made it possible to establish unambiguously that this compound exists only in the form $NH_2{-}C \equiv N$ in the crystalline state, in aqueous solutions, and in certain organic solvents.

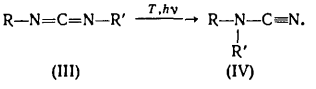
The isomerisation of *N*-phenyl-*N*-tritylcyanamide (I) to *N*-phenyl-*N'*-tritylcarbodiimide (II), observed both in the crystalline state and in solution, has been studied in detail:[43,44]



In both cases, the rate of the process depended on temperature: with increase in temperature, the isomerisation process was accelerated.

The rate of reaction also increases when a non-polar solvent is replaced by a highly polar one, which enabled the authors[43] to propose an ionic isomerisation mechanism.

The reverse isomerisation of disubstituted carbodiimides (III) to the corresponding cyanamides (IV) is accelerated both thermally and photochemically, which has led to the conclusion[45,46] that this process has a radical mechanism:

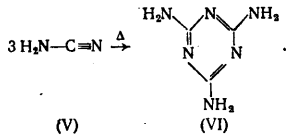


(III) (IV)

The possibility of finding the given compounds in different tautomeric forms depending on the reaction conditions has been confirmed by the results obtained in the study of the alkylation[43–48] and cyclotrimerisation of substituted cyanamides.[8,11,49–61] The alkylation of *N*-monosubstituted cyanamides afforded both *NN*-disubstituted cyanamides[43,44,47,48] and the corresponding carbodiimides[38,43,44,46,48] or mixtures of these products.[38,43,44,48]

III. Cyclotrimerisation of monocyanamides

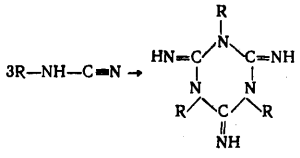
There are few literature data[62–64] on the cyclotrimerisation of cyanamide (V) (T_m = 42 °C) with formation of 2,4,6-triamino-1,3,5-triazine (melamine) (VI), because on heating above the melting point (80–130 °C) cyanamide as a rule dimerises with formation of dicyanodiamide $NH_2-C(=NH)-NHCN$:[50]



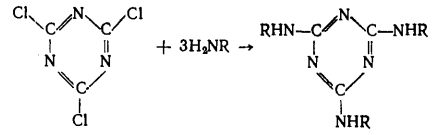
(V) (VI)

The cyclotrimerisation of cyanamide is carried out by heating the latter above 150 °C in solution in tetrahydronaphthalene, diphenyl ether, or a mixture of *m*- and *p*-cresols[62] and also in solution in dimethyl sulphoxide or sulpholan in the presence of an alkali metal or alkaline earth metal hydroxide.[63,64]

The cyclotrimerisation of substituted cyanamides has been frequently reported[49–57,65–67] but until recently the available literature data were contradictory. In some cases the cyclotrimerisation products were isomelamine derivatives,[51,52,55,56,65] whilst in others they were substituted melamines with the normal structure.[53,57,66,67] Thus the cyclotrimerisation of aromatic and aliphatic monocyanamides has been carried out in aqueous or alcoholic solution without a catalyst or in the presence of an alkaline catalyst.[22,49] In all cases, the trimerisation products were the corresponding trisubstituted isomelamines:

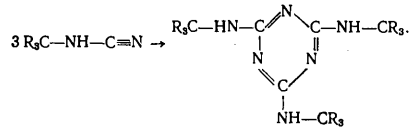


Substituted melamines with the normal structure could be obtained only by condensing cyanuric chloride with the corresponding amine:[22]



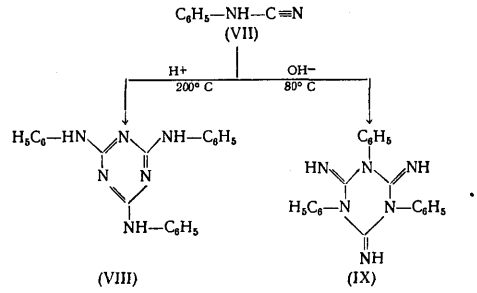
The formation of substituted isomelamines was also observed in the cyclotrimerisation of primary and secondary alkylcyanamides in solution in ethanol.[54] The cyclotrimerisation of compounds having the formula RCO–NR′–CN, where R, R′ = alkyl, arylalkyl, allyl, or methylallyl, in solution in aqueous ethanol in the presence of an alkaline catalyst also leads to the formation of substituted isomelamines.[65]

On the other hand, when the trimerisation of tertiary aliphatic cyanamides was carried out under similar conditions,[53] trisubstituted melamines with the normal structure were obtained:



These literature data permit the conclusion that 2,4,6-triamino-1,3,5-tri-azines are formed more readily if the substituting groups generate steric hindrance to attack by the NH group, as in the case of tertiary alkyls,[53,57,66] 1-adamantyl,[66] and *o*-substituted aryls.[67]

A series of studies have been published[8,11,13,58–61] in which the cyclotrimerisation of phenylcyanamide (VII) was investigated. It was found that, depending on the conditions in the cyclotrimerisation of compound (VII), triphenylmelamine (VIII) and triphenylisomelamine (IX) may be formed:

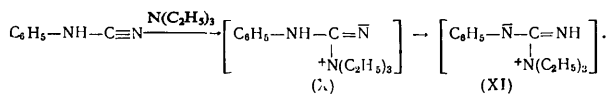


(VIII) (IX)

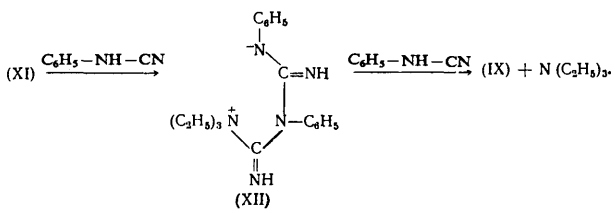
Thus compound (IX) is formed in the cyclotrimerisation of compound (VII) in the melt under mild conditions (20–80 °C), whereas at 200 °C the structure (VIII) is mainly produced.[52] The structure of the final product of the cyclotrimerisation of compound (VII) may be regulated also by the nature of the catalyst. Thus compound (VIII) is formed in the presence of Lewis acids ($SnCl_2$, $ZnCl_2$, $TiCl_4$, etc.), whereas on treatment with basic catalysts (triethylamine, pyridine, triphenylphosphine, etc.) the iso-form (IX) is produced. Lewis acids probably form adducts with compound (VII) having different degrees of substitution of the electron pair involved in the π-bond: ranging from molecular compounds of the type $C_6H_5-NH-CN.MX$ to the ionic structures $C_6H_5-NH-C \equiv N-\overline{M}X$. An increase in the polarisation of the $-C \equiv N$ group tends to accelerate the cyclotrimerisation of compound (VII) with formation of the structure (VIII).

The cyclotrimerisation of compound (VII) catalysed by triethylamine apparently gives rise to the complex of compound (VII) with $(C_2H_5)_3N$ as a reuslt of the nucleophilic attack by the carbon atom of

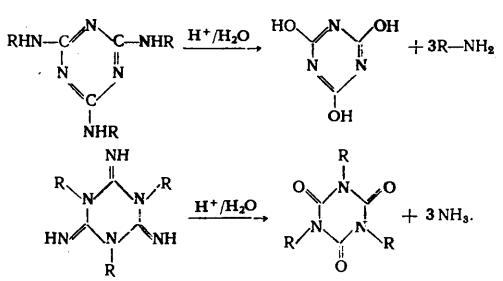
the nitrile group on the nitrogen atom of the tertiary amine:



Of the two tautomeric structures (X) and (XI), compound (XI) is probably more stable. This has been confirmed by IR spectroscopic data, since the intensity of the 2230 cm^{-1} absorption band, characteristic of the vibrations of the $-C \equiv N$ bond of cyanamides,[68] diminishes as triethylamine is added to a solution of compound (VII) in toluene and a band appears at 2130 cm^{-1}, corresponding to the vibrations of the carbodiimide group.[68] Subsequently the complex (XI) apparently combines with two further molecules of compound (VII), forming triphenylisomelamine (IX) via the transition state (XII):[60]



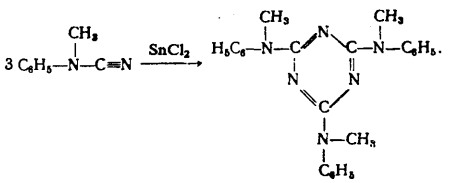
The fundamental difference between the compounds having the isomelamine and melamine structures, obtained as a result of the cyclotrimerisation reaction, is manifested in the products of their hydrolysis: melamine derivatives form, as a result of hydrolysis, cyanuric acid and the corresponding amine, while isomelamine derivatives give rise to the corresponding isocyanurate and ammonia:[11,50,58]



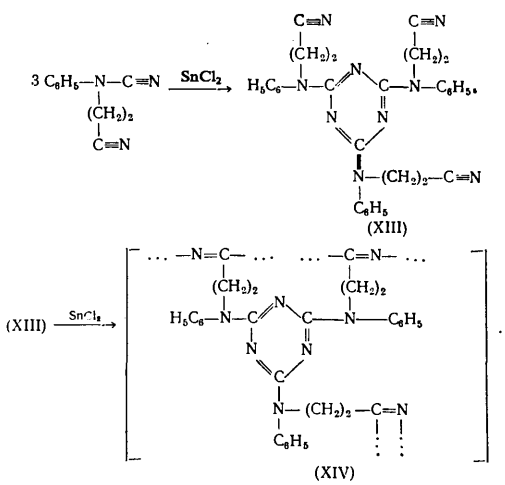
The trimerisation of disubstituted cyanamides was first described by Weith[69] in connection with the synthesis of hexaphenylmelamine by the reaction of diphenylamine with chlorocyanogen, which should proceed via an intermediate stage involving the formation of diphenylcyanamide. 2,4,6-Tri(1-pyrrolyl)-1,3,5-triazine has also been obtained by treating pyrrole with chlorocyanogen.[70]

The kinetics of the cyclotrimerisation of *N*-ethyl-*N*-phenylcyanamide have now been investigated[29] and it has been shown that the presence of the aliphatic substituent in the α-position relative to the nitrile group diminishes the reactivity of the cyanamide group, as a result of which the cyclotrimerisation of this compound proceeds only in the presence of cationic catalysts of the Lewis acid type and leads to the formation of 2,4,6-tris(*N*-ethylphenylamino)-1,3,5-triazine.

The cyclotrimerisation of *N*-methyl-*N*-phenylcyanamide and *N*-cyanoethyl-*N*-phenylcyanamide has also been investigated.[71,72] The cyclotrimerisation of *N*-methyl-*N*-phenylcyanamide[71] was achieved in the melt in the presence of $SnCl_2$:

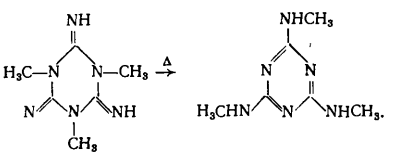


By studying the cyclotrimerisation of *N*-cyanoethyl-*N*-phenyl cyanamide in the presence of $SnCl_2$, the authors[71] showed that, depending on the reaction conditions, not only the corresponding trimer—2,4,6-tris(*N*-cyanoethylamino)-1,3,5-triazine (XIII)—but also the cross-linked polymer (XIV) is formed as a result of the polymerisation of compound (XIII) via the nitrile groups:

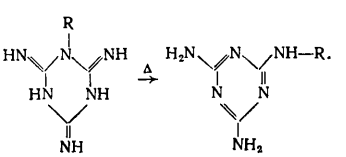


At 30 °C, compound (XIII) is formed preferentially, while at 150 to 280 °C the main product is compound (XIV). Heating of compound (XIII) in the presence of $SnCl_2$ affords compound (XIV).

Data concerning the isomerisation of isomelamine derivatives are of great interest.[11,19,56,58] Thus the isomerisation of trimethylisomelamine, synthesised by Hofmann's method,[73] to trimethylmelamine was carried out by heating trimethylisomelamine at the melting point:[56]



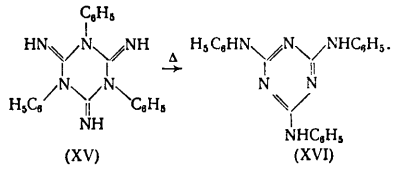
In a study of the influence of elevated temperatures on the reactivity of monosubstituted isomelamines, their conversion into monosubstituted melamines was observed:[74]



The isomerisation occurred in solution in a hydroxylated solvent at a temperature above 80 °C in the presence of 0.1 – 10% of an alkaline catalyst, the yield of the monosubstituted melamine being 95 – 97%.

It has been shown in a study[11,58] of the isomerisation of triphenylmelamine that the substituted isomelamine (XV) isomerises to the melamine (XVI) with the normal structure at a temperature above the

melting point (185 °C); the structure of compound (XVI) does not change on heating to the decomposition temperature. It has also been found that in solution the isomerisation of compound (XV) to (XVI) proceeds at appreciably lower temperatures:[58]



(XV) (XVI)

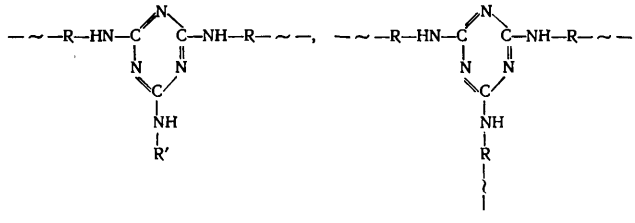
The characteristic features of substituted cyanamides and of the compounds formed on their cyclotrimerisation considered above must undoubtedly be taken into account in the synthesis and study of the properties of polymers based on cyanamides.

IV. Homopolymers of low-molecular-weight cyanamides

The first information about polymers obtained by the polycyclotrimerisation of substituted cyanamides appeared at the beginning of the 1960's and until the 1970's was limited mainly to patent data alone.[4,8,11,13,19,20,23–30,61–69,75]

The synthesis of polymers based on alkyldicyanamides, having the general formula $N \equiv C-NH-(CH_2)_n-NH-C \equiv N$, containing from 2 to 20 methylene groups, has also been described.[76–82] The polymerisation was carried out purely thermally or in the presence of alkaline catalysts by heating one alkyldicyanamide or a mixture of such compounds at the melting point of the monomers for 0.5–1 h.[76] The soluble oligomers thus formed were used as adhesives for the glueing of plastics, varnish coatings, etc. The final hardening was carried out by heating the oligomer to 100 °C. The structure of the polymers was not investigated.

The copolymerisation of bis(cyanamides) having the general formula $NC-NH-R-NH-CN$ with the monocyanamides $R'-NH-CN$ at 60–350 °C in the presence of acid or alkaline catalysts[83] yielded copolymers containing units with the following structure:



Depending on the ratio of the monocyanamide and the bis(cyanamide), both soluble and insoluble cross-linked polymers were obtained.[83]

The polycyclotrimerisation of cyanamides obtained from primary and secondary aromatic diamines was first achieved by Korshak, Pankratov, Vinogradova and co-workers.[61] The principal characteristics of this process were determined[11,58,60] and various properties of network heat-resistant and thermostable polymers based on a large set of bis(cyanamides)[4,8,11,13,20,22,29,58–61,71,72,84–108] were investigated in the studies by these workers.

Investigation of polymers based on bis(4-cyanamidophenyl)-methane, obtained at different temperatures, by IR spectroscopy and also by analysing the hydrolysis products has made it possible to discover[11,84] two types of reactions, as for the model compound phenylcyanamide. At reaction temperatures below the melting point of the initial primary bis(cyanamide), mainly a polymer containing isomelamine fragments is formed, whereas at high temperatures the reaction product is predominantly a polymer having the normal melamine structure.

The polycyclotrimerisation in bulk of secondary N-substituted bis(cyanamides)—bis(4-*N*-methylcyanamidophenyl)methane and bis(4-*N*-ethylcyanamidophenyl)methane—leads to the formation of substituted melamines with the normal structure only, as for the model compound *N*-ethyl-*N*-phenylcyanamide.[11,84] Aliphatic substituents in the α-position relative to the nitrile group diminish the reactivity of the cyanamide group compared with primary N-substituted cyanamides. The polycyclotrimerisation of such compounds takes place in the presence of catalysts of the type of Lewis acids. In contrast to patent data,[75–77,79–81,83,109–118] from which it is difficult to derive a general idea about the influence of the chemical structure of the initial bis(cyanamides) on the properties of the polymers, a number of workers[4,8,11,13,20,28,29,58–61,84–108] carried out a series of systematic investigations in which the influence of the nature of the bridging group between the phenylene moieties and the substituents in the cyanamide group on a number of properties of the polymers was traced under comparable conditions.

Table 1 compares certain properties of the polymers obtained. All the polymelamines investigated were infusible and insoluble close-network polymers, whose network nodes consisted of *sym*-triazine rings connected by the residues of the initial diamines. According to the results of dynamic thermogravimetric analysis of the polymelamines in air, the temperature of the onset of weight loss of these polymers lies within a fairly narrow range (400–420 °C). However, the subsequent course of the thermogravimetric curves of polymelamines with different structures is different. The highest thermal stability is characteristic of polymelamines containing the fluorene group between the phenylene moieties. The polymelamine based on 1,7-bis(4-cyanamidophenyl)carbaborane is characterised by a 5% weight loss on heating to 900 °C in an inert atmosphere.[11,86,87]

According to Hynds et al.,[109] the polymer based on 1,3-dicyanamidobenzene has a decomposition temperature of 464 °C [thermogravimetric analysis (TGA) at a rate of 6 K min^{-1}].

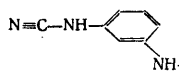
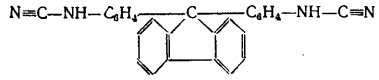
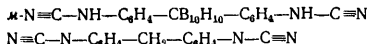
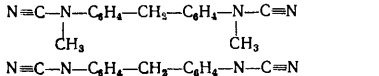
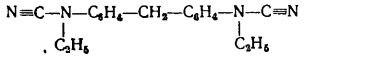
The polymer based on 4,4′-bis(*N*-methylcyanamido)diphenylmethane is characterised by a 50% reduction of weight after heating for 1200 h in air at 260 °C and has a modulus of elasticity equal to 28 800 of kgf cm^{-2}, which remains almost unchanged after 500 h at 260 °C.[111,112,116]

The study of the thermal stabilities of a series of polymers showed that in a helium atmosphere and in air the temperature of the onset of decrease in the weight of polymelamines is approximately the same. However, whereas polymelamines are degraded to the extent of 90% in air at 700 °C, in an inert atmosphere the coke residue at this temperature amounts to 60–80%.[8,11,84,86,87]

In order to deepen the understanding of the processes occurring in aromatic polymelamines on heating, a detailed study has been made also of the thermal degradation of the polymelamine based on bis-(4-cyanamidophenyl)methane and model compounds such as triphenylmelamine, triphenylisomelamine, and melamine.[11,20,88] The data obtained enabled the authors to postulate that the degradation of polymelamine proceeds not with the decomposition of the *sym*-triazine rings of the polymer but with formation of systems consisting of condensed *sym*-triazine rings.

The study of the character of the thermomechanical curves and of the regions corresponding to the useful employment of aromatic poly-

Table 1. The properties of bis(cyanamides) and the aromatic polymelamines based on them*.[94,99–102]

Initial bis(cyanamide) structure	T_m, °C	Network polymers: T_{def}, °C** 5%	T_{def}, °C** 15%	decrease in weight, %*** 400° C	500° C	700° C	Structure
	200—201	420	500	3	20	100	Amorphous
$N\equiv C-NH-C_6H_4-O-C_6H_4-NH-C\equiv N$	218—219	360	420	3	68	100	Amorphous
$N\equiv C-NH-C_6H_4-CH_2-C_6H_4-NH-C\equiv N$	162—163	410	520	1	13	100	Amorphous with signs of crystallinity
	$>T_{decomp}$	440	600	2 (3)	15 (13)	91 (22)	Ditto
	129—130	490	700	1.5 (1)	0 (5)	+3 (5)	»
	154—155	410	490	0.5	19	70	»
	76.5—77	390	460	2 (2)	30 (21)	86 (40)	Amorphous

*The degree of conversion of the cyanamide groups in all the polymers investigated was 90%.

**T_{def} is the temperature corresponding to deformations determined from thermomechanical curves (0.8 kgf cm^{-2} load, heating rate 80 K h^{-1}).

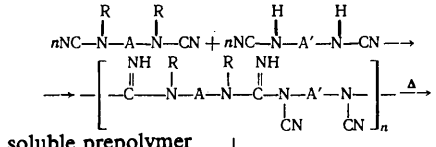
***According to TGA data in air (the values obtained in a helium atmosphere are given in brackets) on heating to the corresponding temperatures (heating rate 4.1 K min^{-1}).

melamines[11,84] showed that these polymers are characterised by a high heat resistance, which is limited by their thermal stability.

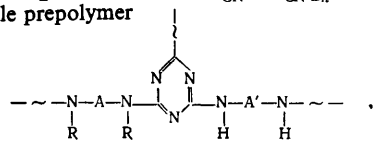
According to X-ray diffraction data, polymelamines have basically an amorphous structure, but a certain amount of order has been observed in some of them (Table 1), which is also characteristic of polycyanurates obtained by the polycyclotrimerisation of the dicyanoethers of bisphenols.[119,120] Thus the presence of a rigid three-dimensional network, formed during the synthesis, in these polymers is not an obstacle to the appearance of ordered structures. Bearing in mind that the ordering of the structure in close-network polmers after the formation of a network is unlikely, it has been suggested that the structures of such polymers are formed during their synthesis.[11,84]

It has been shown[8,11,59,84,85] (Table 2) that polymelamines are also characterised by good physicomechanical parameters. Some of the aromatic polymelamines obtained have been tested as binders for anti-friction materials. It has been demonstrated that these materials have a stable coefficient of friction in the temperature range 200–300 °C.[87]

The synthesis of copolymers based on primary and secondary aromatic bis(cyanamides) has also been achieved in accordance with the scheme



soluble prepolymer



cross-linked polymer

Di(4-aminophenyl)methane was chosen as the starting material for the synthesis of primary and secondary bis(cyanamides). The use of secondary bis(cyanamides) in combination with primary bis(cyanamides) enabled Kray[121] to reduce the rate of polymerisation and to obtain linear prepolymers which can be effectively processed in solution and in the melt. The prepolymers have been used as binders for glass and foam plastics and cast resins and as a base for honeycomb systems.

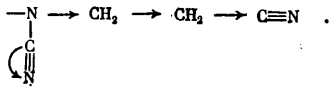
Table 2. Physicomechanical properties of aromatic network polymelamines.[99]

Initial arylbis(cyanamide)	σ_{comp}, kgf cm^{-2}	σ_i, kgf cm^{-2}	Ha_{Br}, kgf cm^{-2}	E_{comp} kgf cm^{-2}
4,4′-Bis(*N*-methylcyanamido)diphenylmethane	1300	1500	21	16 800
4,4′-Bis(*N*-methylcyanamido)diphenylmethane: 9,9′-bis(4-cyanamidophenyl)fluorene = 4 : 1 (molar ratio)	1600	1450	26	27 700
4,4′-Bis-(*N*-ethylcyanamido)diphenylmethane	1400	1350	23	17 600
4,4′-Bis(*N*-ethylcyanamido)diphenylmethane: 9,9′-bis(4-cyanamidophenyl)fluorene = 4 : 1 (molar ratio)	1900	1260	27	23 800

*Ha_{Br} is the Brinell hardness.

The characteristic features of the polycyclotrimerisation of cyanoethylated bis(cyanamides) of different chemical nature have been investigated.[72,91–94] The presence of the electron-accepting N ≡ C

group in the β-position relative to the nitrogen atom of the cyanamide group somewhat increases, compared with *N*-alkylcyanamides, the reactivity of the cyanoethylated bis(cyanamides):



The improvement of the thermal and physicomechanical properties of polymers based on cyanoethylated bis(cyanamides) has been explained by the possibility of additional cross-linking by virtue of the presence of nitrile groups. Thus the impact strength of these polymers is 4–9 kJ m^{-2}, the Brinell hardness is 310–320 MPa, and the density is 1230–1238 kg m^{-3}.[93]

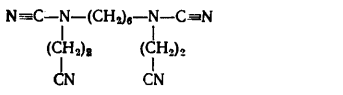
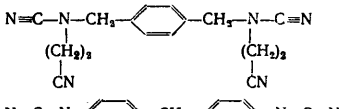
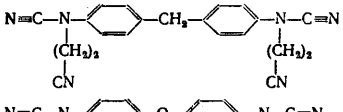
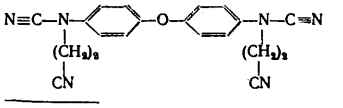
Bearing in mind the results of studies on model compounds, it has been suggested[91–94] that cyanoethylated bis(cyanamides) are polycyclotrimerised at 70–120 °C via the cyanamide groups, while the nitrile groups remain almost unchanged under these conditions. On raising the temperature (150–280 °C), the nitrile groups form polyconjugated



bonds.

Table 3 presents certain thermal characteristics of infusible and insoluble network polymers based on various cyanoethylated bis(cyanamides). The chemical nature of the internodal fragments has an appreciable influence on the properties of these polymers.[92–94]

Table 3. Cyanoethylated bis(cyanamides) and the thermal properties of the polymers based on them.[91–94]

Cyanoethylated bis(cyanamide) structure	Network polymers T_m, °C	n_D^{20}	T_{def}, °C*	$T_{o.d.w.}$, °C**
	—	1.4625	264	200
	—	1.4338	324	200
	65–66	—	300	400
	81–82	—	220	390

*T_{def} is the temperature of the onset of deformation according to thermomechanical studies.

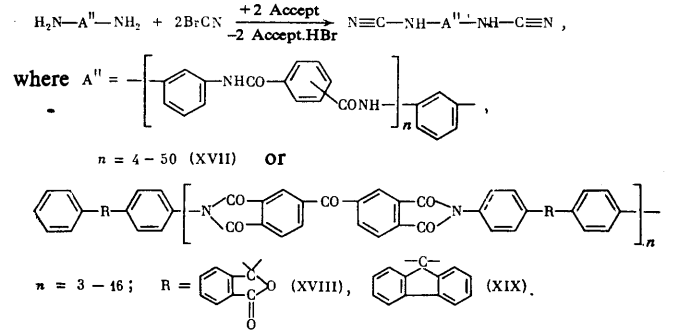
**$T_{o.d.w.}$ is the temperature of the onset of decrease in weight in air according to TGA data.

The high heat resistance and thermal stability as well as good physicomechanical parameters of the polymers obtained and the ability to polymerise without the evolution of volatile products have made it possible to use cyanoethylated bis(cyanamides) as adhesive compositions with heat resistance up to 250–300 °C.[92–94]

V. Polycyclotrimerisation of oligomers with N ≡ C–NH and N ≡ C–NR functional groups

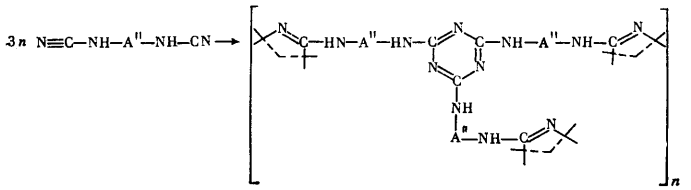
Some of the promising starting compounds for the synthesis of polymelamines by the polycyclotrimerisation reaction are oligomers containing cyanamide groups. Compared with monomeric unsubstituted bis(cyanamides) they have a lower concentration of functional groups and hence the rate of their polymerisation is lower. All these factors make it easy to monitor and to regulate their polycyclotrimerisation. The introduction of thermally stable fragments between the functional groups permits the synthesis of heat resistant and highly thermostable network polymers whose physicomechanical properties can be regulated by altering the length and nature of the oligomer chains.

The synthesis of the oligomers and their polycyclotrimerisation were first studied systematically and the properties of network polymers based on oligobis(cyanamides) were first investigated in Refs. 90, 95–108, 122, and 123. Korshak and co-workers[95–108] synthesised oligomeric bis(cyanamides) by the interaction of oligomers containing terminal NH_2 groups with bromocyanogen in *NN*-dimethylacetamide, which plays the role of both the solvent and the acceptor of the hydrogen bromide evolved, in accordance with the scheme



The properties and certain characteristics of the compounds obtained are presented in Table 4. It is seen from these data that oligomeric bis(cyanamides) have lower softening temperatures than their high-molecular-weight analogues.[124]

Polymelamines differing in the size and chemical nature of the internodal fragments have been synthesised by the polycyclotrimerisation of oligomeric bis(cyanamides) in accordance with the scheme



where A″ are oligomers having the structure shown in Table 4.[90,95–108]

The polycyclotrimerisation of oligoamidobis(cyanamides) was investigated by IR spectroscopy in relation to the oligomer with $n = 4$. The gradual decrease in the intensity of the absorption band of the N–C–NH groups was observed in the course of the polycyclotrimerisation of this compound and was accompanied by the appearance

of absorption bands in the region of 810 and 1560 – 1580 cm^{-1} referring to the vibrations of the *sym*-triazine ring.[105]

Since the concentration of the functional cyanamide groups per unit volume of the reaction system diminishes with increase in the molecular weight of the initial oligomeric bis(cyanamide), it is almost impossible to investigate in this way the cyclotrimerisation process by IR spectroscopy for oligomeric bis(cyanamides) with a higher molecular weight ($n > 10$). The influence of factors such as temperature, reaction time, pressure, and other conditions in processing by compression pressing on the polycyclotrimerisation of oligomeric bis(cyanamides) was therefore monitored from the yield of the gel-fraction of the polymers formed. The study was performed in relation to the oligoaminobis(cyanamide) with $n = 25$ (Table 4).[90,97,98,103,105] The authors recommend that the oligomeric bis(cyanamides) be processed by compression pressing at 320 °C and a pressure of 60 kgf cm^{-2}. The polymers based on other oligoamidobis(cyanamides), synthesised under the given conditions, contain between 93 and 99% of the gel-fraction depending on the length of the oligoamide chain between the cyanamide groups.

Table 4. The properties of oligomeric bis(cyanamides) and the polymelamines based on them.[90,95–108]

n	Initial oligomer		Network polymers		
	T_{soft}, °C*	M_n, found/calc.	content of gel fraction, %	$T_{o.d.w.}$** in air, °C	$T_{o.d.w.}$** in Ar, °C
			(XVII)		
4	280	1 000 1 110	99	410	410
7	280	2 000 1 828	98	405	—
12	280	3 000 3 014	98	400	400
17	280	4 000 4 205	98	400	—
25	290	6 000 6 108	97	400	—
50	290	12 000 12 034	93	400	400
			(XVIII)		
3	230	2 000 2 172	98	500	505
6	240	4 000 3 978	97	495	—
10	240	6 000 6 384	93	495	500
12	245	8 000 7 590	92	490	—
16	250	10 100 9 998	90	490	500
			(XIX)		
3	280	2000 2300	98	500	—

*T_{soft} is the softening temperature determined from thermomechanical curves.
**$T_{o.d.w.}$ is the temperature of the onset of decrease in weight according to TGA data.

The study of the rheological properties of oligoamidobis(cyanamide) melts subjected to a variable load on a capillary viscometer (Table 5) showed that these oligomers are promising materials, capable of being processed by casting under pressure.[98,99]

It has been found[97] that the deformational heat resistance of polymelamines based on oligoamidobis(cyanamides) depends on the size of the internodal network fragment, i.e. on the density of the network. For example, polymelamine based on oligoamidobis(cyanamide) with $n = 4$ softens in the same region as the high-molecular-weight aromatic polyamide with an analogous structure, while the cross-linked polymer has a softening temperature lying above the temperature of the onset of chemical decomposition.

Table 5. The properties of oligoamides with terminal NH_2 groups (a) and of oligoamidobis(cyanamides) (XVII) based on them (b).[98,99]

n	M_n^*	η_{eff}**, P	
		a	b
4	1 000	$0.16 \cdot 10^5$	$0.30 \cdot 10^5$
17	4 000	$0.32 \cdot 10^6$	$0.53 \cdot 10^6$
25	6 000	$0.45 \cdot 10^7$	$0.58 \cdot 10^7$
50	12 000	$0.16 \cdot 10^{10}$	$0.49 \cdot 10^6$

*From terminal NH_2 groups.
**η_{eff} is the effective viscosity of the melt at 320 °C and 6.7×10^7 dyn cm^{-2}.

For a more detailed investigation of the heat resistance of polymelamines, the regions corresponding to their useful employment have been determined for a number of them over a wide temperature range and over a wide range of mechanical stresses. It has been shown that the heat resistance of polymelamines depends on the molecular weight of the internodal network fragment, i.e. on the density of the network. Thus the polymelamine based on oligoamidobis(cyanamide) with $n = 4$ can be used at high mechanical stresses and temperatures in contrast to the other polymers investigated.[97]

Data obtained by dynamic thermogravimetric analysis in air (Table 4) show that the onset of the decrease in the weight of polymelamines based on oligoamidobis(cyanamides) is restricted to a fairly narrow range (400 – 410 °C). However, with increase in the density of the network, i.e. with decrease in the molecular weight of the internodal polymelamine fragments, the onset of the decrease in weight shifts towards higher temperatures.

A comparative study of the thermal stabilities of polymelamines in air and in an inert atmosphere has also been carried out. It has been shown that the temperature of the onset of the decrease in the weight of polymelamines in an inert atmosphere is in the same temperature range as in air. However, whereas in air polymelamine decomposes fully at 700 °C, in an inert atmosphere the amount of coke residue is 60 – 72%.[90,95–108]

The synthesis of polymelamines by the polycyclotrimerisation of bis(cyanamides) tends to form regularly cross-linked thermostable and heat resistant polymers. The polycyclotrimerisation of bis(cyanamides) is characterised by a high selectivity and a high degree of conversion of the cyanamide groups, which is nearly quantitative. The internodal fragments of these polymers are residues of the initial bis(cyanamides).[95–108]

The experimental and theoretically calculated structural parameters of polymelamines based on oligoaminobis(cyanamide) have been compared.[97] The method based on the statistical theory of high elasticity was used to calculate the parameters of the network structure of the polymelamine based on oligobis(cyanamide) with $n = 25$.[97] The experimental number-average molecular weight of the active chain (M_{ce}) and the concentration of the active chains per unit volume of the cross-linked polymer $(V_c/V)_{exp}$ were evaluated from the equilibrium modulus of elasticity E in extension.

Table 6. Parameters of the network structure of the polymelamine based on the oligoamidobis(cyanamide) (XVII).[97]

n	$M_{c\,exp}$, g mol^{-1}	$M_{c\,theor}$, g mol^{-1}	$10^{-4}(V_c/V)_{exp}$, mol cm^{-3}	$10^{-4}(V_c/V)_{theor}$, mol cm^{-3}	$\frac{(V_c/V)_{exp}}{(V_c/V)_{theor}}$
25	5260	6000	2	2.1	0.95

Table 7. Physicomechanical properties of the polymelamines based on oligoamidobis(cyanamides)[97] and oligoimidobis(cyanamides).[107]

n	M_c	Impact strength, kJ m^{-2}	Ha_{Br}*, MPa	σ_i, MPa
		(XVII)		
4	1 000	10	340	80
7	2 000	13	330	95
12	3 000	15	315	116
17	4 000	16	310	120
25	6 000	20	300	128
50	12 000	24	300	145
		(XVIII)		
3	2 000	3	290	80
6	4 000	3	280	82
10	6 000	5	275	85
12	8 000	8	270	92
16	10 000	11	260	110
		(XIX)		
3	2000	3	290	84

*Ha_{Br} is the Brinell hardness.

Table 6 shows, in relation to the polymelamine based on the oligoamidobis(cyanamide) with $n = 25$, that the experimental quantities are virtually identical with the theoretically calculated values, which shows that the degree of completion of the polycyclotrimerisation reaction is nearly quantitative and that the cross-linked polymer formed contains an oligoamide with $n = 25$ as the internodal fragments.[97]

The packing coefficients K have been calculated for certain polymelamines based on oligoamidobis(cyanamides). It was found that the polymelamines have a packing coefficient (0.680–0.690) close to the value determined earlier for linear amorphous polymers ($K = 0.681$).[125] Presumably the polymelamines based on oligoamidobis(cyanamides) are just as close-packed as linear amorphous polymers regardless of the value of M_c.[97]

In order to elucidate the possibility of synthesising polymelamines with specified properties by varying the length of the chain in the initial oligoamidobis(cyanamides) and oligoimidobis(cyanamides),[97,107] the influence of the molecular weights of the internodal fragments on certain physicomechanical characteristics of polymelamines has been studied (Table 7).

The dependence of the electrically insulating properties of the oligoamidobis(cyanamide)-based polymelamines on the effect of temperature, ageing time at different temperatures, and the influence of tropical moisture has been investigated.[100,106,107] Thus the electrically insulating properties of polymelamines based on the oligoamidobis(cyanamides) with $n = 50$ have been investigated as a function of the thermal ageing time at 200° and 250 °C.[100] The studies showed that, after the thermal ageing at 200° and 250 °C for 30 days, the electrically insulating properties of the polymelamines do not change signficantly (Table 8) and that various heat resistant and thermostable articles, used in the electrotechnical industry, can be manufactured from these polymers.

Table 8. Dependence of the electrically insulating properties of the polymelamine based on the oligobis(cyanamide) (XVII) ($n = 50$) on the ageing time.[100]

Conditions	T=200° C			T=250° C			E_{br}, kV mm^{-1}
	tan δ*	ε*	$10^{-15}\rho_V$, Ω cm	tan δ*	ε*	$10^{-15}\rho_V$, Ω cm	
Initial state	0.004	3.3	3	0,004	3.3	3	30
After ageing for							
10 days	0.004	3.6	2	0.004	4.6	5	—
20 days	0.003	3.4	3	0.006	5.1	2	—
30 days	0.004	3.7	1	0.008	5.2	2	25

*At a frequency of 1 MHz.

Table 9. Dependence of the electrically insulating properties of polymelamine based on the oligoamidobis(cyanamide) (XVII) ($n = 50$) on the effect of tropical moisture (38 °C, 98% relative humidity).[107]

Duration of exposure	tan δ*	ε*	$10^{-15}\rho_V$, Ω cm
Initial state	0.004	3.2	3
After exposure to tropical moisture for 10 days	0.007	3.7	8
30 days	0.02	3.7	8

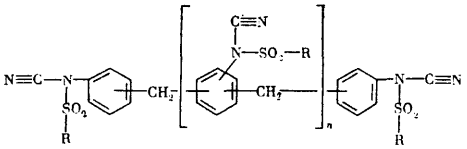
*At a frequency of 1 MHz.

It has been found[100] that the electrically insultating properties of polymelamines based on the oligoamidobis(cyanamide) with $n = 50$ do not change when the polymers are used under the conditions of a tropical climate. The results of these studies are presented in Table 9. Thus the authors[100,106,107] note that the polymelamines investigated exhibit a high heat resistance and thermal stability and have good physicomechanical and electrically insulating parameters at an elevated temperature and under the conditions of a tropical climate and are therefore promising materials for practical use.

Polymelamines, especially aromatic polymelamines, are in most cases highly heat resistant thermostable polymers obtained from a readily available raw material, exhibit an effective adhesion to various materials, and can be readily converted into articles without the evolution of volatile substances.

The preparation of oligomers containing cyanamide groups has been described in a number of studies.[126–128] The authors[126,128] achieved the synthesis of the oligomers by condensing an excess of various diamines with cyanuric chloride, phosphorus trichloride, and phosphoryl chloride. Next the terminal amino-groups were treated with chlorocyanogen in order to obtain cyanamides. The thermoreactive oligomers obtained were cyclotrimerised by the cyanamide groups to prepare heat resistant binders in composite materials.[126–128]

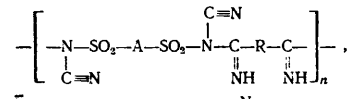
The preparation of α-cyanosulphonamide oligomers having the general formula



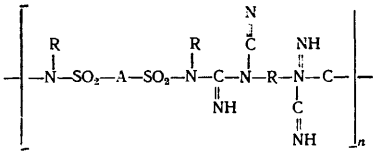
has been described in patents.[129–131] When these thermoreactive oligomers are hardened at 235 °C for 30 min, non-combustible heat resistant polytriazines with T_g = 275 °C are formed;[129] according to differential scanning calorimetric data, the heat of polymerisation is 60–63 cal g^{-1}.[130] The weight losses by the specimen of the composite material based on these oligomers (R = Ph, fillers—fused silica, glass fibre with a fibre length of 6 mm) are respectively 0.32, 0.57, and 4.38% after heating for 500 h at 200°, 225°, and 250 °C.[131]

Oligomeric aromatic polysulphones[132] and polyphosphazenes[133] containing cyanamide groups, and also copolymers of diallylcyanamide with vinyl monomers[134] have been described. Network polymers based on them are obtained by the cyclotrimerisation of the cyanamide groups.

Oligomers having the general formula



(Ref.135)

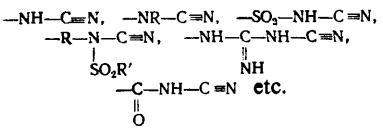


(Ref.136)

have been obtained by the copolymerisation of bis(*N*-cyanosulphonamides) with various bis(cyanamides).[135,136] These thermoreactive polymers, which can be effectively moulded in the melt, are hardened with formation of highly thermostable network polytriazines.

VI. Polymers based on cyanamides

Data are available, mainly of a patent character, for linear and network polymers based on various monomers with the following functional groups:



The polymers have been obtained by the copolymerisation of these monomers with bis(maleic amides),[137,138] diamines,[139–143] ε-caprolactone,[144] nitriles,[145] diamine salts,[146–148] triallyl cyanurate,[149] cyanates,[150–155] and phenols.[156]

There is also information in the patent literature about polymers obtained as a result of the interaction of cyanamides having different sructures with polyamidoacids, polybenzimidazoles, polyquinoxalines, polybenzothiazoles, polyamides, poly(aryl sulphones), and poly(phenylene sulphides), all containing terminal NH_2 groups,[157] and also as a result of reactions with unsaturated polyethers,[158] polybuta-1,2-diene with a molecular weight of 1000–200 000,[159] butadiene–acrylonitrile copolymers,[160] partly cyanomethylated polystyrene,[161] and polyethyleneimine.[162] Network polymers containing oxazolidine fragments are obtained by the reactions of cyanamides with various epoxides.[163–171]

Various cyanamide-based polymers have found applications as binders for filled plastics,[11,59,61,76,84–86,110,111,121,137,138,140,141,158–160,172,173] adhesives,[11,59,61,76,77,81,84–87,109–111] coatings,[11,26,59,61,76,77,81,84–86,109,113,154] films,[26,77,81,86,113,139] and fibres.[75,77,79,113] It has been suggested that polymers based on compounds containing cyanamide groups be used to prepare various thermostable materials—ion-exchange resins,[142,143] electrically insulating materials,[149,158–160,173] cast articles,[11,26,59,61,84,85,109,113,121] and materials for electronic engineering.[174]

References

1. Z Wirpsza *Polymery*, 1970, **15**(1) 57
2. H Kitano, F Tanimoto *Kago-no Reiki*, **25**(2) 135; *Ref. Zh. Khim.*, 1971, 17Zh354
3. H Kitano, F Tanimoto *Kago-no Reiki*, **25**(3) 232; *Ref. Zh. Khim.*, 1971, 18Zh364
4. V A Pankratov, S V Vinogradova, V V Korshak *Usp. Khim.*, 1972, **41**(1) 117 [English translation in *Russ. Chem. Rev.*, 1972(1)]
5. R P Tiger, L I Sarynina, S G Entelis *Usp. Khim.*, 1972, **41**(9) 1672 [English translation in *Russ. Chem. Rev.*, 1972(9)]
6. V V Korshak *Vysokomol. Soedin. Ser. A*, 1974, **16**(5) 926
7. V A Postnikova, Yu L Spirin, A A Blagonravova *Novye Problemy Khimii Vysokomolekulyarnykh Soedinenii* (New Problems in the Chemistry of High-Molecular-Weight Compounds), Izd. Naukova Dumka, Kiev, 1975, p. 58
8. V A Pankratov, S V Vinogradova, V V Korshak *Itogi Nauki i Tekhniko. Khimiya i Tekhnologiya Vysokomolekulyarnykh Soedinenii* (Advances in Science and Engineering. The Chemistry and Technology of High-Molecular-Weight Compounds), Izd. VINITI, Moscow 1974, Vol. II, p. 84
9. V A Pankratov, S V Vinogradova, V V Korshak *Usp. Khim.*, 1977, **46**(3) 530 [English translation in *Russ. Chem. Rev.*, 1977(3)]
10. D Martin, M Bauer, V A Pankratov *Usp. Khim.*, 1978, **47**(10) 1814 [English translation in *Russ. Chem. Rev.*, 1978(10)]
11. V A Pankratov, Doctoral Thesis in Chemical Sciences, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1978, 483 pp
12. R P Tiger, Doctoral Thesis in Chemical Sciences, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1979, 500 pp
13. V A Sergeev, V K Shitikov, V A Pankratov *Usp. Khim.*, 1979, **48** 148 [English translation in *Russ. Chem. Rev.*, 1979(1)]

14. D Martin, R Bacalogly *Organische Synthesen mit Cyansaüreestern*, Akad. Verlag, Berlin, 1980, 227 pp
15. Yu E Doroshenko, A V Samoryadov, V V Korshak *Itogi Nauki i Tekhniko. Khimiya i Tekhnologiya Vysokomelekulyarnykh Soedinenii* (Advances in Science and Engineering. The Chemistry and Technology of High-Molecular-Weight Compounds), Izd. VINITI, Moscow, 1981, Vol. 15, p. 72
16. V V Korshak *Raznozvennost' Polimeriv* (The Heterounit Nature of Polymers), Izd. Nauka, Moscow, 1977, 243 pp
17. V A Pankratov, Ts M Frenkel', A M Fainleib *Usp. Khim.*, 1983, **52**(6) 1018 [English translation in *Russ. Chem. Rev.*, 1983(6)]
18. A K Zhitinkina, N A Shibanova, O G Tarakanova *Usp. Khim.*, 1985, **54**(11) 1866 [English translation in *Russ. Chem. Rev.*, 1985(11)]
19. E N Zil'berman *Reaktsii Nitrilov* (The Reactions of Nitriles), Izd. Khimiya, Moscow, 1972, pp. 27, 62, 374, 381, 387, 389
20. M V Tsirgiladze, Candidate's Thesis in Chemical Sciences, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1980, 153 pp
21. V Migrdichian *The Chemistry of Organic Cyanogen Compounds*, Reinhold Publ. Corp., New York, 1947, p. 102
22. A W Hofmann *Ber.*, 1885, **18**(17) 3217
23. K Sugino, K Shirai, R Kitawaki *J. Org. Chem.*, 1961, **26**(10) 4122
24. French P. 1 305 857; *Chem. Abs.*, 1963, **58** 10088
25. K Sugino, K Shirai, R Kitawaki Japanese P. 11 011; *Chem. Abs.*, 1963, **59** 3778
26. R Kitawaki, K Shirai *J. Chem. Soc. Japan. Ind. Chem. Sec.*, 1964, **67**(9) 1485
27. J Hynds, E J Vickers, J M Phillipson BRD Appl. 1 958 320; *Chem. Abs.*, 1970, **73** 109311
28. V V Korshak, V A Pankratov, D F Kutepov, et al. USSR P. 447 035; *Byull. Izobret.*, 1975(45), 161
29. V A Pankratov, V V Korshak, S V Vinogradova, et al. *Izv. Akad. Nauk SSSR Ser. Khim.*, 1975(10), 2315
30. I Bacaloglu, R Bacaloglu, C Viragh, et al. *J. Prakt. Chem.*, 1975, **317**(6) 907
31. H Kawashi, S Monno, M Wajima, A Takahashi Japanese P. 61-22 060; *Chem. Abs.*, 1986, **105** 79507
32. A E Kreton, I V Smol'yaninov USSR P. 179 229; *Byull. Izobret.*, 1966(5), 19
33. H Boehme, W Stammberger *Chem. Ber.*, 1971, **104**(10) 3354
34. L A Savvina, Ya M Yakovenko *Metody Polucheniya Khimicheskikh Reaktivov i Preparatov* (Methods of Synthesis of Chemical Reagents and Preparations), Izd. Khimiya, Moscow, 1964, No. 10, p. 32
35. V V Korshak, G I Shukurov, D F Kutepov, V A Pankratov *Izv. Akad. Nauk SSSR Ser. Khim.*, 1981(7), 1623
36. L Hunter *Chem. Ind.*, 1941, **60**(1) 32
37. W S Schneider *J. Am. Chem. Soc.*, 1950, **72**(2) 761
38. H Bredereck, K Reif *Chem. Ber.*, 1948, **81**(5) 426
39. A Colson *J. Chem. Soc.*, 1917, **111**(658) 554
40. A Franssen *Bull Soc. Chem. France*, 1928, **44**(3) 117
41. B I Sukhorukov, A I Finkel'shtein *Opt. Spektrosk.*, 1959, **7**(5) 653
42. A I Finkel'shtein, B I Sukhorukov, F I Mushkin *Zh. Fiz. Khim.*, 1963(2), 290 [English translation in *Russ. J. Phys. Chem.*, 1963(2)]
43. K Lempert, J Puskas, L Imre *Acta Chim. Acad. Sci. Hung.*, 1969, **60**(4) 409
44. K Lempert, L Hazai, L Imre *Acta Chim. Acad. Sci. Hung.*, 1972(2), 261
45. I H Boyer, P I Frints *Tetrahedron Lett.*, 1968(28), 3211
46. I H Boyer, P I Frints *J. Heterocycl. Chem.*, 1970, **7**(1) 59
47. W Traube, E Wedelstädt *Ber.*, 1900, **33**(1) 1383
48. K Lempert, I Puskas *Period Polytechn. Chem. Eng.*, 1968, **12**(2) 123
49. A W Hofmann *Ber.*, 1869, **2**(2) 602; 1870 **3**(1), 264; 1872, **5**(2) 695
50. E M Smolin, L Rappoport *s-Triazines and Derivatives*, Intersci. Publ., New York, 1959, p. 349
51. F Kurtzer *J. Chem. Soc.*, 1949(11), 3033
52. H King, A Tonkin *J. Chem. Soc.*, 1946(11), 1063
53. D Keiser, I Hecheimbleiker US P. 2 691 021; *Chem. Abs.*, 1955, **49** 14817
54. W Ericks US P. 2 331 670; *Chem. Abs.*, 1944, **38** 1651
55. R Birkofer *Ber.*, 1942, **75**(4) 429
56. R Kitawaki, K Sugino *J. Org. Chem.*, 1960, **25**(6) 1043
57. S Takenaka, T Sekine *Denki Kagaku Oyobi Kogyo Butsuri Kagaku*, 1968, **36**(12) 863; *Chem. Abs.*, 1969, **70** 92611
58. V V Korshak, D F Kutepov, V A Pankratov, et al. *Izv. Akad. Nauk SSSR Ser. Khim.*, 1973(6), 1408
59. V V Korshak, D F Kutepov, V A Pankratov, et al *Vysokomol. Soedin. Ser. B*, 1974, **16**(3) 156
60. V V Korshak, D F Kutepov, V A Pankratov, et al. *Zh. Vses. Khim. im. D I Mendeleeva*, 1974, **19**(4) 472
61. V A Pankratov, N P Antsiferova, D F Kutepov *XVIII Vsesoyuznaya Konferentsiya po Vysokomolekulyarnym Soedineniyam. Tezisy Dokladov* (The XVIII All-Union Conference on High-Molecular-Weight Compounds. Abstracts of Reports), Izd. Khimiya, Kazan, 1973, p. 175
62. B.P. 654 656; *Chem. Abs.*, 1952, **46** 8682
63. H Michaud, G Ortenburger, W Poshinger,H Roeck BRD Appl., 2 536 689; *Chem. Abs.*, 1977, **86** 140669
64. H Michaud, G Ortenburger, W Poshinger, H Rock Canadian P. 1 055 940; *Chem. Abs.*, 1979, **91** 75075
65. F Lohse, H Zondler Europ. P. 87 393; *Chem. Abs.*, 1983, **99** 196090
66. C G Papaioannou US P. 3 706 741; *Chem. Abs.*, 1973, **78** 72219
67. R McKee *J. Prakt. Chem.*, 1911, **84**(4) 825
68. G Kuzzer, K Dauraghi-Zadek *Chem. Rev.*, 1967, **67**(2) 107
69. W Weith *Ber.*, 1874, **7**(4) 848
70. G Cimmician, M Dennstedt *Ber.*, 1883, **16**(1) 64
71. V V Korshak, V A Pankratov, G I Shukurov, D F Kutepov *Izd. Akad. Nauk SSSR Ser. Khim.*, 1981(3), 681
72. G I Shukurov, V V Korshak, V A Pankratov *Nauchnaya Konferentsiya 'Polimernye Materialy i Ikh Primenenie v Narodnom Knozyaistve' Tezisy Dokladov* (The Scientific Conference on 'Polymeric Materials and Their Applications in the National Economy'. Abstracts of Reports), Izd. Kabardino-Balkar. Gos. Univ., Nal'chik, 1976, p. 17
73. A W Hofmann *Ber.*, 1885, **18**(16) 2755
74. J Thurston US P. 2 480 067; *Chem. Abs.*, 1950, **44** 5926
75. French P. 1 309 517; *Chem. Abs.*, 1963, **58** 10368
76. K Sugino, K Shirai, R Kitawaki Japanese P. 13 898; *Ref. Zh. Khim.*, 1965, 24S275
77. K Sugino, K Shirai, R Kitawaki Japanese P. 13 987; *Ref. Zh. Khim.*, 1965, 24S274
78. K Sugino, K Shirai, R Kitawaki B.P. 100 981
79. K Sugino, K Shirai, R Kitawaki B.P. 100 982

80. K Sugino, K Shirai, R Kitawaki US P. 3291673; *Chem. Abs.*, 1967, **66** 56280
81. K Sugino, K Shirai, R Kitawaki BRD P. 1246239; *Chem. Abs.*, 1967, **67** 91435
82. K Sugino, K Shirai, R Kitawaki BRD P. 1240666
83. C K Ikeda US P. 3308101; *Chem. Abs.*, 1967, **66** 105463
84. V V Korshak, V A Pankratov, S V Vinogradova, et al. *Dokl. Akad. Nauk SSSR*, 1975, **220**(5) 1081
85. V V Korshak, D F Kutepov, S V Vinogradova, et al. USSR P. 413155; *Byull. Izobret.*, 1975(4), 66
86. V V Korshak, S V Vinogradova, V A Pankratov, et al. USSR P. 517599; *Byull. Izobret.*, 1976(22), 76
87. V V Korshak, V A Pankratov, N P Antsiferova, et al. USSR P. 505645; *Byull. Izobret.*, 1976(9) 65
88. M V Tsirgiladze, P N Gribkova, L F Larina, V A Pankratov *Vsesoyuznaya Konferentsiya po Kinetike Fiziko-Khimicheskikh Reaktsii. Tezisy Dokladov* (All-Union Conference on the Kinetics of Physicochemical Reactions. Abstracts of Reports), Izd. OIFKh Akad. Nauk SSSR, Chernogolovka, 1977, p. 108
89. G I Shukurov, V A Pankratov, V V Korshak *Plast. Massy*, 1985(9), 5
90. V A Pankratov, D F Kutepov, G I Shukurov *Plast. Massy*, 1983(2), 12
91. V V Korshak, G I Shukurov, V A Pankratov *Izv. Akad. Nauk SSSR Ser. Khim.*, 1981(7) 1628
92. V V Korshak, S V Vinogradova, V A Pankratov, et al. USSR P. 772167; *Byull. Izobret.*, 1982(1), 266
93. G I Shukurov, V A Pankratov, D F Kutepov, et al. *Plast. Massy*, 1983(12), 10
94. V A Pankratov, G I Shukurov, E N Godovanets *II Vsesoyuznaya Konferentsiya po Issledovaniyu Polimernykh Kompositsionnykh Materialov v Narodnom Khozyaistve. Tezisy Dokladov* (The II All-Union Conference on the Study of Polymeric Composite Materials in the National Economy. Abstract of Reports), Izd. IKhFP Akad. Nauk Uzbek. SSR, Tashkent, 1983, p. 112
95. V V Korshak, S V Vinogradova, V A Pankratov, et al. USSR P. 630877; *Byull. Izobret.*, 1982(23) 307
96. V V Korshak, G I Shukurov, V A Pankratov *Plast. Massy*, 1983(7), 9
97. V V Korshak, V A Pankratov, S V Vinogradova *Plast. Massy*, 1982(3), 28
98. V V Korshak, D F Kutepov, S V Vinogradova *Trudy Moskov. Khim.-Tekhnol. Inst. im. Mendeleeva*, 1980, **110** 124
99. G I Shukurov, V A Pankratov, D F Kutepov, et al. *Vsesoyuznyi Simpozium 'Nauchnye Dostizheniya i Progressivnaya Tekhnologiya Pererabotki Polimerov'. Tezisy Dokladov* (The All-Union Symposium on 'The Scientific Advances and the Progressive Technology in the Processing of Polymers'. Abstracts of Reports), Izd. Nauka, Syzran', 1981, p. 25
100. G I Shukurov, V A Pankratov, D F Kutepov, E N Godovanets *Plast. Massy*, 1983(11), 11
101. V V Korshak, S V Vinogradova, G I Shukurov, et al. *Izv. Akad. Nauk SSSR Ser. Khim.*, 1980(12) 2809
102. V V Korshak, S V Vinogradova, V A Pankratov, et al. USSR P. 704956; *Byull. Izobret.*, 1979(7), 107
103. V V Korshak, S V Vinogradova, V A Pankratov, et al. USSR P. 702034; *Byull. Izobret.*, 1979(5), 110
104. V V Korshak, D F Kutepov, S V Vinogradova, et al. *Trudy Moskov. Khim.-Tekhnol. Inst. im. Mendeleeva*, 1980, **110** 26
105. G I Shukurov, V V Korshak, V A Pankratov *Nauchnaya Konferentsiya 'Polimernye Materialy i Ikh Primenenie v Narodnom Khozyaistve' Tezisy Dokladov* (The Scientific Conference on 'Polymeric Mateirals and Their Applications in the National Economy'. Abstracts of Reports), Izd. Kabardino-Balkar. Gos. Univ., Nal'chik, 1982, p. 44
106. G I Shukurov, V A Pankratov, D F Kutepov, V V Korshak *Plast. Massy*, 1983(7), 11
107. G I Shukurov, V A Pankratov *Mezhvedomstvennoe Seminar-Soveshchanie 'Pererabotka, Destruktsiya i Strabilizatsiya Polimernykh Materialov'. Tezisy Dokladov* (Interdepartmental Seminar-Conference on 'The Processing, Degradation, and Stabilisation of Polymeric Materials'. Abstracts of Reports), Izd. Irfon. Dushanbe, 1983, p. 119
108. G I Shukurov, V A Pankratov *Nauchno-Teknicheskaya Konferentsiya 'Ekspluatatsionnye Svoistva Konstruktsionnykh Materialov'. Tezisy Dokladov* (The All-Union Scientific-Technical Conference on 'The Operating Properties of Constructional Materials'. Abstracts of Reports), Izd. Kabardino-Balkar. Gos. Univ., Nal'chik, 1984, p. 84
109. J Hynds, J M Phillipson, E J Vickers B.P. 1322332
110. J Hynds, E J Vickers, J M Phillipson B.P. 1269335
111. B A Langager US P. 3779997
112. B A Langager US P. 3817920
113. H D Schminke, E Grigat, R Pütter US P. 3642725
114. J Ebiling BRD P. 2433938
115. French P. 2265769
116. B A Langager B.P. 1453105
117. J Hynds, E J Vickers, J M Phillipson BRD Appl. 1958320; *Chem. Abs.*, 1970, **73** 109311
118. Japanese Appl. 75-128800; *Chem. Abs.*, 1976, **85** 124691
119. V V Korshak, V A Pankratov, D Ya Tsvankin, et al. *Vysokomol. Soedin. Ser. B*, 1974, **16**(5) 324
120. V A Pankratov, G I Shukurov, D F Kutepov, E N Godovanets *Plast. Massy*, 1984(10), 59
121. R J Kray *Soc. Plast. Ind. Reinforc. Plast and Compos. Inst. XXX Annu. Conf., Reinforc. Plast.-Milestone., Washington DC 4–7 February 1975*, New York Acad. Sci., New York, P.C. 19/I–C19/8
122. Japanese Appl. 58-71923; *Chem. Abs.*, 1983, **99** 196014
123. *Res. Discl.*, 1978(171), 16
124. L N Fomenko, V D Gerasimov, G A Kuznetsov, L B Sokolov *Plast. Massy*, 1970(3), 27
125. G L Slonimskii, A A Askadskii, A A Kitaigorodskii *Vysokomol. Soedin. Ser. A*, 1970, **12**(2) 494
126. R Sundermann, G Rottloff, E Grigat BRD Appl. 2546372; *Ref. Zh. Khim.*, 1978, 4S323
127. R Sundermann, C Rottloff BRD Appl. 2534890; *Ref. Zh. Khim.*, 1978, 5S315
128. R Sundermann, G Rottloff BRD Appl. 2546369; *Ref. Zh. Khim.*, 1978, 5S318
129. R J Kray BRD Appl. 2745521; *Chem. Abs.*, 1978, **89** 25336
130. R J Kray US P. 4150051
131. S Kadziura, S Wada, S Suzuki, T Ito Japanese Appl. 57-170958; *Ref. Zh. Khim.*, 1983, 18S509
132. T Kakurai, N Igarashi, T Senao Japanese Appl. 57-202322; *Ref. Zh. Khim.*, 1984, 2S529
133. W L Hergenrother, A F Halasa US P. 4175181
134. Y Iwakura, K Uno, K Tsuruoka Japanese P. 46-3175; *Ref. Zh. Khim.*, 1971, 23S396

135. R Sundermann, G Rottloff, G E Grigat BRD Appl. 2 533 127; *Ref. Zh. Khim.*, 1978, 6S314
136. R J Kray US P. 3 944 526
137. Japanese P. 57-207 645; *Chem. Abs.*, 1983, **99** 23546
138. M Ono, A Takahashi, T Sugawara, et al. Japanese P. 61-246 234; *Chem. Abs.*, 1987, **106** 139497
139. U Kreutzer, J Galinke BRD Appl. 2 022 492; *Chem. Abs.*, 1972, **76** 113868
140. A Takahashi, M Ono, R Tada, et al Europ. P. 102 052; *Chem. Abs.*, 1984, **101** 8181
141. Japanese P. 59-196 393; *Chem. Abs.*, 1985, **102** 186027
142. Japanese P. 60-37 524; *Chem. Abs.*, 1985, **103** 14661
143. M Ono, A Takahashi, W Kawamoto, et al. Japanese P. 61-04778; *Chem. Abs.*, 1986, **105** 62242
144. K Sugawara, A Takahashi, M Ono, et al Europ. P. 153 603; *Chem. Abs.*, 1986, **104** 34946
145. T Seo, T Kakurai, T Noguchi *Kobunshi Kagaku.*, 1973, **30**(340) 451, 518; *Ref. Zh. Khim.*, 1974, 5S246
146. F L Rose, G Swain US P. 2643232
147. K Sugino, K Shirai, R Kitawaki Japanese P. 37-13899; *Ref. Zh. Khim.*, 1965, 24S276
148. R Kitawaki, K Shirai, K Sugino *Bull. Chem. Soc. Jpn.*, 1968, **41**(6) 1461
149. Japanese P. 58-125 719; *Chem. Abs.*, 1983, **99** 213560
150. R Sundermann, G Rottloff, E Grigat BRD Appl. 2 533 119; *Ref. Zh. Khim.*, 1978, 5S316
151. R Sundermann, G Rottloff, E Grigat BRD Appl. 2 533 121; *Ref. Zh. Khim.*, 1978, 6S311
152. R Sundermann, G Rottloff, E Grigat, R Pütter BRD Appl. 2 533 122; *Ref. Zh. Khim.*, 1978, 6S312
153. R Sundermann, G Rottloff, E Grigat BRD Appl. 2 533 126; *Ref. Zh. Khim.*, 1978, 5S314
154. R Sundermann, G Rottloff BRD Appl. 2 546 355; *Ref. Zh. Khim.*, 1978, 5S317
155. R Sundermann, G Rottloff, E Grigat BRD Appl. 2 549 569; *Ref. Zh. Khim.*, 1978, 8S379
156. H Izumi, M Nakai Japanese Appl. 76-62 895; *Chem. Abs.*, 1976, **85** 95150
157. R Seltzer, P D Sherman US P. 3 943 107
158. Japanese P. 60-94 422; *Chem. Abs.*, 1985, **103** 179165
159. Japanese P. 59-157 130; *Chem. Abs.*, 1985, **102** 150338
160. Japanese P. 60-94 423; *Chem. Abs.*, 1985, **103** 216341
161. T Seo, T Kakurai, T Noguchi *Chem. High Polym.*, 1973, **30**(334) 76
162. B.P. 1 531 273
163. W Seide, D Helm BRD Appl. 2 459 792; *Chem. Abs.*, 1976, **85** 109511
164. P Bornmann, H Michaud, J Seeholzer BRD Appl. 2 649 402; *Chem. Abs.*, 1978, **89** 25445
165. R Seltzer US P. 4 140 658; *Chem. Abs.*, 1979, **90** 118001
166. G Bihlmayer, J Krick BRD Appl. 2 743 015; *Chem. Abs.*, 1979, 20270
167. G Bihlmayer, J Krick Austrian P. 351 772; *Chem. Abs.*, 1979, 141717
168. R Seltzer, J F DiPrima, W S Durell US P. 4 168 364; *Chem. Abs.*, 1979, **91** 212228
169. E H Catsiff, H B Dee, J F DiPrima, R Seltzer *ACS Polym. Prepr. Div. Polym. Chem.*, 1981, **22**(2) 111
170. S A Zahir *Adv. Org. Sci. Technol.*, 1982, 4 83; *Chem. Abs.*, 1983, **98** 145085
171. Japanese P. 58-71 923; *Chem. Abs.*, 1983, **99** 196014
172. S Kaziura, S Wada, S Suzuki Japanese P. 56-54 994; *Ref. Zh. Khim.*, 1983, 18S510
173. Japanese P. 57-170 923; *Chem. Abs.*, 1983, **98** 144656
174. Japanese Appl. 81-73 492; *Chem. Abs.*, 1981, **95** 134061

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Condensing agents in polycondensation

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ABSTRACT. The advances have been examined and trends noted in the development of a new method of synthesis of heterochain polymers which has been called "direct polycondensation" and is based on the interaction of monomers under mild conditions in the presence of various condensing agents. The latter form reactive derivatives with one of the monomers, which then react *in situ* with the monomer of the opposite nature. It has also been shown that the condensing agents can be used successfully in the synthesis of activated dicarboxylic acid diesters and diamides, which are promising electrophilic monomers for the synthesis of a wide variety of heterochain polymers under the conditions of low-temperature polycondensation in solution. The possibilities of the synthesis of polymers by the "biochemical" activation of monomers, i.e. using enzymes as "condensing agents", are discussed.

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I. Introduction

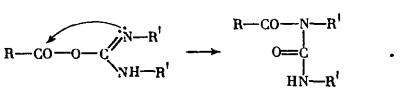
The polycondensation of dicarboxylic acids with diamines, diols, and other difunctional and polyfunctional nucleophiles proceeds as a rule only at high temperatures (up to 250–300 °C) and at a low rate and is accompanied by numerous side reactions leading to the decomposition of the functional groups and the breakdown of heterounit structures.[1] In a number of instances, for example, when aromatic diamines are used in polycondensation, high-molecular-weight polymers are not formed even at the high temperatures stated above.[2]

One of the most effective and widely used methods of overcoming the above difficulties consists in the employment of the corresponding acid halides (mainly dichlorides), which are distinguished by a high reactivity and which permit the synthesis of high-molecular-weight heterochain polymers at low temperatures (–30 to + 50 °C).[3–5] However, each individual acid dichloride must be synthesised and brought to the required condition, which involves additional expense. The high hydrolytic instability of acid dichlorides, which, apart from the destruction of the functional groups, leads to the evolution of hydrogen chloride, causes corrosion of the apparatus. The synthesis of acid dichlorides therefore requires additional complex apparatus made of corrosion-resistant materials.

In the light of the foregoing, the idea of employing a wide variety of reagents the so called condensing agents (CA), leading to the activation of one of the monomers (more precisely either electrophilic or nucleophilic functional groups) with their subsequent polycondensation *in situ* under mild conditions in organic solvents, is extremely attractive.

In synthetic organic chemistry, CA have been known for a fairly long time. A wide variety of halogen transferring agents ($SOCl_2$, PCl_3, $POCl_3$, etc.,[6] hexachlorocyclotriphosphazene,[7] cyanuric chloride,[8] picryl chloride,[9,10] picryl fluoride,[11] $SiCl_4$,[12–14] and $TiCl_4$[15]), carbonates,[16,17] sulphites,[18] carbodiimides,[19] a wide variety of phosphorus derivatives.[20–29] including derivatives immobilised on monomeric carriers,[30,31] polyphosphates,[32] as well as other compounds[33–35] have been used as highly effective CA. The employment of the above CA permits the successful solution of many complex synthetic problems, especially when water-soluble CA are used (see, for example, Woodward et al.[33] and Kemp and Chien[34]), which make it possible to form the amide bond or bonds of a similar nature in an aqueous medium. The employment of the above agents in peptide chemistry[12,14,18,20–22,25,26,33,34,36–40] and oligonucleotide chemistry[41] for the construction of peptide and phosphodiester bonds under mild conditions without the preliminary activation of the reactants has proved especially fruitful. This approach had hardly been used for polycondensation systems up to the beginning of the 1970's. A possible reason for this may be sought in the nature of the condensing agents commonly employed at the time in the peptide and nucleotide chemistry (dicyclohexylcarbodiimide, carbonyldiimidazole, etc.), which tended to undergo side reactions involving the destruction of the functional groups. This factor may not be so significant in the synthesis of individual low-molecular-weight substances (at worst it leads to a decrease in the yield) but is of primary importance in the synthesis of high-molecular-weight compounds, while the single-channel nature of the reaction (i.e. the absence of side processes involving chain termination) is a decisive factor for the attainment of high molecular weights.

The CA employed to construct the amide or ester bond form an activated intermediate with an electrophile (carboxylic acid, CO_2, or CS_2—see below) or a nucleophile; this then reacts further with a substrate of the opposite nature. The main requirement which must be met by such intermediate activated compounds is a sufficiently high stability (lifetime) and a low tendency to rearrange or undergo similar side reactions involving the destruction of the functional group. For example, the main disadvantage of carbodiimides as CA is the high tendency of the intermediate activated adduct to rearrange to an inactive acylurea:[19]



The introduction of various phosphorus compounds (both trivalent and pentavalent) as CA into the polymer chemistry made it possible to solve successfully the problem of the synthesis of high-molecular-weight polymers under the conditions of "direct polycondensation".

Subsequently other CA without phosphorus were also proposed. The prospects for the employment of various enzymes belonging to the class of hydrolases as CA are being discussed.

II. Phosphorus compounds as condensing agents

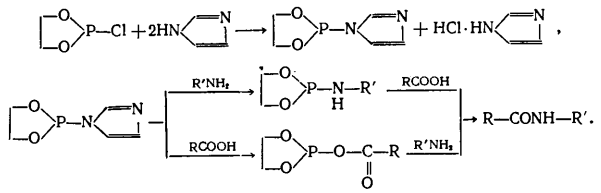
Phosphorus compounds, especially pyrophosphoric acid esters, were used as early as the 1950's–1960's in polycondensation (of the AB type) as CA for the synthesis of regularly alternating polypeptides. For example, polypeptides[20–22] with a molecular weight up to 25 000[22] were synthesised using tetraethyl pyrophosphate. However, up to the 1970's no systematic studies in the field of "direct polycondensation", involving also other "usual" monomers (among them those of the AA–BB type) were performed.

At the beginning of the 1970's, two groups of investigators (Ogata and co-workers and Yamazaki and Higashi) published almost simultaneously a series of communications on the successful use of phosphorus compounds as CA for the direct polycondensation of dicarboxylic acids with diamines and diols to form the corresponding polyamides and polyesters and initiated thereby systematic studies on a new promising field of synthesis of polymers.

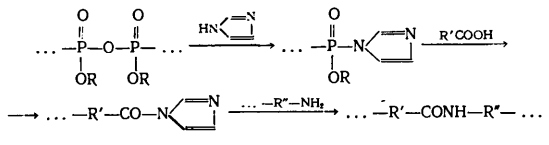
In their first publications, Ogata and co-workers[42,43] described the use of triphenyl phosphite $P(OPh)_3$ in the presence of imidazole as the CA and a somewhat modified version of the method proposed by Mitin and co-workers for the synthesis of peptides.[23] The authors suggest that the polycondensation proceeds with formation of an intermediate mixed anhydride, which reacts further with the diamine to form a polyamide:[43]

$$HOOC{-}R{-}COOH + 2P(OPh)_3 \xrightarrow{\text{imidazole}} (PhO)_2P{-}O{-}CO{-}R{-}CO{-}O{-}P(OPh)_2.$$

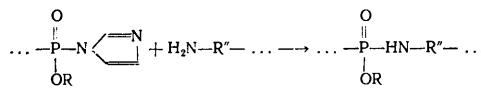
The mechanism and kinetics of the polycondensation reaction have been investigated in detail.[44] Apart from $P(OPh)_3$, its chloro-, methyl-, and methoxy-substituted analogues as well as 2-chloro-1,3,2-dioxaphosphorane (ethylene phosphorochlorodite) were used in the above reaction. The dioxaphosphorane reacts with imidazole to form 2-(1-imidazolyl)-1,3,2-dioxaphosphorane, which is capable, in its turn, of activating both an electrophile and a nucleophile:



In subsequent studies,[45] other phosphorus compounds were also used to synthesise polyamides, namely polyphosphoric acid esters (polyphosphates) in combination with imidazole. The mechanism of the activation put forward by the authors includes the formation of an acylimidazole, which has an exceptionally high acylating potential:

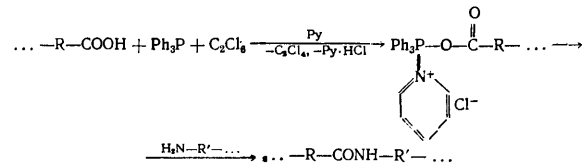


However, together with the reaction investigated, the formation of a relatively inactive phosphamide takes place at an appreciable rate, which is apparently in fact the main cause of the arrest of chain growth:



However, we cannot fully exclude chain termination due to the alkylation of amines, because it is known that phosphoric acid esters are fairly vigorous alkyl group transferring agents.[46]

The triphenylphosphine plus organic polyhalide condensing system[24,25] modified by pyridine[47–52] proved to be very successful. The proposed activation mechanism is as follows in this instance:



The above condensing system has been used to synthesise polyamides[46,48,52] and polyesters.[47,50]

Triphenylphosphine dichloride (plus a tertiary amine), which is in all probability actually an intermediate in the interaction of triphenyl phosphine with C_2Cl_6 when the reaction is carried out in accordance with the above scheme, has also been used successfully to synthesise polyesters.[53] A characteristic feature of this system is the possibility of regenerating the CA, which is important from the standpoint of the practical application of the method:

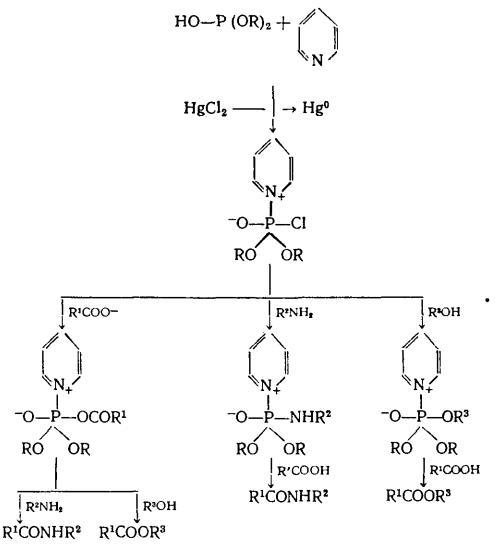
$$n\text{HOOCArCOOH} + n\text{HOAr'OH} \xrightarrow{2Ph_3PCl_2,\ B_N}$$
$$\longrightarrow {-}[{-}\text{COArCOOAr'O}{-}]_n{-} + Ph_3PO + B_N\cdot HCl,$$
$$Ph_3PO + COCl_2 \text{ (or ClCOCOCl)} \longrightarrow Ph_3PCl_2 + CO_2 + (CO);$$
$$B_N = \text{tertiary amine.}$$

High-molecular-weight polyesters based on bisphenol A and isophthalic acid (η_{int} = 2.24 dl g^{-1}) and *m*-hydroxybenzoic acid (η_{int} = 2.33 dl g^{-1}) have been obtained using phosphorus compounds, the best results being achieved in the presence of polymeric matrices—poly-2-vinyl- and poly-4-vinyl-pyridines or polyepoxyethane.[51]

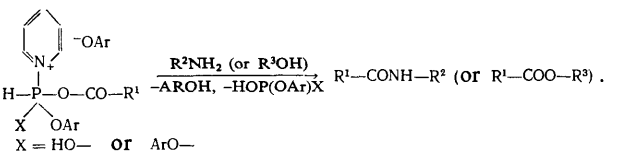
As regards the synthesis of polyamides, in the presence of the $P(OPh)_3$–imidazole system[42–44] low-molecular-weight polyamides with $\eta_{int} < 0.4$ dl g^{-1} were obtained from aliphatic monomers (salts of type AG). This is apparently due to the formation of appreciable amounts of comparatively inactive phenyl esters of carboxylic acids when imidazole is used as the tertiary amine in systems of this kind.[44] The polyphosphate–imidazole system also leads only to the synthesis of low-molecular-weight polyamides ($\eta_{int} < 0.3$ dl g^{-1}) for reasons discussed above.[45] The η_{int} for aliphatic polyamides was raised to 0.76 dl g^{-1} using the PPh_3–organic halide–pyridine system.[52] The system proved to be suitable for the synthesis of aromatic polyamides[47,49,50] especially of poly-*p*-benzamide, whose η_{int} was raised to 5.16 dl g^{-1}.[59] (For the halides employed, see Table 3 below.)

Since 1972, another group of investigators (Yamazaki, Higashi, and co-workers) also undertook systematic studies of a wide variety of phosphorus-containing condensing systems and of their employment both in the direct polycondensation and in peptide synthesis.[54–107] In their first publications, the authors established that the *N*-phosphonopyridinium derivative in the presence of an oxidant ($HgCl_2$) is

extremely reactive towards nucleophiles and activates carboxy- (interacting in the form of the carboxylate anion), amino-, and hydroxy-groups leading to the formation of the corresponding amides and esters on subsequent aminolysis, alcoholysis, or acidolysis:[54,56–58]

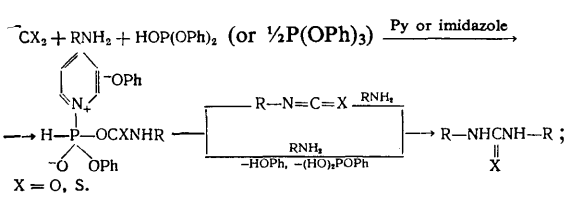


It was subsequently established that phosphates, in particular di- and tri-aryl phosphites, react with carboxylic acids, in the presence of pyridine but without an oxidant, to form the corresponding activated derivatives capable of further interaction with nucleophiles under mild conditions:[55]



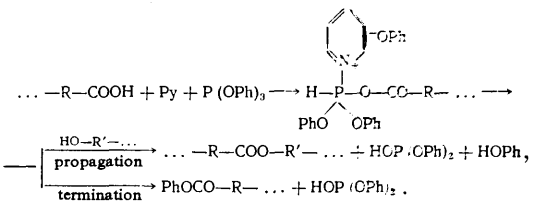
Apart from phosphites, other phosphorus compounds can also be used in similar reactions—phosphinites (R_2P-OAr), phosphonites [$R-P(OAr)_2$], phosphonates [$R-P(O)(OAr)_2$], etc., which are presented in Table 1. Only the aryl esters are effective.[65] We may note that the promoting role of pyridine and imidazole (and also of other bases having properties similar to theirs—Table 2) is in all cases significant. Promoting functions are also performed by *N*-methylpyrrolidinone (*N*-MD) (which is in addition the most suitable solvent in the processes indicated) and tetramethylurea. Various organic halides (Table 3) as well as metal salts, particularly LiCl and $CaCl_2$ (Table 4), quaternary ammonium salts, and tertiary amine hydrochlorides (Table 5) are also effective promoting agents in the reactions of aryl phosphites described above.

The main advantages of the systems examined include the fact that the reaction is performed in one stage by adding the CA directly to the mixture of the electrophile and the nucleophile. It is essential to note that, apart from carboxylic acids, in the presence of pyridine or imidazole aryl phosphites form activated derivatives with CO_2 (or CS_2), which leads to the "direct" synthesis of the corresponding ureas:[64]

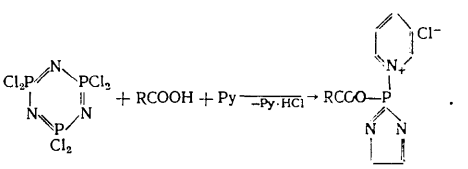


Various halogen-containing phosphorus compounds, namely $PhOPCl_2$,[69,70] $EtOPCl_2$, $PhPCl_2$, $(PhO)_2PCl$, $(EtO)_2PCl$, etc.,[70] have likewise been used as CA in order to synthesise ureas from CO_2. In the synthesis of polyureas, for example, from di(4-aminophenyl)-methane (t = 40 °C, P_{CO_2} = 20 atm), the systems $P(OPh)_3$ + imidazole in dimethylformamide (η_{ln} = 0.37 dl g^{-1}) and $HOP(OPh)_2$ in pyridine (η_{ln} = 2.24 dl g^{-1}) proved to be the most effective. The $PhOPCl_2$ system in pyridine made it possible to synthesise polyureas at atmospheric CO_2 pressure (η_{ln} = 0.4–0.5 dl g^{-1}).[69]

Aryl phosphites, which are excellent CA in the processes indicated above (in the synthesis of polyamides or their analogues), proved to be relatively ineffective in the synthesis of polyesters, which has been attributed to chain termination as a result of the competing intramolecular esterification reaction:[83]



The best CA in the synthesis of polyesters are pentavalent phosphorus compounds containing a phosphorus–chlorine bond. Thus polyesters (η_{ln} = 0.2–0.8 dl g^{-1}) have been synthesised successfully in the presence of hexachlorocyclotriphosphazene.[75,85,89] It is believed that the reaction proceeds via *N*-phosphinopyridinium derivatives:



Polyesters with higher molecular weights have been obtained by employing the $(PhO)_2P(O)Cl-LiCl$ system in pyridine,[98,101,103] best results being achieved in the presence of *NN*-disubstituted amides (forming Vilsmeier adducts with the CA),[101,103] especially dimethylformamide. The same system has been used successfully to synthesise

Table 1. The phosphorus compounds used as CA.

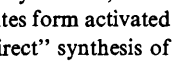
No.	Phosphorus compound	Effect*	Refs.
	Phosphorus (III) compounds		
1	$P(OH)_3$	–	[66]
2	$HO-P(-OC_2H_5)_2$	–	[66]
3	$HO-P(-OC_4H_9)_2$	–	[66]
4	$HO-P(-OCH_3)(-O\overset{+}{N}H_4)$	–	[66]
5	$HO-P(-OC_2H_5)_3+I_2$	++	[139]
6		++	[55, 59–61, 63, 64, 66–68, 71–73, 78, 84, 92, 119, 121]
7	$P(-OC_2H_5)_3$	–	[43, 66, 67]
8	$P(-OC_4H_9)_3$	–	[66]
9		++	[94]
10		++	[42–44, 62, 63, 66, 67, 71–80, 82, 83, 87, 92, 95, 96, 99, 100, 109–119, 121–123, 127, 133, 134, 140–148, 153, 155–158]

Table 1 (contd.)

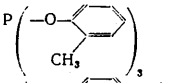
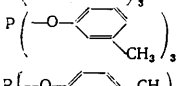
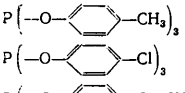
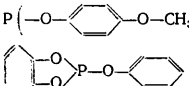
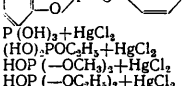
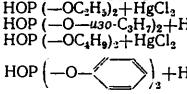
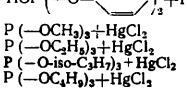
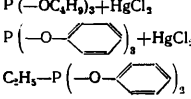
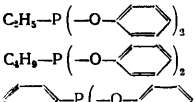
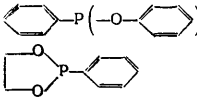
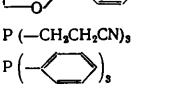
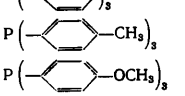
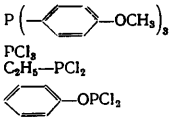
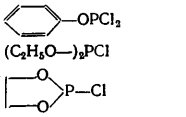
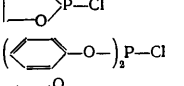
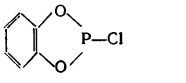
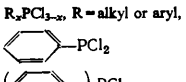
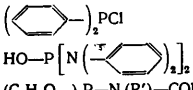
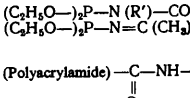
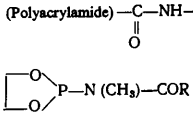
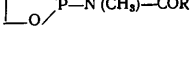
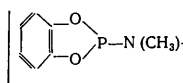
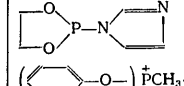
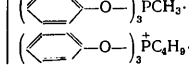
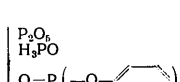
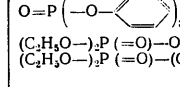
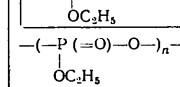
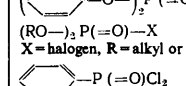
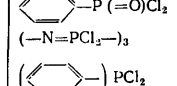
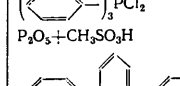
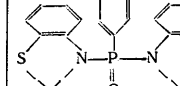
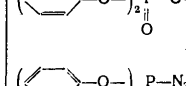
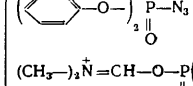
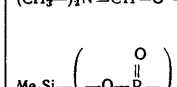
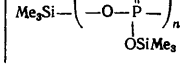
No.	Phosphorus compound	Effect*	Refs.
	Phosphorus (III) compounds		
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12		++	[44, 62, 66, 67, 72, 119, 121, 122]
13		++	[44, 62, 66, 67, 72, 119, 121, 122]
14		++	[44, 62, 66, 67, 119, 121, 122]
15		++	[44]
16		++	[43]
17	$P(OH)_3+HgCl_2$	++	[57]
18	$(HO)_2POC_2H_5+HgCl_2$	++	[57]
19	HOP $(-OCH_3)_3+HgCl_2$	+	[56]
20	HOP $(-OC_2H_5)_2+HgCl_2$	++	[56]
21	HOP $(-O-uзo\text{-}C_3H_7)_2+HgCl_2$	++	[56]
22	HOP $(-OC_4H_9)_2+HgCl_2$	++	[56]
23		++	[56, 59, 92]
24	$P(-OCH_3)_3+HgCl_2$	−	[56]
25	$P(-OC_2H_5)_3+HgCl_2$	+	[56]
26	$P(-O\text{-iso-}C_3H_7)_3+HgCl_2$	++	[56]
27	$P(-OC_4H_9)_3+HgCl_2$	+	[56, 66]
28		++	[56, 92]
29		++	[67, 72, 92, 122]
30		++	[122]
31		++	[122]
32		−	[43]
33	$P(-CH_2CH_2CN)_3$	++	[52]
34		++	[47—51, 86, 130, 151, 152]
35		+	[52]
36		+	[52]
37	PCl_3	++	[70, 127]
38	$C_2H_5-PCl_2$	++	[70]
39		++	[69, 70, 128, 129]
40	$(C_2H_5O-)_2PCl$	+	[70]
41		++	[44, 131, 132]
42		+	[70]
43		+	[70, 83]
44	R_xPCl_{3-x}, R = alkyl or aryl, $x = 1-3$	++	[70, 83, 119, 130]
45		++	[70, 83, 119, 130]
46		++	[83, 119]
47		++	[122]
48	$(C_2H_5O-)_2P-N(R')-COR$, R′ = H−, CH_3−	++	[102, 104]
49	$(C_2H_5O-)_2P-N=C(CH_2)-O-P(-OC_2H_5)_2$	++	[104]
50		++	[104]
51		++	[102]

Table 1 (contd.)

No.	Phosphorus compound	Effect*	Refs.
	Phosphorus (III) compounds		
52	 R = H, CH_3, OC_2H_5, CF_3, $(C_2H_5O)_2P$	++	[102]
53		++	[44]
54		++	[74]
55		++	[74]
	Phosphorus (V) compounds		
56	P_2O_5	++	[135]
57	H_3PO	−	[43]
58		−	[43]
59	$(C_2H_5O-)_2P(=O)-O-P(=O)(-OC_2H_5)_2$	++	[20—22, 45, 81]
60	$(C_2H_5O-)_2P(=O)-(O-P(=O)-)_n-$ OC_2H_5 $-P(=O)(-OC_2H_5)_2$ $n=1,2$	++	[45, 81]
61		++	[45]
62	$-(-P(=O)-O-)_n-$ OC_2H_5	++	[81]
63	PCl_5	−	[70]
64	$O=PCl_3$	−	[70]
65		++	[97, 98, 101, 103, 105—107, 120, 124, 125]
66	$(RO-)_2P(=O)-X$ X = halogen, R = alkyl or aryl	++	[120]
67		−	[70]
68	$(-N=PCl_2-)_3$	++	[75, 85, 89, 92, 119, 123]
69		+	[53]
70	$P_2O_5+CH_3SO_3H$		[160, 161]
71		++	[137]
72		++	[138]
73		++	[154]
74		++	[206]
75		++	[159]

Remarks. (++)—the product is formed in a yield > 50%; (+)—the product is formed in a yield ⩽ 50%; (−)—the product is formed in a yield < 10−15% or is not formed at all.

*The table indicates the tendency of the CA towards the formation of a product in a particular yield because in many instances they were tested only in model reactions; compounds forming a product in a yield exceeding 50% are as a rule effective in polycondensation.

Table 2. The bases tested in direct polycondensation by the phosphorylation method.*

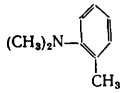
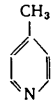
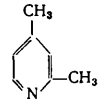
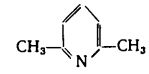
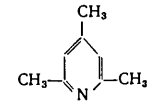
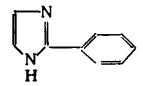
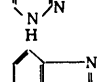
Base	Effect	Refs.
$(C_2H_5)_3N$	—	[43—45, 49, 51, 63, 66, 70, 119, 120, 137]
	—	[44]
	—	[49]
	+	[43, 44, 49—51, 59—77, 83, 84, 87, 90—92, 95—101, 103, 105—107, 109—120, 122—134, 139, 141—150, 153, 156—158]
	+	[49, 51, 52, 63, 66, 67, 70, 76, 99, 119, 122]
	+	[49, 51, 52, 63, 66, 67, 70, 76, 99, 119, 122]
	+	[44, 49, 51, 52, 63, 66, 67, 70, 76, 99, 119, 122]
	+	[49, 99]
	+	[67, 70, 122]
	+	[44, 49, 63, 66, 67, 70, 76, 122]
	+	[99]
	+	[49, 51, 155]
	+	[120]
	+	[42—45, 55, 63, 66, 67, 81, 86, 94, 99, 119, 139]
	+	[44, 45, 120]
	+	[44]
	+	[120]
	+	[44, 45]
	+	[45]
	+	[44, 45]

Table 2 (contd.)

Base	Effect	Refs.
$(CH_3)_2N—CO—N(CH_3)_2$	+	[49]
N-Methylpyrrolidinone	+	[49]
Hexamethylphosphoramide	—	[49]
KOH	—	[43]

*Trivalent phosphorus compounds—di- and tri-aryl phosphites and triphenylphosphine—were used as the CA.

Table 3. The organic halides tested as promoting additives in direct polycondensation by the phosphorylation method.

Halide	Effect	Refs.
CH_3I	+	[74] *
C_6H_5Br	+	[74] *
CCl_4	+	[47, 51, 52, 86]
CBr_4	+	[47, 51, 52]
CI_4	+	[52]
$CHBr_3$	+	[52]
$Cl_3C—CCl_3$	+	[47—52]
$Cl_3C—CO—CCl_3$	+	[47, 51, 52]
$Cl_3C—CO—O—C_6H_4—O—CO—CCl_3$	+	[47, 51]
$Cl_3C—CO—O—uso\text{-}C_3H_7$	+	[ ]
$Cl_2CH—CO—O—uso\text{-}C_3H_7$	—	7]
$ClCH_2—CO—O—uso\text{-}C_3H_7$	—	7]
$Br_3C—SO_2—Ph$	+	[47]

*$(PhO)_3P$ was used as the CA by Yamazaki et al.,[74] while in the remaining cases Ph_3P was employed.

Table 4. The metal salts and complexes tested as promoting additives in direct polycondensation by the phosphorylation method.*

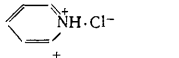
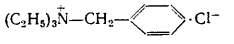
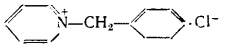
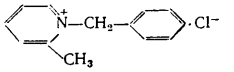
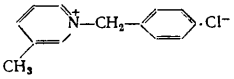
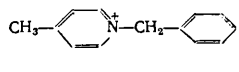
Additive	Effect	Refs.
LiCl	++	[67, 68, 72, 76—80, 82, 87, 92, 95—98, 103—106, 109, 113, 122, 127, 133—135, 140—150, 153, 156—158]
LiBr	+	[79, 105, 119, 120, 122]
LiF	—	[79]
$LiNO_3$	—	[79]
KBr	+	[79]
KI	+	[151]
KSCN	—	[67, 68, 72, 79, 92]
$CaCl_2$	++	[67, 68, 72, 79, 87, 92, 95, 96, 116—122, 135]
$CaCl_2 \cdot H_2O$	+	[67, 68, 72, 92]
$CaBr_2$	+	[121, 122]
$MgCl_2$	+	[44, 67, 68, 72, 79, 92, 119, 120, 135]
$NiCl_2$	—	[79]
$ZnCl_2$	+	[67, 68, 72, 79, 92]
$CuCl_2$	+	[44]
$Cu(OCOCH_3)_2$	+	[44]
LiAcAc	—	[67, 68, 72]
$Cu(AcAc)_2$	+	[44]
$Ni(AcAc)_2$	+	[44]
$Mg(AcAc)_2$	+	[44]
$Co(AcAc)_2$	+	[44]
$Zr(AcAc)_4$	+	[44]
$Fe(AcAc)_2$	—	[44]

Remarks. ++—strong effect, +—weak effect, —no effect; AcAc = acetylacetonate; when introduced in small amounts (up to 4 mol%), acetylacetonates exhibit a catalytic effect; greater amounts (up to 100%) inhibit the reaction.

**Mainly trivalent phosphorus compounds—di- and tri-arylphosphites— were used as the CA.

various polyamidoesters (η_{ln} up to 1.93 dl g^{-1}).[103] It has the advantage, apart from those already mentioned, that the CA (diphenyl phosphorochloridate) can be regenerated by treating the diphenyl phosphate formed with thionyl chloride.

Table 5. The salts of tertiary amines used as promoting additives in direct polycondensation by the phosphorylation method in the presence of $(PhO)_3P$.

Salt	Effect	Refs.
$(C_2H_5)_3\overset{+}{N}H\cdot Cl^-$	++	[88, 99]
	++	[88, 99]
$(CH_3)_4\overset{+}{N}\cdot Cl^-$	+	[88]
$(C_2H_5)_4\overset{+}{N}\cdot Cl^-$	++	[88]
$(C_2H_5)_4\overset{+}{N}Br^-$	+	[88]
$(C_2H_5)_4\overset{+}{N}\cdot I^-$	+	[88]
$(C_4H_9)_4\overset{+}{N}\cdot Cl^-$	+	[88]
	++	[88]
	++	[88]
	++	[88]
	++	[88]
	++	[88]

Remarks. ++—strong effect; +—weak effect.

Yamazaki and co-workers[104] used a polymeric derivative of *N*-acylphosphoramidite (compound No. 50 in Table 1) as the CA for the synthesis of dipeptides. The use of similar compounds in polycondensation would be of interest, since this would greatly facilitate the removal of polycondensation side products from the reaction mixture and also the regeneration of the CA.

Using the above CA as well as a number of others, Yamazaki, Higashi, and co-workers achieved the syntheses of various high-molecular-weight film- and fibre-forming heterochain polymers: AA–BB and AB polyamides,[59,67,68,72,76–79,82,84,87,88,90–92,94,97,99,100,102,103,106] polyhydrazides,[78,84] polyaminoacids (α and β) and regularly alternating polypeptides,[55,60,62,63,71,80,92] AA–BB and AB polyesters,[75,81,83,86,89,92,97,98,100,101,103,105–107] and polyureas and polythioureas.[61,66,68,69,73,92,93] (Many CA proved to be effective also in the synthesis of peptides.[54,55,63,65,104]) The influence of various factors—the structure of the monomers, temperature, and the nature of the CA, promoting agents, and solvents—on the yield and the molecular weight characteristics of the target products has been investigated. These aspects of the process have been described in detail in the literature.[92,108] Here we shall mention only that high-molecular-weight polyamides can be obtained from aromatic diamines by the proposed direct polycondensation methods. Aliphatic diamines lead to the synthesis of low-molecular-weight polymers, which are relatively unpromising from the practical point of view. This has been attributed to the side interaction of the above diamines with the phosphorus compounds employed.

Subsequent communications by other investigators were devoted both to the solution of specific problems involving the application of condensing systems enumerated above and to the search for a series of new phosphorus-containing CA suitable for polycondensation designed to synthesise heterochain polymers of different classes.

Preston and co-workers[109–118] synthesised polyamides and polyhydrazides using the $P(OPh)_3-Py-LiCl$ system, having extended the Yamazaki–Higashi reaction to various aromatic diamines, dicarboxylic acids, and their hydrazides. It is of interest to note that they succeeded in synthesising poly-*p*-phenyleneterephthalamide with $\eta_{ln} = 6.2$ dl g^{-1} by means of direct polycondensation.

Azuma and co-workers[119–126] synthesised aromatic polyesters[119,120,124–126] and polyamides[121–123] using various diaryl phosphites, triaryl phosphites, chlorophosphines, hexachlorocyclotriphosphazene, chlorodiphenyl phosphate, etc.

A simplified method of synthesis of polyamides, where $P(OPh)_2$ was obtained from phenol and PCl_3 in solution in pyridine, has been described.[127] Without isolating $P(OPh)_3$, the reaction solution was used subsequently as the CA in the polycondensation of aromatic diamines with aromatic dicarboxylic acids. Polyamides with $\eta_{ln} \simeq 1.0$ dl g^{-1} were obtained.

Phosphorus compounds have been used to synthesise heterochain polymers by direct polycondensation,[130–132] including polyureas and polythioureas.[131,132] In the synthesis of the latter, ethylene phosphorochloridite was used as the CA.

Multiblock copolymers containing arylamide and polyoxyethylene fragments have been obtained in the presence of the $P(OPh)_3-Py-LiCl/CaCl_2$ system.[133]

The method of direct polycondensation in *N*-MP [the $P(OPh)_3-Py-LiCl$ system] has been used[134] to synthesise polyamides from *NN'*-terephthaloylbis-β-alanine (a diamidodicarboxylic acid whose dichloride is not obtainable) and hexamethylene diamine. However, despite the use of a wide variety of polymeric matrices [poly(ethylene oxide), poly-*N*-vinylpyrrolidinone, poly-4-vinylpyridine], only a low-molecular-weight polymer with $[\eta] = 0.14$ dl g^{-1} was obtained, which is typical for an aliphatic diamine.

P_2O_5 has been used as the CA for the synthesis of polyamides from aromatic diamines and dicarboxylic acids (both aromatic and aliphatic).[135] The reaction was performed in *N*-MP in two stages—initially a mixed anhydride of dicarboxylic acid and P_2O_5 was obtained (80 °C, 1 h), then the diamine was introduced into the solution and the polycondensation was carried out at 20 °C. Polyamides with $\eta_{int} = 0.18-0.85$ dl g^{-1} were obtained. However, it is essential to note that phosphorus pentoxide dehydrates aliphatic amides with formation of keten imines,[136] which can give rise to complications when aliphatic dicarboxyic acids are used. *NN*-Phenylene phosphonobis[2(3*H*)-benzothiazolone][137] and 1,2-benzoisoxazol-3-yl diphenyl phosphate[138] (Nos. 71 and 72 in Table 1) have also been used to synthesise polyamides.

A method of synthesis of various poly-α-aminoacids with a degree of polycondensation of approximately 50 using the $HOP(OC_2H_5)_2/I_2$ system in the presence of pyridine or imidazole as the CA has been described.[139]

The synthesis of polyamides, polyamidoimides, and polyamidohydrazides using the $P(OPh)_3-Py-LiCl$ system has also been described.[140–143] We may note that polyamides, distinguished by a satisfactory thermal stability, have been synthesised from cyclic aliphatic dicarboxylic acids.

Aharoni and co-workers[144–146] investigated thoroughly the mechanism of the polycondensation reaction with participation of phosphites and concluded that the formation of the *N*-phosphinopyridinium salt or of a mixed anhydride of the carboxylic and phosphorous acids, postulated in the studies examined above, does not occur. The diametrically opposite reaction mechanism, involving the formation of an intermediate aminodiphenoxyphosphine, was proposed:

$$P(OPh)_3 + H_2N{-}R{-}\ldots \xrightarrow[-PhOH]{} (PhO)_2P{-}NH{-}R{-}\ldots \xrightarrow{HOOC{-}R'{-}\ldots} \longrightarrow \ldots {-}R'{-}CONH{-}R{-}\ldots$$

In other words, according to the above workers,[144–146] the nucleophile and not the electrophile is activated, as would follow from the mechanism proposed by Yamazaki and Higashi. Their experimental data[144–146] are fairly convincing, but the role of pyridine solely as a promoting agent is not altogether clear. If pyridine functions only as a proton transferring agent, as suggested by the authors, then the same role could be played more successfully by other bases for example by hexamethylphosphoramide, which, however, is ineffective in the processes indicated (Table 2).

The polyamide extrusion process at 280–300 °C in the presence of small amounts (0.5–1.0%) of $P(OPh)_3$, accompanied by a sharp increase in the molecular weight of the polymer, proposed by Aharoni et al.,[145] is noteworthy.

Korshak and co-workers were the first to use the phosphorylation reaction in order to obtain high-molecular-weight polyamidophenylquinoxalines[147] and silicon-containing aromatic polyamides.[148] Polyamides with quinoxaline units have been synthesised by direct polycondensation using $P(OPh)_3$.[149,150]

A number of other studies have also been published in which a wide variety of heterochain polymers have been synthesised using phosphorus compounds as the CA: PPh_3 for the synthesis of polyesters,[151] PPh_3,[152] and $P(OPh)_3$[153] for the synthesis of polyamidoimides, and $(PhO)_2P(O)-N_3$[154] and $P(OPh)_3$[155–158] for the synthesis of regularly alternating polydipeptides and poly-α-aminoacids.

An interesting reaction involving the synthesis of polyamidines by the reaction of aromatic diamines with benzoic acids using poly(trimethylsilyl phosphate) as the CA, has been described.[159] An amide is formed in the first stage, reacting subsequently with the free amino-group to form the amidine bond:

$$\ldots {-}Ar{-}NH_2 + HOOCAr' \xrightarrow[-H_2O]{Me_3Si{-}\left(-O{-}\overset{\displaystyle O}{\overset{|}{P}}{-}\right)_{OSiMe_3}{-}OSiMe_3} \longrightarrow \ldots {-}Ar{-}NHCO{-}Ar'{-}\ldots \xrightarrow[-H_2O]{H_2N{-}Ar{-}\ldots} \ldots {-}Ar{-}NH{-}\overset{\displaystyle Ar'}{\overset{|}{C}}{=}N{-}Ar{-}\ldots$$

The $P_2O_5-CH_3SO_3H$ mixture has also been used in recent years as the CA in the reaction medium.[160,161] This system is particularly effective in the synthesis of polybenzazoles.

Thus it follows from the foregoing that the direct polycondensation reaction using phosphorus compounds has developed vigorously during the last 10–15 years. The phosphorus compounds proposed as the CA are listed in Table 1. Analysis of the available data shows that, bearing in mind their availability and the results achieved, diphenyl and triphenyl phosphites are the most common and promising substances among trivalent phosphorus compounds, while among pentavalent phosphorus compounds the most promising substance is diphenyl phosphorochloridate, which has the advantage that it can be regenerated after the reaction (see above).

When phosphorus compounds are used as the CA, promoting agents play a significant role, as already mentioned above (Tables 2–5). The exceptionally marked effect of a wide variety of polymers (Table 6), capable of forming hydrogen bonds with the monomers, must be especially emphasised. It was shown for the first time in a number of studies[51,76,77,80] that the introduction of polymers of the above type into the reaction solution increases significantly the rate of polycondensation and the molecular weight of the target polymers. The matrix effects of the added polymers consist in increasing the local concentration of the reactants and possibly in the attainment of their mutually convenient orientation in space. These considerations may be supported, for example, by the formation of high-molecular-weight polyaminoacids directly from free α-aminoacids (Val, Leu, Phe, Met) under direct polycondensation conditions $P(OPh)_3$ + LiCl] using poly-*N*-vinylpyrrolidinone (PDP) with molecular weights of 10^4, 4×10^4, and 3.6×10^5 as the matrix.[80] It has been established that the molecular weight of the final polyaminoacid increases with increasing molecular weight of the PDP and amounts to approximately 0.1 of the latter. In all probability, the matrix influences not only the molecular weight of the polyaminoacid synthesised but also the course of the reaction, directing it towards the formation of a linear polymer. The synthesis of poly-β-alanine from the free aminoacid has also been achieved under similar conditions.[80]

Table 6. The polymers tested as matrices in direct polycondensation by the phosphorylation method.

Polymer-matrix	Polymers synthesised	Phosphorus-containing agent	Effect*	Refs.
Poly(ethylene oxide)	Polyamides	$P(OPh)_3$, $HOP(OPh)_2$	+	[77, 82, 92, 121, 123, 134]
"	Polyesters	PPh_3, $(PhO)_2P(O)Cl$	+	[51, 107]
"	Poly-α-amino-acids	$P(OPh)_3$	+	[156, 157]
Poly(ethylene oxide)-poly(propylene oxide) block copolymer	Polyamides	$P(OPh)_3$, $HOP(OPh)_2$	+	[121]
Poly-*N*-vinyl-pyrrolidinone	Polyamides	$P(OPh)_3$, $HOP(OPh)_2$	+	[82, 92, 121, 134]
"	Polyesters	$(PhO)_2P(O)Cl$	+	[107]
"	Polyaminoacids (α and β)	$P(OPh)_3$	+	[80]
Poly-2-vinyl-pyridine	Polyesters	PPh_3	+	[51]
Poly-4-vinyl-pyridine	Polyamides	$P(OPh)_3$	+	[76, 82, 92, 123, 134]
"	Polyesters	PPh_3, $(PhO)_2P(O)Cl$	+	[51, 107]
"	Poly-α-amino-acids	$HOP(OC_2H_5)_2+I_2$	+	[139]
Poly-*N*-*p*-tolyl-maleimide	Poly-α-amino-acids	$P(OPh)_3$	+	[158]
Polystyrene	Polyesters	PPh_3	—	[51]

*Increases the rate of reaction or the molecular weight of the polymer synthesised.

It is essential to note that, in contrast to matrix polymerisation, the characteristic features of which have been thoroughly investigated,[162] matrix polycondensation is a new and little investigated field. The reasons for this should apparently be sought in the inapplicability of the traditional low-temperature polycondensation methods in matrix synthesis, mainly owing to the unduly high reactivity of the monomers employed (acid dichlorides, bischloroformates, diisocyanates, etc.), capable of interacting irreversibly with the polymers used as the

matrices. The development in recent years of "high order" polycondensation methods leads to interesting prospects for the investigation of the matrix polycondensation in which there are, from our point of view, considerable possibilities for polymer chemistry.

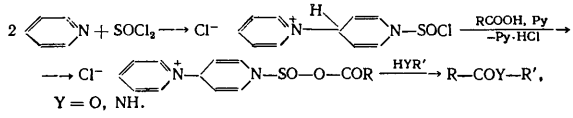
III. Phosphorus-free condensing agents

One of the first CA used successfully as early as the end of the 1950's[163,164] for the synthesis of polyhydroxyacids under the conditions of high-temperature polycondensation was thionyl chloride. The first communications about the applicability of $SOCl_2$ as the CA under the conditions of low-temperature polycondensation in the synthesis of polyamides were published by Ueda et al.[165] in 1978. Subsequently a series of studies devoted to this problem were published.[159,166–172] Regardless of the reaction conditions and the nature of the solvents and acceptors employed (tertiary amines) and also the method used to introduce the reactants, polyamides with $\eta_{int} \leqslant 0.6$ dl g^{-1} were obtained in the majority of cases.

A study devoted to the synthesis of polyesters (together with polyamides) under the conditions of low-temperature polycondensation using $SOCl_2$ as the CA was published in 1980.[166] Subsequently the synthesis of polyesters by the above method was achieved also by Maiti and co-workers,[170] who used dicarboxylic acid salts instead of the free acids themselves and also by Elias and co-workers.[173–175] Only low-molecular weight polyesters were obtained in most cases. Best results have been published by Elias and Warner,[173] who synthesised a polyester with $[\eta] = 0.96$ dl g^{-1} from 3-(*p*-hydroxyphenyl)propionic acid.

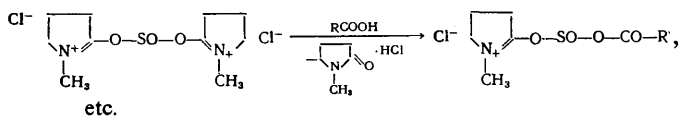
In the studies quoted, the polycondensation in the presence of $SOCl_2$ was carried out predominantly in two stages: the dicarboxylic acid was treated initially with a stoichiometric amount of $SOCl_2$ and then a nucleophile and a hydrogen chloride acceptor were added to the resulting solution. When the reactants are added in this order, the reaction proceeds via intermediate acid dichlorides and is apparently accompanied to a large extent by the side processes characteristic of the latter,[2–4] which is in fact the reason for the low molecular weights of the final polymers.

It has been established[176] that polyesters with much higher molecular weights (with η_{ln} up to 5.56 dl g^{-1}) are obtained when the mixture of dicarboxylic acid and the bisphenol (or an aromatic hydroxyacid) is treated with the complex $SOCl_2$.Py prepared beforehand at a low temperature. The authors suggest that the complex is converted on treatment with the carboxylic acid into the corresponding mixed anhydride, which then interacts with the nucleophile:



In other words, when the reactants are introduced in this sequence, the reaction proceeds via a different, non-acid dichloride pathway and is free from the disadvantages of the latter.

It has been found that the complex of $SOCl_2$ with *N*-MP is an effective CA.[177] In this case, the reaction proceeds via a mechanism involving the formation of a Vilsmeier adduct:



Various arenesulphonyl chlorides (Table 7), used in 1982–1983[178–180] for the direct polycondensation of aromatic dicarboxylic acids with bisphenols, proved to be excellent CA. It has been established that, in the presence of pyridine alone, arenetosylates, leading to chain termination, are formed as side products together with the ester. This undesirable process was suppressed by adding to the reaction system dimethylformamide[180] as well as other amides—diethylformamide, dimethylacetamide, and *N*-MP[181]—forming Vilsmeier adducts ($R_2\overset{+}{N}$ = $CR'-O-SO_2ArCl^-$) with arenesulphonyl chloride in the presence of pyridine. For example, the polycondensation of hydroxybenzoic acid using the tosyl chloride–dimethylformamide–pyridine system afforded polyesters with η_{ln} up to 2.52 dl g^{-1}.[180] The successes achieved can be attributed to the fact that the polycondensation in the presence of arenesulphonyl chloride proceeds with formation of electrophiles (mixed anhydrides) showing a small tendency to undergo side reactions:[178]

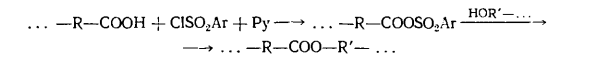
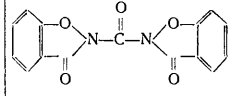
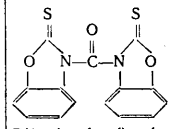
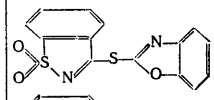
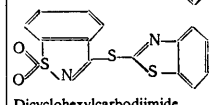
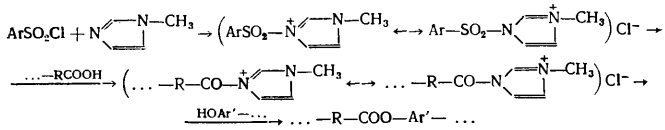


Table 7. Condensing agents (phosphorus-free) used in direct polycondensation.

No.	Condensing agent	Refs.
1	$SOCl_2$	[152, 165—177]
2	CH_3SO_2Cl	[178, 179]
3	$C_6H_5SO_2Cl$	[178, 179, 188]
4	*p*-$CH_3C_6H_4SO_2Cl$	[178—191]
5	2,4,6-$(CH_3)_3C_6H_2$—SO_2Cl	[178, 179, 186, 188]
6	*p*-Cl–$C_6H_4SO_2Cl$	[178, 179, 186, 188]
7	C_6H_5—CH_2—SO_2Cl	[186]
8	Picryl chloride	[192—194]
9	$SiCl_4$	[196—198]
10	$TiCl_4$	[199]
11		[200]
12		[201]
13	Di(*p*-nitrophenyl) carbonate	[202, 203]
14	Bis(2,4-dinitrophenyl) carbonate	[202, 203]
15		
16		[204, 205]
17	Dicyclohexylcarbodiimide	[206]
18	2-Chloro-1-methylpyridinium iodide	[209]
19	Chymotrypsin	[217, 218]
20	Lipase	[220]

It has been shown[182] that *N*-methylimidazole is an effective base in the polycondensation reactions indicated. The authors suggest that the reaction proceeds via the following mechanism in its presence:

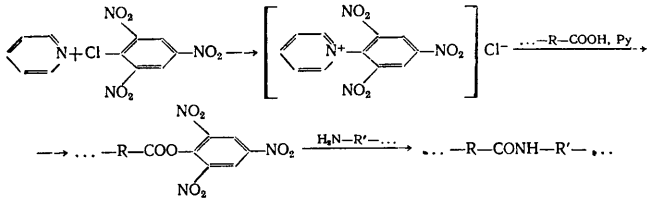


Subsequent studies[183] established that the formation of arenetosylates in the presence of pyridine can also be suppressed by the gradual introduction of phenol into a solution of the acid and tosyl chloride in pyridine. The rate at which the reagent is added has a corresponding significant influence on the molecular weight of the polyester synthesised. For example, when the duration of the addition of bisphenol A to the solution of isophthalic acid and tosyl chloride in pyridine at 120 °C is increased (from 20 to 60 min), the molecular weight of the polymer increases from 14 000 to 54 000.

A different version of polycondensation in the presence of tosyl chloride, also leading to the synthesis of high-molecular-weight polyesters, has been proposed. According to this procedure, a solution of tosyl chloride in pyridine is gradually added to a solution of the dicarboxylic acid and a bisphenol in a mixture of pyridine and dimethylformamide preheated to 120 °C over a period of 5 min.[184]

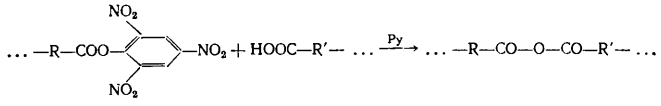
Arenesulphonyl chlorides have been used successfully to synthesise polyamides, polyesters, and polyamidoesters[185–187] and also polyesterimides.[188–191]

Picryl chloride has been used as the CA for the synthesis of polyamides[192,193] and polyesters.[192] The polymers obtained had comparatively low viscosity characteristics (η_{int} = 0.04–0.55 dl g^{-1}), although in a number of instances the viscosity of the polyamides could be raised to 0.87 dl g^{-1}.[193] On the basis of the data obtained in the study of a model reaction, the authors suggest that the reactions proceed with formation of an intermediate activated ester:

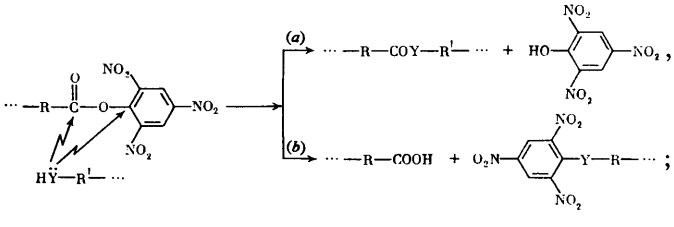


This mechanism is supported by the fact that the reaction does not occur when pyridine is replaced by triethylamine.

The formation of the carboxylic acid anhydride, in all probability as a result of the interaction of the intermediate ester with the carboxy-group, has also been observed in this process:[194]



However, the reaction could hardly be the case of the chain termination because, instead of one reactive group (activated ester group), another no less reactive (anhydride) group is produced. The aromatic nucleophilic substitution reaction (*b*), leading to the formation of relatively inactive trinitrophenyl derivatives and competing with the main reaction (*a*), constitutes a greater danger from this point of view:

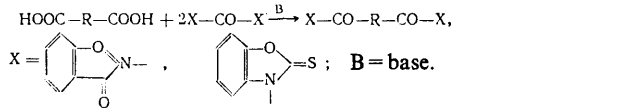


Y = O, NH.

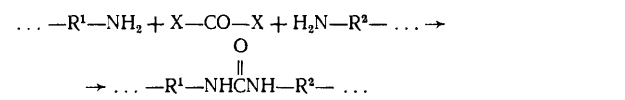
Such a reaction has been observed, for example, in the synthesis of polyamides by the polycondensation of activated nitrophenyl dicarboxylate esters with diamines, its probability increasing sharply with increase in the number of nitro-groups in the phenolic part of the ester.[195] Chain termination as a result of the formation of the trinitrophenyl derivative is also possible as a result of the interaction of the nucleophiles directly with picryl chloride or its pyridinium salt.

$SiCl_4$ proved to be an effective CA in the direct synthesis of aromatic polyamides.[196–198] Poly-*p*-benzamide with η_{ln} up to 1.97 dl g^{-1} has been obtained in its presence. $TiCl_4$ can also be used as the CA for the synthesis of polybenzamides (η_{ln} up to 0.14 dl g^{-1}).[199] The formation of SiO_2 and TiO_2 accompanies these reactions, which leads to interesting prospects for the "direct" synthesis of filled materials.

Varoius activated derivatives of carbonic acid and benzazoles (Nos. 10 and 11 in Table 7) have been used as CA in the synthesis of polyamides.[200,201] This resulted in the formation of polyamides with η_{ln} up to 0.5 dl g^{-1}. The polyamides were synthesised in two stages: the dicarboxylic acid was initially treated with the above reagent in an organic solvent in order to activate it:



The diamine was then added to the solution and the polycondensation was carried out. We may note that, if the first stage of the reaction is not quantitative, the residual CA interacts with the diamine to form urea, which leads both to a heterounit structure and to a deviation from equimolar proportions of the functional groups:



This apparently accounts for the low viscosity characteristics of the polyamides obtained. The synthesis of high-molecular-weight polyureas by the reaction of the closest analogues of compounds Nos. 11 and 12 (Table 7)—bis(*p*-nitrophenyl carbonate) and bis(2,4-dinitrophenyl carbonate) (Nos. 13 and 14)—with diamines can serve as evidence supporting the above explanation.[202,203] Incidentally, these processes can also be placed in the category of "direct polycondensation" because the reaction proceeds with formation of an intermediate activated compound (an isocyanate), reacting *in situ* with the free amine.

3-(2-Benzoxazolylthio)benzoisothiazole 1,1-dioxide and 3-(2-benzothiazolylthio)benzoisothiazole 1,1-dioxide (Nos. 15 and 16 in Table 7) have been used to synthesise polyamides by a single-stage method.[204,205] However, the above compounds have no special advantages over the appreciably more readily available CA listed above and in addition lead to the synthesis of low-molecular-weight polymers ($\eta_{int} \leqslant 0.3$ dl g^{-1} for the polyisophthalamides synthesised).

CA have been used successfully to obtain a wide variety of polymers with functional groups. For example, the synthesis of activated polyesters by treating chloro- and nitro-substituted hydroxyacids with dicyclohexylcarbodiimide in dimethylformamide has been described.[206] The polyesters obtained were used for a wide variety of purposes in peptide synthesis.[206–208] Polyesters and polyamides, suitable as polyazoradical initiators in the polymerisation of vinyl monomers, in particular, for the synthesis of block copolymers, have been synthesised by the polycondensation of azobiscyanopentanoic acid with diols and diamines using 2-chloro-2-methylpyridinium iodide as the CA.[209]

The applications of CA in polycondensation are not restricted to processes involving the direct synthesis of polymers. A wide variety of CA—dicyclohexylcarbodiimide,[210,211] $SOCl_2$,[212] trifluoroacetic acid anhydride,[211,212] triaryl phosphites,[211] and diaryl carbonates[211]—have been used successfully to obtain activated dicarboxylic acid diesters. The condensing agents Nos. 15 and 16 (Table 7) have also been used to synthesise *NN'*-bis(2-benzothiazolyl)benzene-1,3-dicarbothioate and 3,3'-isophthaloylbis(2,3-dihydro-2-thioxobenzoxazole)—an activated thioester and an activated amide of isophthalic acid respectively.[205] Activated diesters and diamides are promising polycondensation monomers for the synthesis of heterochain polymers of various classes—polyamides, polyhydrazides, polyesters, polybenzazoles, etc. Many of the CA listed in Tables 1 and 7 are suitable for the synthesis of the above monomers. The choice of a specific CA is determined by the problem formulated and also by its practical usefulness. We may note that this procedure is in many cases irreplaceable and makes it possible to synthesise activated diesters and the corresponding monomers from dicarboxylic acids to which the methods of the "direct" and traditional low-temperature polycondensation are inapplicable. For example, high-molecular-weight film- and fibre-forming polysuccinamides have been synthesised for the first time via activated diesters.[213] They are of interest from the practical point of view as self-annihilating polymers. Only low-molecular-weight polyamides have been obtained from succinic acid by direct polycondensation methods.[59] The use of activated diesters is more promising also for the synthesis of polyamides from highy basic aliphatic diamines.[212,213]

IV. Enzymes as condensing agents

It is known that under appropriate conditions the chemical equilibrium in reactions catalysed by enzymes can be displaced towards the desired product.[214] This applies also to enzymes of the class of hydrolases which under certain conditions, mainly in a non-aqueous organic medium, can be "compelled" to form heterobonds (amide and ester bonds) instead of cleaving (hydrolysing) them. This approach has acquired increasing importance in organic chemistry, for example, in the synthesis of esters,[215] peptides,[216] etc. Together with a high stereoselectivity, the advantage of enzymes is that they are used in catalytic amounts (in contrast to the chemical CA introduced in stoichiometric amounts) and are not consumed, i.e. they are virtually "eternal" CA, provided, of course, that conditions preventing their inactivation are created.[214]

In recent years studies devoted to the use of enzymes also for the solution of purely "polymeric" problems have appeared in the literature. For example, the use of chymotrypsin for the synthesis of high-molecular-weight multiblock copolymers with oligo(ethylene oxide) and oligopeptide segments[217] and the application of enzymes to the synthesis of polyaminoacids[218] have been described. The lipase-catalysed polycondensation of hydroxyacids has been achieved.[219] A short review discussing the possibilities and the prospects for the synthesis of polymers with the aid of enzymes has been published.[220]

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Summarising the data described in the review, one may conclude that the employment of CA opens a new and extremely interesting and promising chapter in the field of polycondensation. The use of CA permits the successful solution of complex problems, which it is sometimes difficult to achieve with the aid of traditional methods of synthesis. Among the principal disadvantages of the proposed CA one should include mainly their extensive consumption and the formation of equally large amounts of fairly toxic low-molecular-weight polycondensation products which are difficult to recycle and which give rise to a series of problems, including environmental ones.

Taking into account the foregoing, those systems are promising which could be readily separated, after the completion of the process, from the reaction mixture and regenerated by an appropriate treatment or, what would be even more promising, those which could be used again without additional treatment. It may be that solutions of these problems can be achieved by creating "microreactors" in the form of CA (analogous to those employed in Refs. 30, 31, 104), for example polymeric arenesulphonyl chlorides, aryl phosphites and phosphorochloridates, etc., covalently attached to polymeric supports (soluble or insoluble). It would also be of interest to attach such reagents covalently to polymers playing the role of matrices in polycondensation. Enzymes as well as artificial enzyme-like systems immobilised on polymeric carriers or in inverted micelles (possibly covalently cross-linked for stability) can also be included among promising "microreactors". The application of the above constructions might open the way to a more universal variety of direct polycondensation, which would permit syntheses under milder conditions and independently of the nature of the monomers and would promote the practical realisation of this new and promising method of synthesis of polymers.

References

1. V V Korshak, S V Vinogradova *Ravnovesnaya Polikondensatsiya* (Equilibrium Polycondensation), Izd. Nauka, Moscow, 1968, 444 pp
2. D A Holmer, O A Pickett, J H Saunders *J. Polym. Sci. A-1*, **1972**, **1547**
3. V V Korshak, S V Vinogradova *Neravnovesnaya Polikondensatsiya* (Non-equilibrium Polycondensation), Izd. Nauka, Moscow, 1972, 696 pp
4. P W Morgan "*Condensation Polymers: by Interfacial and Solution Methods*" (Translated into Russian), Izd. Khimiya, Leningrad, 1970, 448 pp
5. L B Sokolov *Osnovy Sinteza Polimerov Metodom Polikondensatsii* (Fundamentals of the Synthesis of Polymers by the Polycondensation Method), Izd. Khimiya, Moscow, 1979, 265 pp
6. C Weygand, G Hilgetag *Organisch-chemische Experimentierkunst* (Translated into Russian), Izd. Khimiya, Moscow, 1968, p. 350
7. L Caglioti, M Poloni, G Rosini *J. Org. Chem.*, 1968, **33** 2979
8. K Venkataraman, D R Wagle *Tetrahedron Lett.*, 1979, 3037
9. S Takimoto, J Inanaga, T Katsuki, et al. *The National Meeting of the Chemical Society of Japan*, Prepr. 1975, Vol. 33, p. 908
10. S Takimoto, J Inanaga, T Katsuki, et al. *Bull. Chem. Soc. Jpn.*, 1981, **54** 1470
11. K Inomata, H Kinoshita, H Fukuda, et al *Bull. Chem. Soc. Jpn.*, 1978, **51** 1866
12. L Birdofer, A Ritter *Liebigs Ann. Chem.*, 1958, **B612** 22
13. T H Chan, L T L Wong *J. Org. Chem.*, 1969, **34** 2766
14. T H Chan, L T L Wong *J. Org. Chem.*, 1971, **36** 850
15. J D Wilson, H Weingarten *Can. J. Chem.*, 1970, **48** 118
16. H A Staab, W Rohr *New Methods of Preparative Organic Chemistry*, Verlag, Weinheim, 1967, Vol. 5, p. 64
17. H Ogura, T Kobayashi, K Shimizu, et al. *Tetrahedron Lett.*, 1979, 4745
18. N Yamazaki, F Higashi, M Niwano *Tetrahedron*, 1974, **30** 1319

19. D M Brown *Advances in Organic Chemistry* (Translated into Russian), Izd. Mir, Moscow, 1966, Vol. 3, p. 79
20. S G Waley *J. Chem. Soc.*, 1955, 517
21. H Kataoka, S Sakakihara, H Tani *Bull. Chem. Soc. Jpn.*, 1958, **31** 802
22. N S Andreeva, V A Debabov, M M Millionov, et al. *Biofizika*, 1961, **6** 244
23. Yu V Mitin, O V Glinskaya *Tetrahedron Lett.*, 1969, 5267
24. L E Barstow, V J Hruby *J. Org. Chem.*, 1971, **36** 1305
25. R Appel, L Willms *Chem. Ber.*, 1979, **112** 1057
26. T Shioiri, K Ninomiya, S Yamada *J. Am. Chem. Soc.*, 1972, **94** 6203
27. H Ogura, S Nagai, K Takeda *Tetrahedron Lett.*, 1980, 1467
28. M Ueda, H Oikawa *J. Org. Chem.*, 1985, **50** 760
29. M Ueda, A Mochizuki, J Hiratsuka, et al. *Bull. Chem. Soc. Jpn.*, 1985, **58** 3291
30. C R Harrison, P Hodge, B J Hunt, et al. *J. Org. Chem.*, 1983, **48** 3721
31. R A Amos, R W Emblidge, N Havens *J. Org. Chem.*, 1983, **48** 3598
32. J H Adams, J R Lewis, J G Paul *Synthesis*, 1979, 429
33. R B Woodward, R A Olofson, H Mayer *J. Am. Chem. Soc.*, 1961, **83** 1007
34. D S Kemp, S W Chien, *J. Am. Chem. Soc.*, 1967, **89** 2743
35. M A Ogliaruso, J F Wolfe, *The Chemistry of Acid Derivatives* (Edited by S Patai), Wiley, New York, 1979, p. 474
36. B Belleau, G Malek *J. Am. Chem. Soc.*, 1968, **90** 1651
37. Y S Klausner, M Bodabsky *Synthesis*, 1972, 453
38. E Schroeder, K Luepke *Peptides* (Translated into Russian), Izd. Mir, Moscow, 1967, Vol. 1, 496 pp
39. C H Stammer *Amino Acids Peptides and Related Compounds* (Edited by D H Hey et al.), Butterworth, London, 1973, p. 135
40. H D Jakubke, H Jeschkeit *Amino Acids, Peptides, and Proteins* (Translated into Russian), Izd. Mir, Moscow, 1985, 455 pp
41. H Kössel, H Seliger *Fortschr. Chem. Org. Naturst.*, 1975, 298
42. N Ogata, H Tanaka *Polym. J.*, 1971, **2** 672
43. N Ogata, H Tanaka *Polym. J.*, 1972, **3** 365
44. N Ogata, H Tanaka *Polym. J.*, 1974, **6** 461
45. N Ogata, K Sanui, M Harada *J. Polym. Soc. Polym. Chem. Ed.*, 1979, **17** 2401
46. D G Thomas, J H Billman, C E Davis *J. Am. Chem. Soc.*, 1946, **68** 895
47. G-C Wu, H Tanaka, K Sanui, et al. *J. Polym. Sci. Polym. Chem. Ed.*, 1981, **19** 343
48. N Ogata, K Sanui, H Tanaka, et al. *Polym. J.*, 12981, **13** 989
49. G-C Wu, H Tanaka, K Sanui, et al. *Polym. J.*, 1982, **14** 571
50. G-C Wu, H Tanaka, K Sanui, et al. *Polym. J.*, 1982, **14** 797
51. S Yasuda, G-C Wu, H Tanaka, et al. *J. Polym. Sci. Polym. Chem. Ed.*, 1983, **21** 2609
52. N Ogata, K Sanui, S Tan *Polymer J.*, 1984, **16** 569
53. S Kitayama, K Sanui, N Ogata *J. Polym. Sci. Polym. Chem. Ed.*, 1984, **22** 2705
54. N Yamazaki, F Higashi *Tetrahedron Letters*, 1972, 415
55. N Yamazaki, F Higashi *Tetrahedron Letters*, 1972, 5047
56. N Yamazaki, F Higashi *Bull. Chem. Soc. Jpn.*, 1973, **46** 1235
57. N Yamazaki, F Higashi *Bull. Chem. Soc. Jpn.*, 1973, **46** 1239
58. N Yamazaki, F Higashi *Synthesis*, 1974, 436
59. N Yamazaki, F Higashi *J. Polym. Sci. Polym. Lett. Ed.*, 1974, **12** 185
60. N Yamazaki, F Higashi, J Kawabata *Macromol. Chem.*, 1974, **175** 1825
61. N Yamazaki, F Higashi, T Iguchi *J. Polym. Sci. Polym. Lett. Ed.*, 1974, **12** 517
62. N Yamazaki, F Higashi, J Kawabata *J. Polym. Sci. Polym. Lett. Ed.*, 1974, **12** 2149
63. N Yamazaki, F Higashi *Tetrahedron*, 1974, **30** 1323
64. N Yamazaki, F Higashi, T Iguchi *Tetrahedron Lett.* 1974, 1191
65. N Yamazaki, M Niwano, J Kawabata, et al. *Tetrahedron*, 1975, **31** 665
66. N Yamazaki, T Iguchi, F Higashi *J. Polym. Sci., Polym. Chem. Ed.*, 1975, **13** 785
67. N Yamazaki, M Matsumoto, F Higashi *J. Polym. Sci., Polym. Chem. Ed.*, 1975, **13** 1373
68. N Yamazaki, F Higashi *Am. Chem. Soc. Polym. Prepr.*, 1976, **17** 157
69. N Yamazaki, T Tomioka, F Higashi *J. Polym. Sci. Polym. Lett. Ed.*, 1976, **14** 55
70. N Yamazaki, T Tomioka, F Higashi *Bull. Chem. Soc. Jpn.*, 1976, **49** 3104
71. N Yamazaki, J Kawabata, F Higashi *J. Polym. Sci. Polym. Chem. Ed.*, 1977, **15** 1511
72. N Yamazaki, F Higashi US P. 411 837 4, 1979
73. N Yamazaki, S Nakahama, F Higashi *Am. Chem. Soc. Polym. Prepr.*, 1978, **19** 81
74. N Yamazaki, M Yamaguchi, H Kakinoki, et al. *Synthesis*, 1979, 355
75. F Higashi, K Koichi, M Sekizuka, et al. *J. Polym. Sci. Polym. Lett. Ed.*, 1980, **18** 385
76. F Higashi, M Goto, Y Nakano, et al. *J. Polym. Sci. Polym. Chem. Ed.*, 1980, **18** 851
77. F Higashi, Y Nakano, M Goto, et al. *J. Polym. Sci. Polym. Chem. Ed.*, 1980, **18** 1099
78. F Higashi, N Kokubo *J. Polym. Sci. Polym. Chem. Ed.*, 1980, **18** 1639
79. F Higashi, M Goto, H Kakinoki *J. Polym. Sci. Polym. Chem. Ed.*, 1980, **18** 1711
80. F Higashi, K Sano, H Kakinoki *J. Polym. Sci. Polym. Chem. Ed.*, 1980, **18** 1841
81. F Higashi, K Kubota, M Sekizuka *Macromol. Chem. Rapid Commun.*, 1980, **1** 457
82. F Higashi, Y Taguchi *J. Polym. Sci. Polym. Chem. Ed.*, 1980, **18** 2875
83. F Higashi, N Kokubo, M Goto *J. Polym. Sci. Polym. Chem. Ed.*, 1980, **18** 2879
84. F Higashi, M Ishikawa *J. Polym. Sci. Polym. Chem. Ed.*, 1980, **18** 2905
85. F Higashi, Y Ito, K Kubota *Macromol. Chem. Rapid Commun.*, 1981, **2** 29
86. F Higashi, T Murakami *Macromol. Chem. Rapid Commun.*, 1981, **2** 273
87. F Higashi, Y Aoki, Y Taguchi *Macromol. Chem. Rapid Commum.*, 1981, **2** 329
88. F Higashi, K Sano, T Murakami *Sen-i Gakkaishi, J. Soc. Fiber Sci. Technol. Jpn.*, 1981, **37** 87
89. F Higashi, K Kubota, M Sekizuka, et al. *J. Polym. Sci. Polym. Chem. Ed.*, 1981, **19** 2681
90. F Higashi, Y Taguchi, N Kokubo, et al. *J. Polym. Sci. Polym. Chem. Ed.*, 1981, **19** 2745
91. F Higashi, Y Taguchi *J. Polym. Sci. Polym. Chem. Ed.*, 1981, **19** 3345
92. N Yamazaki, F Higashi *Polymerization Processes, Adv. Polym. Sci.* Berlin, Springer, 1981, **38** 1

93. N Yamazaki, F Higashi *Org. Bio-Org. Chem. Carbon Dioxide*, 1982, 153, *Chem. Abs.*, 1982, **97** 145291h
94. K Yamaguchi, G Bokichi, W Kawanobe, et al. *J. Polym. Sci. Polym. Chem. Ed.*, 1982, **20** 1185
95. F Higashi, S Ogata, Y Aoki *J. Polym. Sci. Polym. Chem. Ed.*, 1982, **20** 2081
96. F Higashi, N Akiyama, S Ogata *J. Polym. Sci. Polym. Chem. Ed.*, 1983, **21** 913
97. F Higashi, A Hoshio, J Kiyoshige *Macromol. Chem. Rapid. Commun.*, **4** 371
98. D Higashi, A Hoshio, J Kiyoshige *J. Polym. Sci. Polym. Chem. Ed.*, 1983, **21** 3241
99. F Higashi, A Mochizuki *J. Polym. Sci. Polym. Chem. Ed.*, 1983, **21** 3337
100. F Higashi *Kobunshi*, 1983, **32** 438
101. F Higashi, Y Yamada, A Hoshio *J. Polym. Sci. Polym. Chem. Ed.*, 1984, **22** 2181
102. W Kawanobe, K Yamaguchi, G Bokicki, et al *J. Polym. Sci. Polym. Chem. Ed.*, 1984, **22** 2371
103. F Higashi, A Hoshio, H Ohtani *J. Polym. Sci. Polym. Chem. Ed.*, 1984, **22** 3983
104. W Kawanobe, K Yamaguchi, S Nakahama, et al. *Macromol. Chem.*, 1985, **186** 1803
105. F Higashi, A Hoshio, et al *J. Polym. Sci. Polym. Chem. Ed.*, 1985, **23** 69
106. F Higashi, M Ozawa, A Hoshio, et al *J. Polym. Sci. Polym. Chem. Ed.*, 1985, **23** 1699
107. F Higashi, Y Yamada *J. Polym. Sci. Polym. Chem. Ed.*, 1985, **23** 2709
108. V A Vasnev, A L Rusanov, M L Keshtov, et al. *Itogi Nauki i Tekhniki. Khimiya i Tekhnologiya Vysokomolekulyarnykh Soedinenii* (Advances in Science and Engineering. The Chemistry and Technology of High-Molecular-Weight Compounds), Izd. VINITI, Moscow, 1987, Vol. 23, p. 3
109. J Preston, W L Hofferbert Jr. *J. Polym. Sci. Polym. Symp.*, 1978(65), 13
110. J Preston, W L Hofferbert Jr. *Amer. Chem. Soc. Polym. Prepr.*, 1978, **19**(2) 87
111. J Preston, W L Hofferbert Jr. *J. Appl. Polym. Sci.*, 1979, **24** 1109
112. J Asrar, J Preston, W R Krigbaum *Am. Chem. Soc. Polym. Prepr.*, 1981, **22**(1) 60
113. J Asrar, J Preston, W R Krigbaum *J. Polym. Sci. Polym. Chem. Ed.*, 1982, **20** 79
114. J Asrar, J Preston, A Ciffrri, et al. *J. Polym. Sci. Polym. Chem. Ed.*, 1982, **20** 373
115. J Preston, W R Krigbaum, R Kotek *J. Polym. Sci. Polym. Chem. Ed.*, 1982, **20** 3211
116. W R Krigbaum, R Kotek, J Preston *J. Polym. Sci. Polym. Chem. Ed.*, 1984, **22** 873
117. W R Krigbaum, R Kotek, Y Mihara, et al. *J. Polym. Sci. Polym. Chem. Ed.*, 1984, **22** 4044
118. W R Krigbaum, R Kotek, Y Mihara, et al. *J. Polym. Sci. Polym. Chem. Ed.*, 1985, **23** 1907
119. H Kagiki, F Azuma Japanese P. 56-45921; *Ref. Zh. Khim.*, 1982, 6S459P
120. F Azuma Japanese P. 57-136668; *Ref. Zh. Khim.*, 1985, 1S388P
121. H Kakinoki, F Azuma Japanese P. 53-141134; *Ref. Zh. Khim.*, 1981, 23S354P
122. S Yamadzaki, F Azuma Japanese P. 56-27306; *Ref. Zh. Khim.*, 1983, 21S439P
123. F Azuma *Kobunshikako. Polym. Appl.*, 1984, **33** 171
124. F Azuma Japanese P. 58-167768; *Ref. Zh. Khim.*, 1986, 7S510P
125. F Azuma Japanese P. 59-85505; *Ref. Zh. Khim.*, 1986, 22S492P
126. F Azuma Japanese P. 59-186057; *Ref. Zh. Khim.*, 1987, 9S568P
127. C Chiriac, J K Stille *Macromolecules*, 1977, **10** 710
128. C Chiriac *Rev. Romaine Chim.*, 1981, **26** 1001
129. C Chiriac *Polym. Bull.*, 1984, **11** 371
130. C Chiriac, D Craescu, F Chiriac, et al. *Mater. Plast.*, 1985, **22** 147
131. C Chiriac *Polym. Bull.*, 1986, **15** 65
132. C Chiriac *Polym. Bull.*, 1986, **16** 143
133. Y Imai, M Kajiama, S Ogata, et al. *Polym. J.*, 1985, **17** 1173
134. B S Curatolo, G P Cottey US P. 4556697
135. M Ueda, N Kawaharasaki *Macromol. Chem. Rapid Commun.*, 1983, **4** 801
136. C L Stevens, G H Singhal *J. Org. Chem.*, 1964, **29** 34
137. M Ueda, A Mochizuki *Macromolecules*, 1985, **18** 2353
138. M Ueda, H Oikawa *J. Polym. Sci. Polym. Chem. Ed.*, 1985, **23** 1607
139. L Le Guilly, A Breck, G Spach *Macromol. Chem.*, 1978, **179** 2829
140. M J Nanjan, D Jayarakash *J. Polym. Sci. Polym. Chem. Ed.*, 1983, **21** 1227
141. G Simonecsu, V Bulacovschi *Tezisy Dokladov VIII Mezhdunarodnyi Simpozium. Polimery-83. Varna, 13–15 Octyabrya 1983 g.* (Abstracts of Reports at the VIII International Symposium Polymers-83, Varna, 13–15 October, 1983), p. 74
142. V Bulacovschi, C I Simonescu *J. Macromol. Sci. A.*, 1985, **22** 561
143. M Minami, M Tanifuchi B.P. 1383480 *Chem. Abs.*, 1975, **83** 115715t
144. S M Aharoni *Macromolecules*, 1982, **15** 1311
145. S M Aharoni, W Hammond, J S Szobota, et al. *J. Polym. Sci. Polym. Chem. Ed.*, 1984, **22** 2567
146. S M Aharoni, W Hammond, J S Szobota, et al *J. Polym. Sci. Polym. Chem. Ed.*, 1984, **22** 2579
147. V V Korshak, E S Krongauz, M N Belomoina *Vysokomol. Soedin*, 1984, **26B** 793
148. V V Korshak, A L Rusanov, L M Khananashvili, et al. *Tezisy Dokladov VI Vsesoyuznoi Konferentsii po Khimii i Primeneniyu Kremniiorganicheskikh Soedinenii. Riga, 22–24 Aprelya, 1986* (Abstracts of Reports at the VII All-Union Conference on the Chemistry and Applications of Organosilicon Compounds, Riga, 22–24 April, 1986), p. 97
149. F Akutsu, H Hayashi, M Miura, et al. *Makromol. Chem. Rapid Commun.*, 1985, **6** 475
150. K Nagakubo, F Akutsu, M Miura Japanese P. 60-91769; *Ref. Zh. Khim.*, 1987, 20S489P
151. T Morimoto, K Nisiuti Japanese P. 58-220353; *Ref. Zh. Khim.*, 1986, 12S569P
152. S S Ray, A K Kundu, M Ghosh, et al. *Eur. Polym. J.*, 1985, **21** 131
153. G I Nosova, M M Koton, L A Laius, et al. *Vysokomol. Soedin*, 1987, **29A** 1871
154. B Nakajima, N Nishi *Polym. J.*, 1981, **13** 183

155. M Tessier, E Marechal *Eur. Polym. J.*, 1986, **22** 877
156. L N Mikhailova, I A Klopotova, I N Tikhomirova, et al *Vestn. Leningr. Univ. Ser. 4. Fizika. Khim.*, 1986(1), 114
157. L N Mikhailova, I A Klopotova, I N Tikhomirova *Vestn. Leningr. Univ. Ser. 4. Fizika. Khim.*, 1987(1) 55
158. I A Klopotova, L N Mikhailova, I V Pletneva *Vestn. Leningr. Univ. Ser. 4. Fizika. Khim.*, 1987(2), 121
159. S Ogata, M Kakimoto, Y Imai *Macromol. Chem. Rapid Commun.*, 1985, **6** 835
160. M Ueda, M Sato, A Mochizuki *Macromolecules*, 1985, **18** 2723
161. M Ueda, S Yokote, M Sato *Polym. J.*, 1986, **18** 117
162. V A Kabanov, I M Papisov *Polimerizatsiya Ioniziruyushchikhsya Monomerov* (Polymerisation of Ionising Monomers), Izd. Nauka, Moscow, 1975, 224 pp
163. T Kametani, K Fukumoto, Y Nomura *Chem. Pharm. Bull.*, 1959, **7** 641
164. T Kametani, K Fukumoto *Yakugaki Zasshi.*, 1960, **80** 1188 *Chem. Abs.*, 1960, **55** 3589b
165. M Ueda, S Aoyama, M Konno, et al *Macromol Chem.*, 1978, **179** 2089
166. Y Imai, S Aoyama, T-Q Nguyen, et al. *Macromol. Chem. Rapid Commun.*, 1980, **1** 655
167. S Das, S Maiti *Macromol. Chem. Rapid Commun.*, 1980, **1** 403
168. A Ray, A Das, S Maiti *Macromol. Chem. Rapid Commun.*, 1981, **2** 333
169. S Maiti, A Ray *Macromol. Chem. Rapid Commun.*, 1981, **2** 649
170. A Ray, V K Bhattacharya, S Maiti *Macromol. Chem. Rapid Commun.*, 1982, **3** 205
171. A Ray, Y V Rao, V K Bhattacharya, et al. *Polym. J.*, 1983, **15** 169
172. M Ueda, N Kawaharasaki, M Takeda *Kobunshi Ronbunshu.*, 1984, **41** 261
173. H-G Elias, R J Warner *Macromol. Chem.*, 1981, **182** 681
174. H-G Elias, J-H Tsao, J A Palacios *Macromol. Chem.*, 1985, **186** 893
175. H-G Elias, J A Palacios *Macromol. Chem.*, 1985, **186** 1027
176. F Higashi, T Mashimo *J. Polym. Sci. Polym. Chem. Ed.*, 1986, **24** 1717
177. F Higashi *Kobunshi*, 1986, **35** 1098
178. F Higashi, N Akiyama, T Koyama *J. Polym. Sci. Polym. Chem. Ed.*, 1983, **21** 3233
179. F Higashi, N Akiyama, I Takahashi, et al. *J. Polym. Sci. Polym. Chem. Ed.*, 1984, **22** 1653
180. F Higashi, I Takahashi, N Akiyama, et al. *J. Polym. Sci. Polym. Chem. Ed.*, 1984, **22** 3607
181. F Higashi, T Mashimo *J. Polym. Sci. Polym. Chem. Ed.*, 1985, **23** 2999
182. F Higashi, M Ozawa, T-C Chang *J. Polym. Sci. Polym. Chem. Ed.*, 1985, **23** 1361
183. F Higashi, T Mashimo *J. Polym. Sci. Polym. Chem. Ed.*, 1985, **23** 2715
184. F Higashi, T Mashimo, I Takahashi, et al. *J. Polym. Sci. Poly. Chem. Ed.*, 1985, **23** 3095
185. F Azuma Japanese P. 59-197 423; *Ref. Zh. Khim.*, 1986, 7S511P
186. F Azuma Japanese P. 58-167 767; *Ref. Zh. Khim.*, 1986, 8S569P
187. F Azuma Japanese P. 59-85 506; *Ref. Zh. Khim.*, 1986, 22S482P
188. R Takazawa Japanese P. 59-39 692; *Ref. Zh. Khim.*, 1986, 15S474P
189. R Takazawa Japanese P. 59-27 193; *Ref. Zh. Khim.*, 1986, 16S489P
190. R Takazawa Japanese P. 59-46 603; *Ref. Zh. Khim.*, 1986, 17S585P
191. R Takazawa Japanese P. 59-46 604; *Ref. Zh. Khim.*, 1986, 17S586P
192. H Tanaka, G-C Wu, Y Iwanaga, et al. *Polym. J.*, 1982, **14** 331
193. H Tanaka, G-C Wu, Y Iwanaga, et al *Polym. J.*, 1982, **14** 635
194. H Tanaka, Y Iwanaga, G-C Wu, et al. *Polym. J.*, 1982, **14** 643
195. R D Katsarava, D P Kharadze, L M Avalishvili, et al. *Vysokomol. Soedin.*, 1986, **28B**, 433
196. P Strohriegl, W Heitz, G Weber *Macromol. Chem. Rapid Commun.*, 1985, **6** 111
197. W Heitz, P Strohriegl BRD P. 3 400 236
198. W Heitz, P Strohriegl BRD P. 3 400 237
199. M Spies, P Strohriegl, W Heitz BRD P. 3 505 903
200. M Ueda, H Oikawa, et al *Bull. Chem. Soc. Jpn.*, 1983, **56** 2485
201. M Ueda, N Kawaharasaki, Y Imai *Bull. Chem. Soc. Jpn.*, 1984, **57** 85
202. M M Zaalishvili, R D Katsarava, T M Kartvelishvili USSR P. 905 228; *Byull. Izobret.*, 1982(6), 116
203. R D Katsarava, T M Kartvelishvili, Yu A Davydovich, et al. *Dokl. Akad. Nauk SSSR*, 1982, **226** 363
204. M Ueda, N Kawaharasaki, Y Imai *Synthesis*, 1982, 933
205. M Ueda, N Kawaharasaki, Y Imai *Macromol. Chem. Rapid Commun.*, 1982, **3** 881
206. F H C Stewart *Austral. J. Chem.*, 1978, **31** 2523
207. F H C Stewart *Austral. J. Chem.*, 1979, **32** 405
208. F H C Stewart *Austral. J. Chem.*, 1981, **34** 2013
209. K Matsukawa, A Ueda, H Inoue, et al. *Chem. Express*, 1987, **2** 33
210. C G Overberger, J Sebenda *J. Polym. Sci. A-1.*, 1969, **7** 2875
211. R D Katsarava, D P Kharadze, L M Avalishvili, et al. *Izv. Akad. Nauk Gruz. SSR Ser. Khim.*, 1982, **8** 102
212. R D Katsarava, D P Kharadze, L M Avalishvili, et al. *Macromol. Chem. Rapid Commun.*, 1984, **5** 585
213. R D Katsarava, D P Kharadze, L M Avalishvili, et al *Macromol. Chem.*, 1986, **187** 2053
214. Yu A Khmel'nitskii, A V Levashov, N A Klyachko, et al *Usp. Khim.*, 1984, **53** 545 [English translation in *Russ. Chem. Rev.*, 1984(4)]
215. Y Inada, H Nishimura, K Takahashi, et al *Biochem. Biophys. Res. Commun.*, 1984, **122** 845
216. K Inoue, K Watanabe, K Morihara, et al. *J. Am. Chem. Soc.*, 1979, **101** 751
217. A Leonhardt, F Gutzler, G Wegner *Macromol. Chem. Rapid Commun.*, 1982, **3** 461
218. C Selvi, M Baboulene, V Speziale, et al. *J. Chem. Technol. and Biotechnol.*, 1985, **B35** 282
219. S Matsumura, J Takahashi *Macromol. Chem. Rapid Commun.*, 1986, **7** 369
220. S Fukui *Kobunshi*, 1986, **35** 535

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Chromonic mesophases

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ABSTRACT. The chemical characteristics, structure, and physical properties of one of the most important types of lyotropic liquid crystals—chromonic mesophases—are examined. These liquid crystals are formed in solutions of large planar molecules and have a columnar structure. Chromonic mesophases are observed most often in solutions of dyes and medicinal drugs. The formation of mesophases is preceded by the aggregation of the molecules. The characteristics of this process are also examined in the review.

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I. Introduction

Liquid crystals have been known for more than 100 years but have entered the mainstream of the scientific and technical progress only during the last two decades—their optical properties proved to be convenient for the manufacture of simple and inexpensive indicating devices with a low power consumption. This led to a wide scale development of both chemical and physical and biological studies on liquid crystals.

By virtue of the unique combination of the properties of a liquid (the absence of translational order and hence fluidity and finite viscosity) and a crystal (the presence of orientational order and hence anisotropy of the physical properties), liquid crystals have become a favourite object in the study of the influence of structural order on the physicochemical properties of substances. It was found that liquid crystal (mesomorphic) properties are manifested by organic compounds in almost all classes. Furthermore, regardless of their chemical nature, a definite set of types of ordering proved to be typical for compounds of all classes, namely nematic with orientational order in only one direction, cholesteric with the same property but having in addition a helical superstructure in the direction at right angles to that of the orientational order, and smectic with the same properties as the nematic type of order but with layered order in a plane perpendicular to the direction of the orientational order. On the other hand, the chemical nature of the substance imparts detailed features to the canonical structural types. Thus the structural element for aromatic compounds is the molecule (sometimes the dimer), while for amphiphilic compounds it is a micelle consisting of tens of hundreds of molecules. A columnar order is characteristic of discotic molecules where a superstructure is produced as a result of the orientation of specific axes along a definite direction. Polymeric liquid crystals sometimes form a nematic mesophase with a hexagonal superstructure and twisted smectic mesophases.

The existence of dye and medicinal drug mesophases has been known for a long time but they have not attracted the attention of chemists or physicists. As early at 1916, Gaubert[1] found that a series of substances capable of forming thermotropic mesophases on fusion produced them when their solutions in ether, toluene, chloroform, carbon disulphide, etc. were evaporated. He later showed[2] that liquid crystals are formed also on evaporation of solutions of certain substances which do not give rise to mesophases on fusion. There is no doubt that all the liquid crystals obtained by this procedure are lyotropic, i.e. they were formed only when a highly concentrated solution was generated as a result of evaporation.

Among the substances investigated, there were also a number of dyes. Lyotropic liquid crystals were observed for anisylidene-*p*-aminoazotoluene,[1] tetrazine,[2] Brilliant Croceine,[3] Methylene Blue, and Neutral Red.[4] However, the structures of the mesophases of these compounds were not established and the above studies therefore remained unnoticed by specialists in the field of liquid crystals and had no influence on the further development of research into the physical chemistry of mesophases. Subsequently, in the 1940's–1950's, studies on the lyotropic mesomorphism of these compounds became of current interest for some time in connection with the vigorous investigation of the influence of the aggregation process in aqueous solutions of dyes on their absorption spectra, but, owing to the lack of interest in liquid crystals in general, they did not receive due development.

The study of the lyotropic mesomorphism of medicinal drugs began as early as the 1920's. The first drugs in which liquid crystal properties were discovered were apparently salvarsan and neosalvarsan.[5] However, these features were studied independently of the study of the liquid crystal properties of dyes and did not find an apparent practical application.

In recent years the situation has changed. The study of the structures of dye and drug mesophases showed that here there is a new type of mesormorphism. It was called chromonic mesomorphism, the name of the antiasthmatic drug sodium cromoglycate—a typical representative of this type of liquid crystal. It became clear in subsequent years that chromonic mesophases constitute one of the subgroups of lyotropic viscotic liquid crystals which are characterised by a column arrangement of planar molecules. Among them one can differentiate viscotic substances proper whose molecules have a symmetrical disc shape.[6–11] On the other hand, chromonic mesophases form planar molecules with a low symmetry having the form of a plank (sanidic). They can therefore be referred to also as sanidic mesophases. Incidentally, certain mesophases have been recently discovered among high-molecular-weight compounds.[12]

Chromonic mesophases have found a practical application. Thus it has been discovered that their lyotropic mesomorphism has a direct

bearing on the dyeing process[13,14] and the therapeutic effect of preparations.[15] Other technical applications of these mesophases have also been found.[16,17] All this has promoted the appearance of much interest in chromonic mesophases.

This review is devoted to the consideration of the present state of the problem of the lyotropic chromonic mesomorphism. Attention is concentrated on the conditions in the formation of mesophases, their structure, and its relation to the chemical structure of molecules and with physicochemical properties.

II. The aggregated state as the premesophase

The formation of the chromonic mesophase cannot be understood without considering its initial stage, the aggregation of molecules in aqueous solutions. This phenomenon is well known and has been studied mainly in relation to dyes.[18–21] It has been shown that the aggregation resembles to some extent micelle formation. There exists a critical concentration (we shall refer to it as the CCA—the critical concentration for aggregation), after the attainment of which a whole series of physical parameters, such as electrical conductivity,[19,22,23] the activity coefficient,[24] and the NMR spectra,[25] change sharply. Below the CCA, single molecules are present in solution, while above it they are aggregates. Typical CCA of certain dyes are listed in Table 1. Evidently the CCA depends not only on temperature but also on the nature of the electrolyte present. This indicates an appreciable role of electrostatic forces in the aggregation process. The CCA also depends on the length of the alkyl chain of the dye. Thus, in the case of 4-alkylamino-1-aminoanthraquinone-2-sulphonic acid, the increase in the length of the alkyl chain from 1 to 4 units (from methyl to butyl) diminishes the CCA at 40 °C in the presence of 0.05 M NaCl from 3.31×10^{-3} to 1.41×10^{-3} M, i.e. by a factor greater than 2. On the other hand, the introduction of 4 M urea into the same dyes increases the CCA almost by a factor of 4.[27] All this indicates that the aggregation process is influenced also by hydrophobic interaction.

Table 1. The values of the CCA for aqueous solutions of certain dyes.[26]

Dye	Electrolyte and its concentration, M	CCA, 10^{-4} M	
		30° C	40° C
Chlorazol Sky Blue FF	0.2 NaCl	2.8	4.0
	0.13 NaCl	5.0	6.2
	0.13 KCl	0.89	1.2
Congo Red	0.025 NaCl	3.0	5.2
	0.025 KCl	2.3	4.0
Benzopurpurine 4B	0.025 NaCl	2.6	4.9
	0.025 KCl	2.2	4.1

An important characteristic of the aggregation process is the aggregation number, i.e. the number of molecules in the aggregate. It is determined by many methods. The average aggregation number $\overline{N}_n$, defined as

$$\overline{N}_n = \sum_i (n_i M_i) \Big/ \sum_i n_i, \qquad (1)$$

where n_i is the number of molecules of type i having a molecular weight M_i, can be found from the rate of diffusion.

As a rule, aggregation begins with dimerisation. This process is accompanied by the absorption of heat. The thermodynamic data for certain typical dyes are presented in Table 2. They make it possible to regard dimerisation as a first-order phase transition which has become diffuse as a result of the finite size of the aggregates, as happens in micelle formation.[29] This can be readily seen from Fig. 1, which illustrates the dependence of the aggregation number of a dye, the sodium salt of 1-amino-4-butylaminoanthraquinone-2-sulphonic acid, on concentration. The aggregation number was calculated from the diffusion coefficient found by the polarographic method.[27] A large proportion of the data on the aggregation numbers of various dyes have been obtained by this procedure.[30–35] Table 3 lists the aggregation numbers for Direct Fast Orange SE in the presence of 2 g litre^{-1} NaCl at different concentrations and temperatures. Two typical tendencies are manifested here: $\overline{N}_n$ increases with increase in the dye concentration and diminishes with increase in temperature. At a given temperature, aggregation is intensified after a time. Thus the aggregation number of Benzo Light Red 8 BL at a concentration of 0.5 g litre^{-1} in the presence of 1.0 g litre^{-1} of NaCl increases by 30% in a week and by 100% in a month.[33] The origin of this behaviour can be understood from general considerations and needs no comment.

Table 2. Thermodynamic characteristics of the dimerisation reactions of certain dyes at 25 °C.[28]

Dye	ΔF, kcal mol^{-1}	ΔH, kcal mol^{-1}	ΔS, cal mol^{-1} K^{-1}
Orange P	−4.28	−10.48	−20.8
Thionine	−4.10	−6.82	−9.10
Methylene Blue	−5.17	−5.90	−0.77
Rhodamine 6G	−4.57	−8.6	−13.5

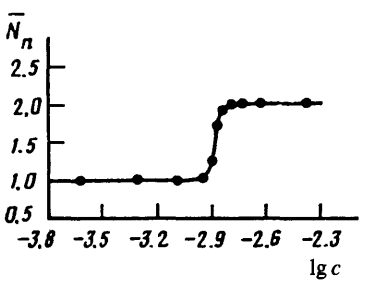


Figure 1. Dependence of the average aggregation number $\overline{N}_n$ on the concentration c of the sodium salt of 1-amino-4-butylaminoanthraquinone-2-sulphonic acid in the presence of 0.05 M NaCl at 30 °C.[20]

Table 3. The aggregation numbers for Direct Fast Orange SE.[33]

T, °C	c, g litre^{-1}	$\overline{N}_n$	T, °C	c, g litre^{-1}	$\overline{N}_n$
25	0.05	39	60	0.05	9
	0.1	43		0.1	10
	0.2	53		0.2	13
	0.5	64		0.5	17

As already mentioned, the presence of an electrolyte in the solution has a significant influence on the aggregation process. Fig. 2 presents the dependence of the aggregation numbers of certain dyes on the NaCl concentration.[36] It is readily seen that the electrolyte concentration has a greater effect on $\overline{N}_n$ than the concentration of the dye itself. Thus an increase in the concentration of benzopurpurine 4B from 0.005 to 0.01 wt.% does not lead to an increase in the aggregation number, which remains 6, but an increase in the NaCl concentration from 0.01 to 0.02 wt.% increases $\overline{N}_n$ from 6 to 400.[30]

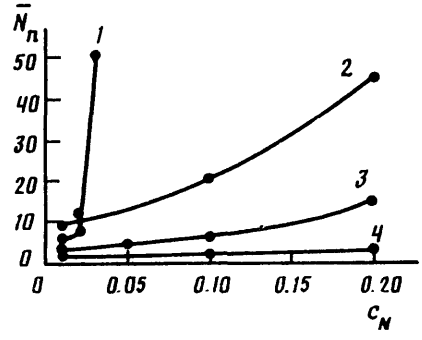


Figure 2. Dependence of the average aggregation number for dyes on the NaCl concentration: (*1*) benzopurpurine 4B; (*2*) Congo Red; (*3*) Chicago Blue; (*4*) Orang P.[36]

The weight-average aggregation number can be found by the classical light scattering method:

$$\overline{N}_w = \sum_i (n_i M_i^2) \Big/ \sum_i (n_i M_i), \qquad (2)$$

It is not identical with the $\overline{N}_n$ found by the diffusion method.[37,38] Thus $\overline{N}_n$ = 552 and $\overline{N}_W$ = 2621 for benzopurpurine 4B in the presence of 0.04 M KCl at 25 °C.[39] Whereas the average aggregation number yields the actual average number of aggregated molecules, the weight-average aggregation number reflects only the maximum degree of aggregation. The discrepancy between $\overline{N}_n$ and $\overline{N}_W$ therefore indicates the polydispersity of the aggregates in the given solution. The knowledge of both aggregation numbers makes it possible to plot a diagram illustrating the distribution of the micelles with respect to size.[40]

The aggregation process has a significant influence on the absorption spectra of dyes.[19–21] The presence of a long-wavelength absorption band *M* and a shorter-wavelength band D with a lower intensity is typical for the monomeric form of the dye. A still shorter-wavelength low intensity band *H* is sometimes also manifested. When aggregates are formed, the intensity of the band M falls but those of the bands H and D increase. An example of this kind is illustrated in Fig. 3, which presents the absorption spectra of a solution of pseudoisocyanine chloride.

A deviation from the Beer–Lambert law is also a sign of the appearance of aggregates in solution, although the degree of deviation is not linked directly to the aggregation number.[41]

Dye solutions at concentrations above the CCA exhibit flow birefringence. This effect has been observed for benzopurpurine 4B both in the absence of an electrolyte[42] and in the presence of 0.05 M NaCl.[43] Hence it was concluded that the aggregates are large highly anisometric particles. Under certain conditions, they can be observed under an ultramicroscope.[43] Similar conclusions were reached also in the interpretation of the absorption spectra.[44]

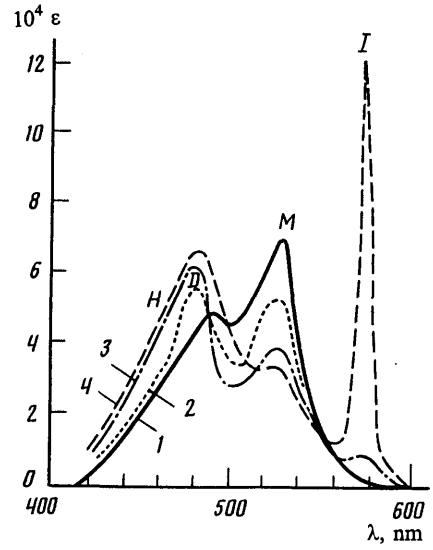


Figure 3. Absorption spectra of aqueous solutions of pseudoisocyanine chloride at 25 °C and different molar concentrations: (*1*) 1.3 × 10^{-5}; (*2*) 1.3 × 10^{-3}; (*3*) 7.1 × 10^{-3}; (*4*) 1.4 × 10^{-2}.[21]

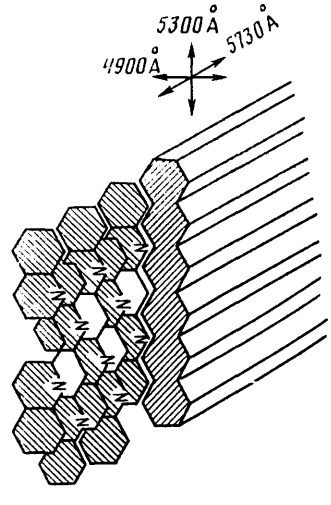


Figure 4. A model of the packing of pseudoisocyanine molecules in the aggregate; above—schematic illustration of optical trichroism.[46]

The question arises what these aggregates represent. In order to answer it, it is essential to say a few words about the structure of the molecules of the dyes considered. In the majority of cases, the molecules of ionogenic dyes have a planar form, although the oxygen and hydrogen atoms of terminal groups such as SO_3, OH, or NH_2 project upwards or downwards from the main plane of the dye. In aqueous solutions, these hydrophilic groups are in contact with water

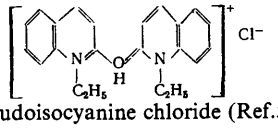
molecules, which inevitably leads to the mutual contact of the hydrophobic hydrocarbon skeletons of the molecules. As a result, the dye molecules are arranged like coins in a stack.[45,46] Specific details of such packing are naturally different for different dyes. Thus in the case of pseudoisocyanine dyes each successive molecule in the stack is displaced relative to the preceding one in such a way that the nitrogen atom in the quinoline ring lies above the carbon atom of the methylidyne group. This model[46] explains satisfactorily the trichroism of the absorption spectra (Fig. 4).

The question arises what retains the molecules in the aggregates. There exists the view[41] that these are van der Waals dispersion forces. However, according to other ideas,[47] hydrogen bonds play the main role here. The latter model presupposes the insertion of two water molecules between the dye molecules for each layer. These molecules form hydrogen bonds with the oxygen or nitrogen atoms of the dye. This view has found support in investigations[48,49] where it was shown that the aggregation of dyes in non-aqueous solutions is also accompanied by the formation of hydrogen bonds.

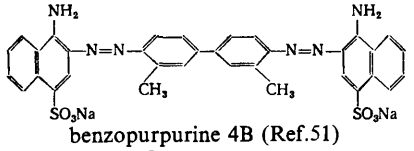
III. Dye mesophases

With increase in the dye (and also electrolyte) concentration, the degree of association also increases, leading ultimately to the precipitation of the solid phase. So long as the aggregates are small, their motion is uncorrelated, since they do not experience steric hindrance. The solution remains isotropic and birefringence arises only in flow. On the other hand, when the aggregates grow so much that they begin to "interfere" with one another, their motion acquires a correlated character. They can now move only together, since the orientation of one aggregate in one way or another specifies the orientation of all the others. Spontaneous birefringence arises. Such a phase is a lyotropic liquid crystal phase.

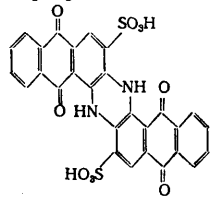
Fairly numerous dyes whose aqueous solutions have chromonic phases are now known. The chemical formulae and names of the most typical liquid crystals are presented below:



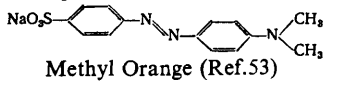
pseudoisocyanine chloride (Ref.50)



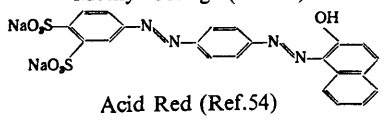
benzopurpurine 4B (Ref.51)



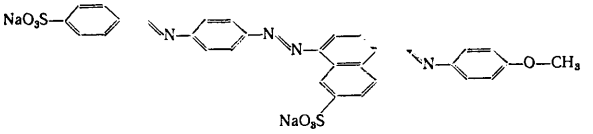
disulphoindanthrone (Ref.52)



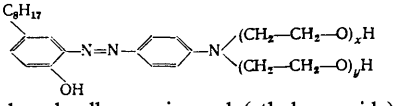
Methyl Orange (Ref.53)



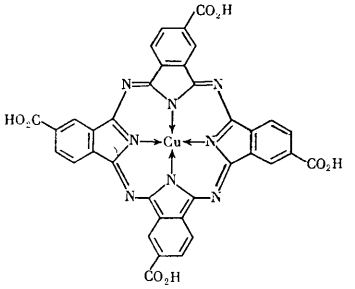
Acid Red (Ref.54)



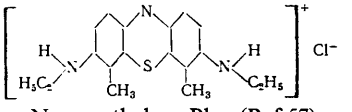
Sirius Supra Brown (Ref.54)



p-t-Octylphenol yellow amine poly(ethylene oxide) (Ref.55)



Copper-tetracarboxyphthalocyanine (Ref.56)

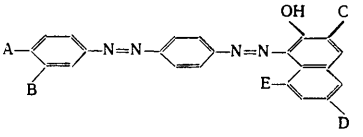


Novomethylene Blue (Ref.57)

It is readily seen that the liquid crystal dyes belong to different groups. They include cyanine, anthraquinone, and azo-dyes. They are represented by different water-soluble forms—salts and acids. One of the compounds is a dye possessing surface-active properties. It is related to a long-chain hydroxyethylated alcohol,[55] which also forms liquid crystals. Finally, the penultimate dye—copper-tetracarboxyphthalocyanine[56]—represents the large class of metal-containing porphyrins.

All the dyes indicated above have large planar molecules. Thus the length of the benzopurpurine 4B molecule is 24 Å whilst that of disulphoindanthrone is 14 Å. The width of the latter is 8 Å, whilst its thickness, like that of all such planar molecules, is approximately equal to the diameter of the carbon atom (3.4 Å). As already stated, such molecules can be readily arranged in stacks.

The question of the influence of the chemical structure on the ability of the dye to form the liquid crystal phase has acquired considerable importance in this connection. Such influence has been investigated[54] in relation to diazo-dyes having the general formula



(I)

The combinations of the substituents A, B, C, D, and E in various compounds are indicated in Table 4.

Distinct mesophases are formed by the dyes (I) and (IV) over a fairly wide concentration range. The formula of the latter dye (Acid Red) was indicated above. The dye (V) affords a mesophase over a narrow concentration range. The remaining dyes do not form mesophases. Hence one may conclude that the addition of sulpho-groups to the benzene fragment favours the formation of a mesophase to a greater extent than their addition to the naphthalene fragment.

The following rules have been formulated as a result of detailed studies of the influence of chemical structure on the liquid crystal properties of dyes.[58] If the dye molecule consists of one or two planar fragments linked by a twofold axis and has a symmetry point group C_2 or higher and the planar fragments of the molecule have at the same time a single possible conformation, the inogenic hydrophilic groups are such that, at a pH greater or smaller than a certain value pH_0, the dye acquires an appreciable solubility ($\sim 10^{-2}$ M) due to the dissociation of these groups, all the hydrophilic groups are located only on the periphery of the molecular plane, i.e., the planar part from the molecule is hydrophobic, and on the plane and along the periphery of the molecules there are no groups capable of preventing the formation of dimers and multimers, i.e. the molecular planes are capable of sliding freely past one another without experiencing steric hindrance whose overcoming would require the expenditure of an energy greater than kT, then conditions exist (pH, ionic strength, temperature, and concentration ranges) such that the dye forms a lyotropic liquid crystal phase in an aqueous electrolyte solution. An obligatory requirement is also that the adsorption of electrolyte ions does not entail the breakdown of the above conditions.

Although these rules are in fact fairly general, they were found to be well justified in the search for new chromonic mesophases.[59]

Table 4. Substituents in diazo-dyes having the general formula (I).

Compound	A	B		D	E
(I)	SO_3Na	H	H	H	H
(II)	H	H	H	SO_3Na	H
(III)	H	H	H	H	SO_3Na
(IV)	SO_3Na	SO_3Na	H	H	H
(V)	H	H	SO_3Na	SO_3Na	H
(VI)	H	H	H	SO_3Na	SO_3Na
(VII)	H	H	SO_3Na	SO_3Na	SO_3Na
(VIII)	H	H	H	H	H

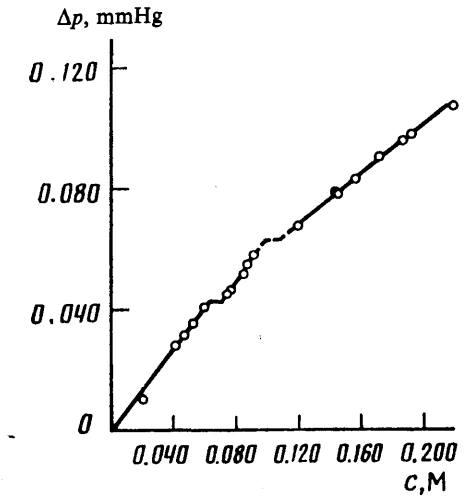


Figure 5. Dependence of the decrease in the vapour pressure of an aqueous solution of the dye Naphthol Yellow S on its concentration at 20 °C.[60]

Like the appearance of aggregates, the formation of the mesophase is a critical process and is accompanied by a sharp alteration of a number of physical properties when both the concentration and the temperatue are varied. In both cases a first-order phase transition take place. Fig. 5 shows how the vapour pressure of an aqueous solution of Naphthol Yellow S decreases as a function of its concentration at 20 °C.[60] Two anomalous sections can be readily seen at ~0.06 and 0.01 M. At low concentrations, an aggregated isotropic solution exists. With increase in concentration, a liquid crystal solution, separated into two phases, arises (see below).

A similar situation occurs also when the temperature is altered. Fig. 6 presents the temperature variation of the specific conductance of a 0.1 M aqueous solution of the disulphoindanthrone dye.[52] Above 32 °C, an isotropic solution exists in which two chromonic mesophases are formed in succession on cooling. The electrical conductivity undergoes pronounced changes at the phase transition points.

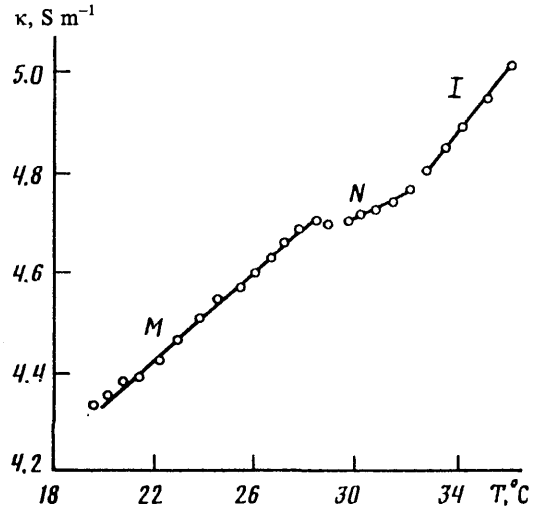


Figure 6. Temperature dependence of the specific conductance κ of a 0.1 M solution of disulphoindanthrone: *M*—hexagonal mesophase; *N*—nematic mesophase; *I*—isotropic phase.[52]

The positions of the points corresponding to transitions to mesophases on the concentration and temperature scales are naturally determined by the nature of the dye and the solvent. This can be represented most fully by phase diagrams (see below). However, in order to provide an idea about the order of magnitude of the quantities, Table 5 lists the critical concentrations at which typical dyes form mesophases at room temperature. On comparing the data in Table 5 with the values of the CCA listed in Table 1, it is readily seen that the transition to the mesophase is completed at concentrations which exceed on average the CCA by two orders of magnitude.

The formation of mesophases in dye solutions is characterised not only by the appearance of double refraction but also by a change in the transmission spectrum—a new narrow band (the so called *J*- or *Z*-band) appears in the long-wavelength region. It is readily seen in Fig. 3. Partial polarisation and fluorescence are observed in this part of the spectrum.[44–46,50]

The formation of a liquid crystal is accompanied by yet another interesting effect—the appearance of induced optical activity. It has been observed[61] in an aqueous solution of 1,1'-diethyl-2,2'-carbocyanine iodide after the addition of NaCl. The optical activity is due to the linear dichroism arising as a consequence of the ordering of the supermolecular structures. It appeared only after the cell had been rotated around its longitudinal axis.

Table 5. Critical concentrations for the formation of chromonic mesophases by typical dyes in aqueous solutions at room temperature.[52,60]

Dye	Critical concentration, 10^{-2} M
Amaranth	3.8—4.2
Naphthol Yellow S	6.2—7.0
Potassium Methyl Orange	2—10
Pseudoisocyanine chloride	1
Disulphoindanthrone	10
Benzopurpurine 4B	1—10

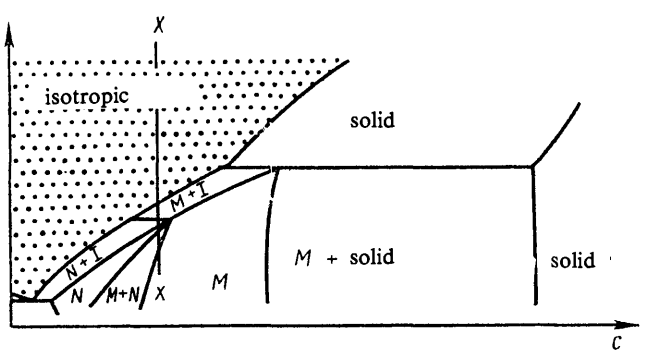


Figure 7. Typical phase diagram of chromonic mesophases.[54]

The appearance of the chromonic mesophase entails the appearance of spontaneous birefringence and of characteristic textures which differ little from the textures of the usual thermotropic liquid crystals (see below).

There are altogether still few complete phase diagrams for binary dye–water systems. A phase diagram which is to some extent typical is illustrated in Fig. 7.[54] Leaving aside the solid phases, we shall consider the sequence of mesophases arising on heating along the *X–X* line in the above diagram. For the typical dye Sirius Supra Brown, this line corresponds to a concentration of 16 wt.%. At room temperature, the dye forms the mesophase *M*. It follows from the analysis of the X-ray diffraction patterns for this phase that the thickness of the dye molecule is 3.4 Å and the parameters of the hexagonal cell are 40 and 23 Å, i.e. are in the ratio $1 : 1/\sqrt{3}$.

A model of such hexagonal structure is illustrated in Fig. 8. It was constructed taking into account the real rectangular structure of the dye molecule. Although the centres of the columns are arranged in accordance with the hexagonal law, in fact the structure should be more correctly regarded as being of the "chevron" orthorhombic type. This thickness of the layer of counterions and water between the columns of the dye molecules is then 10—20 Å.

In certain dyes, the hexagonal mesophase has a more complex nature. For example, four varieties of the mesophase *M* have been found in Acid Red. At room temperature and a dye concentration of 14 wt.%, the usual mesophase *M* is produced. However, when it is heated to 50 °C, lens-shaped regions, resembling the sodium caprylate "sticks" are formed.[62] This is the second hexagonal mesophase. On further heating, the lens-shaped regions merge, forming an island type texture, which belongs to the third hexagonal phase. Above 90 °C, the lens-shape regions reappear, giving rise to a network texture. This is the fourth mesophase *M*. However, presumably not all the formations described above are really mesophase *M*. Analysis of the textures described by Jones and Kent[63] suggests that at least the high-temperature phase is nematic (*N*).

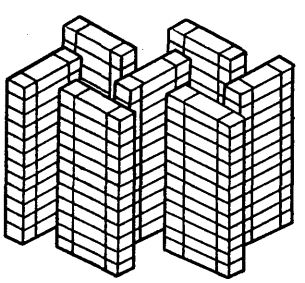


Figure 8. A model of a hexagonal chromonic mesophase *M*.[54]

This mesophase *N*, is clearly manifested on the phase diagram presented in Fig. 7 only beyond the two-phase region (along the *X–X* line). It has a typical Shchlieren texture with appreciable planar regions (see below). In the nematic mesophase *N*, the columns of the dye molecules are fairly free. They are structural units like the anisometric micelles in micellar nematic phases.[64] On the X-ray diffraction patterns of the mesophases *N*, only one reflection, permitting the estimation of the thickness of the dye molecules, can be observed.[65,66] The number of such molecules in each column is $10^3 - 10^6$ depending on the concentration and temperature.[66]

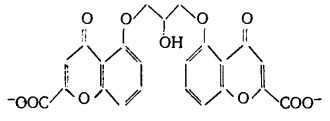
A few words have to be said about the chromonic phases of the porphyrins. Copper compounds are sparingly soluble in water but in the presence of NH_4OH (pH 10—12) both nematic and hexagonal phases are clearly manifested.[56,67,68] A nematic mesophase has been found[69] also in cobalt(II)-phthalocyanines.

In conclusion, we may mention the behaviour of the chromonic phases of dyes at high concentrations. At the critical concentration of the dye or the electrolyte, a solid phase is precipitated from the lyotropic mesophase. Structural and electron microscope studies have shown[17,65,66] that it has no crystal structure but exhibits double refraction. It is, as it were, a "frozen" chromonic phase in which the columns are oriented in parallel. Such a solid phase is characterised by a high dichroism and is used to manufacture polaroids.[16,17,70]

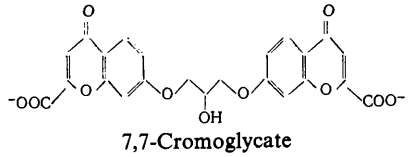
IV. Medicinal drug mesophases

We shall turn initially to mesophases of compounds whose properties are close to those examined in the previous Section. We shall deal with the derivatives of naphthylaminedisulphonic acids[71] related to the widely familiar dye Congo Red. Many of these derivatives are highly active agents against trypanosomes, the simplest parasites in human and animal blood and tissues. Many of them possess liquid crystal properties. The sodium salt of *N*-(*m*-aminobenzoyl)-2-naphthylamine-5,7-disulphonic acid, the tetrasodium salt of *N*-(*m*'-aminobenzoyl-*m*-aminobenzoyl)-2-naphthylamine-6,8-disulphonic acid, the disodium salt of *N*-(*m*'-nitrobenzoyl-*m*-aminobenzoyl)-2-naphthylamine-6,8-disulphonic acid, and also free *N*-(*m*'-nitrobenzoyl-*m*-aminobenzoyl)-2-naphthylamine-4,8-disulphonic acid may serve as examples. It is of interest to note that there exists a distinct correlation between the therapeutic effect and the affinity of these compounds for cotton in dyeing.[71] This shows that there is a single mechanism of their action: the medicinal drugs add equally readily to chemically similar groups in copper and trypanosomes, blocking the reproduction of the latter.

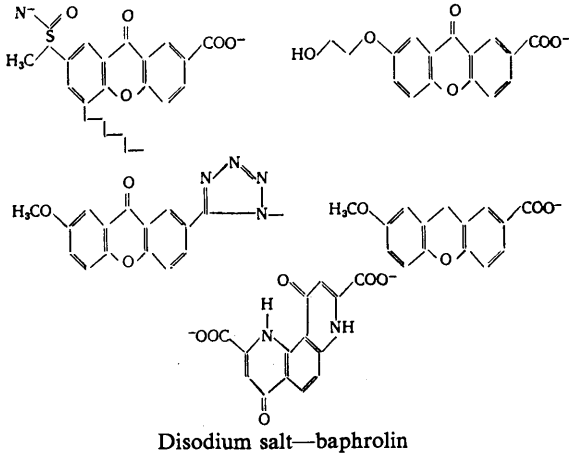
A large group of antiasthmatic drugs also form chromonic mesophases. These are mainly the sodium salts of non-steroid anions, whose structures are presented below:[15,72,73]



Cromoglycate. Disodium salt—cromolyn, intal, sodium cromoglycate (DSCG)



7,7-Cromoglycate



Disodium salt—baphrolin

Examination of the structures of these compounds makes it possible to differentiate the following general features:[15] (1) all the compounds have rigid planar aromatic nuclei containing benzopyrone or isoelectronic benzopyridone groups; (2) there are two hydrophilic groups at the opposite ends of the molecule in all these compounds, one of the groups representing an acid residue and the other either yet another acid residue or another group capable of forming a hydrogen bond. These groups do not have a permanent position: in some cases, they are linked directly to the pyrone ring, whereas in others they are linked to a neighbouring ring.

We may note that the benzopyrone and beonzopyridone structures can have an appreciable dipole moment if the molecule contains in the ring an oxygen atom which carries a large positive charge. For this reason, such an atom does not form hydrogen bonds.

The mesophases of these compounds are formed for the same reason as the mesophases of the dyes examined above. Here too water molecules play a major role (see above).

Like dyes, antiasthmatic drugs possess two main chromonic mesophases—nematic (*N*) and hexagonal (*M*). These phases have been investigated in greatest detail in relation to sodium cromoglycate (DSCG).

The phase diagram for the DSCG–H_2O system (Fig. 9) has been frequently investigated,[72,74–76] being gradually refined and amplified. On the whole, it resembles the phase diagrams for chromonic dyes (cf. Fig. 7), but there are also certain differences. A common feature is the existence of a premesophase region where aggregates, usually dimers, are formed. At room temperature, aggregation begins when the DSCG concentration reaches approximately 5 wt.%.[77] On the other hand, in the concentration range 5–25 wt.%, the aggregation of molecules is already manifested when the temperature of the system exceeds by 10–15 °C the temperature of the region of the mesophases.[78]

As for dyes, there are two chromonic mesophases—nematic (*N*) and hexagonal (*M*)—in the DSCG–H_2O system. The presence of extensive two-phase regions is also a common feature of these two diagrams.

Table 6. The enthalpies and temperatures of the $N + I \rightarrow I$ transitions in aqueous 13 wt.% DSCG solution.[79]

NaCl concentration, M	pH	ΔH, cal g^{-1}	Transition temperature, K
—	6.9	0.39	314.9
—	6.5	0.49	314.4
—	6.0	0.40	313.2
—	5.0	0.36	313.7
10^{-6}	—	0.40	310.2
10^{-5}	—	0.54	309.9
10^{-4}	—	0.58	310.0
10^{-3}	—	0.54	307.4
10^{-2}	—	0.40	309.9
10^{-1}	—	0.49	314.7
0.5	—	0.54	323.0
1.0	—	0.43	330.5
1.5	—	0.62	334.9

The positions of the mesophases on the phase diagram depend on the pH of the solution and on the concentration of the added salts.[79] This conclusion is well illustrated by Table 6, which lists the temperatures and enthalpies of the transition to the isotropic phase at different pH and NaCl concentrations. It is seen from the table that the pH has only a weak influence on the enthalpy and temperature of the transition. On the other hand, the influence of the salt concentration is very appreciable, the transition temperature falling initially and then increasing as the concentration rises. A similar effect was found also after the addition of KCl and LiCl. The minimum transition temperature corresponds to a different salt concentration: 10^{-3} M for NaCl, 10^{-4} M for KCl, and 10^{-5} M for LiCl. It is of interest to note that the crystal-nematic phase transition temperature also increases only slightly with increasing concentration of the salts investigated.[79]

The principal difference between dyes and the DSCG – H_2O system is the presence on the phase diagram of the latter of a new smectic mesophase, with a hitherto unknown structure, at low temperatures (–4 °C) before the transition to the solid phase.[80] It is designated as III in Fig. 9. Measurement of the enthalpy of the transition with the aid of a differential scanning calorimeter (DSC) permitted the hypothesis[75] that in fact two mesophases III exist. However, analysis of the NMR spectra and optical observations have not so far confirmed this hypothesis.

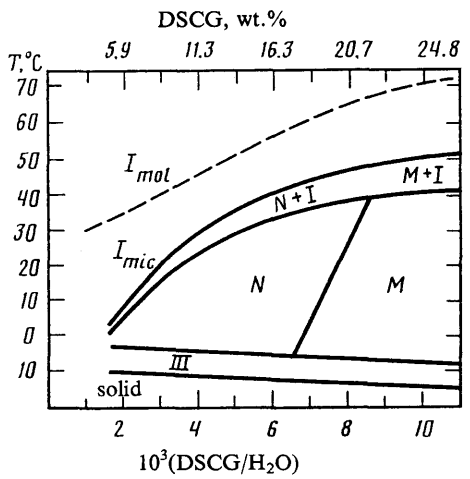


Figure 9. Phase diagram of the DSCG – H_2O system: *M*—hexagonal mesophase; *N*—nematic mesophase; *I*—isotropic phase; I_{mol}—isotropic molecular phase; I_{mic}—isotropic micellar phase.[72]

The mesophase III is satisfactorily manifested following the addition of ethylene glycol or glycerol to the system. The starting point of the solid phase to give the mesophase (III) then diminishes and the temperature of the transition to the nematic phase increases. Thus the region of the existence of the mesophase (III) expands. This made it possible to find the thermodynamic characteristics of the phase transitions in this system with the aid of the DSC. As for thermotropic liquid crystals, fusion to give the mesophase is a first-order phase transition accompanied by large heat and entropy changes. On the other hand, the transitions between the mesophases and between the mesophase and the isotropic liquid have all the features of weak first-order phase transitions. With increase in the glycerol content, the heat changes diminish and the transition temperatures increase.

New mesophases have also been found in the 7,7-cromoglycate (7,7-DSCG) – H_2O system.[73] At temperatures below the temperature of the existence of the mesophase *N* (in the 7,7-DSCG concentration range form 3 to 25 wt.%), an extensive region of a birefringent gel phase (the phase *R*), having a network structure, was discovered. The texture of this phase is illustrated in Fig. 10*a*. In the same temperature range as for the phase *N* but with a salt content above 15 wt.%, the more ordered and denser phase *S* was found (Fig. 10*b*).

The mesophases *N* and *M* give rise to readily identifiable optical textures (Figs. 10*c* and 10*d*), typical for chromonic mesophases.[15,72–75] Their structure was investigated by small angle X-ray diffraction analysis[74,76,81] and NMR.[76,78,80,82]

We shall consider primarily the shape of the DSCG molecule. Here there is no unanimous view as yet. In the first study concerned with the solid phase,[72,74] a planar molecular structure was postulated although it was also suggested[74] that at high water concentrations the planar configuration can hardly persist as a consequence of the possibility of the free rotation of one end of the cyclic system relative to the other about the –CH– bond. However, light scattering and magnetic double refraction data[77] have not confirmed this hypothesis even in the concentration range 0.3 – 3 wt.% (isotropic solution). The planar configuration is likewise supported by the formation of hydrogen

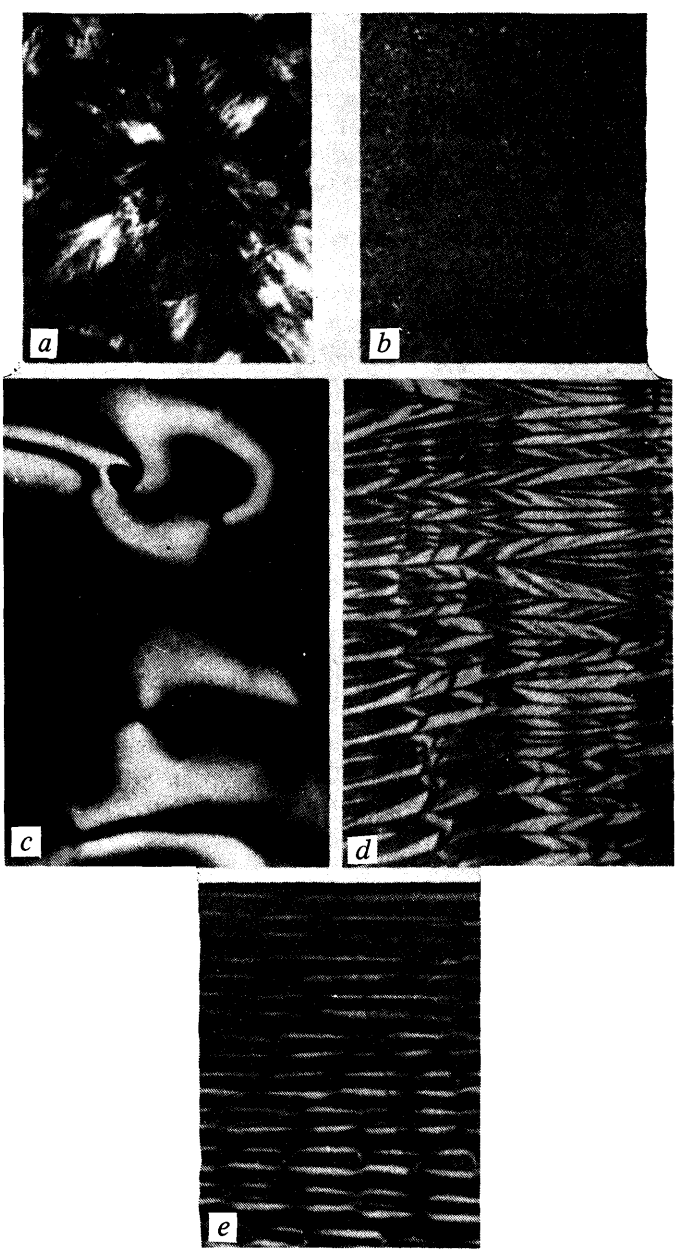


Figure 10. Textures of chromonic mesophases: (*a*) *R*; (*b*) *S*; (*c*) *N*; (*d*) *M*; (*e*) "bamboo".[15,73,79]

bonds between the water molecules and the hydroxy- and carbonyl groups of the DSCG molecules. This is indicated by the pronounced hygroscopicity of solid DSCG and the presence of an appreciable amount of bound water in the mesophases.[72,74] However, the non-coplanarity of the chromonium rings (the angle between them is 53°) was observed in a later study,[83] where the detailed structure of DSCG was found. It may be that such non-coplanarity is characteristic only of the solid phase.

Important information about the structure of DSCG was obtained by small angle X-ray diffraction.[74] Reflections with the ratios $1:1/\sqrt{3}:1/\sqrt{4}$ are clearly manifested in the phase *M*, which indicates hexagonal packing. In addition there is a reflection corresponding to a distance of 3.4 Å, which is interpreted at the identity parameter along the long axis of the column, i.e. as the thickness of the DSCG molecule. If it is assumed that the columns have a circular cross-section, then it is easy to calculate their diameter and the distance between them. Thus in solution at a DSCG concentration of 20 wt.% at room temperature the column diameter is 16 Å and the distance between the columns is 43.3 Å. The nematic mesophase gives rise to only one reflection corresponding to a distance of 3.4 Å, which indicates the breakdown of hexagonal packing.

Thus the structure of the mesophases in the DSCG–H_2O system corresponds to the chromonic type. However, bearing in mind the size of the DSCG molecules and the diameter of the columns, presumably[84] four molecules are accommodated in the cross-section of the chromonic columns, the polar ends of the molecules projecting to the outside (Fig. 11*a*).

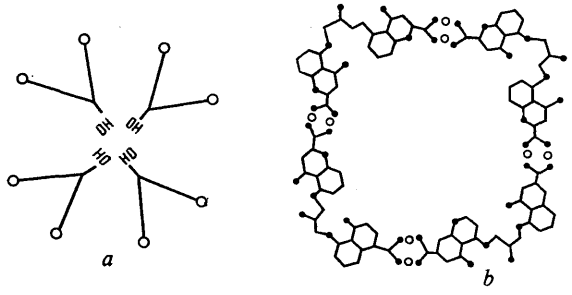


Figure 11. Models of the packing of DSCG molecules in chromonic columns: (*a*) cylindrical model;[84] (*b*) square model.[85]

However, this simple structure agrees poorly with the high moisture absorption capacity of the mesophases. Density measurements have shown[72] that in the mesophase *M* there are 9 water molecules for each DSCG molecule, while in the mesophase *N* there are 260 water molecules. Taking into account these data and other information about the structural features of the system, another hypothesis has been put forward concerning the structure of the columns,[85] according to which 4 DSCG molecules, linked to hydrated sodium ions, form hollow rings (Fig. 11*b*). These rings are superimposed on one another, as in the usual chromonic columns, forming square hollow columns filled with water. In the nematic phase, the columns are distributed freely, while in the mesophase *M* they are packed in accordance with the hexagonal law, as shown in Fig. 12.

The latter model was fully accepted by Hartshorne and Woodard,[86] although the square form of the chromonic columns was rejected.

The chromonic type of the structure of the DSCG mesophases was confirmed by X-ray diffraction.[76] The phase (III) was investigated in the same study. It was found that it too is made up of columns, but more detailed data were not obtained. The study of all the phases in the DSCG–H_2O system by ^2H, ^{17}O, and ^{23}Na NMR showed[76,78,80] that in all the mesophases the anisotropy of the diamagnetic susceptibility $\psi_a = \psi_{\parallel} - \psi_{\perp}$, where $\psi_{\parallel}$ and $\psi_{\perp}$ are diamagnetic susceptibilities along and at right angles to the director, is negative. This means that the planar DSCG molecules are arranged perpendicularly to the column axes, like the molecules in the chromonic phases of dyes.

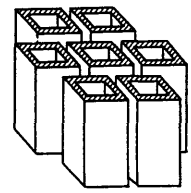


Figure 12. A model of the packing of columns in the mesophase *M* of the DSCG–H_2O system.[85]

A second important result is the fact that the quadrupolar splitting in the ^2H and ^{17}O spectra of the D_2O molecules and in the ^{23}Na spectrum changes sharply on transition from the phase (III) to the phases *N* or *M* and varies linearly on transition from *N* to *M*. The quadrupolar splitting on the ^2H and ^{17}O spectra on transition to the mesophase *N* or *M* diminishes under these conditions, while that in ^{23}Na spectra increases. A detailed study[78] of the NMR spectra of the ^{23}Na atoms showed that, following the addition of NaCl to the system, the quadrupolar splitting in all the phases initially falls to zero and then changes sign and increases again. This makes it necessary to postulate that the Na^+ ions occupy two different types of positions in the structure, to which splittings of different sign correspond. They can be found both in the columns (the binding of the DSCG molecules) and in the surrounding water. In the initial system, almost all the Na^+ ions are in the first positions. After the addition of NaCl, most of the Na^+ ions pass to the surrounding water, which in fact diminishes the quadrupolar splitting.

A study[82] of the influence of NaCl on the ^2H NMR spectra of D_2O led to the conclusion that there is only an increase in the stability of the mesophases and the associated impairment of the quadrupolar splitting. The increase in stability was explained by the weakening of the repulsion of the DSCG molecules as a result of the shielding effect of Na^+ ions. The absence of two different doublets in the NMR spectrum of D_2O, which should have been observed according to the model illustrated in Fig. 11*b*, was also noted. However, this finding can be readily accounted for also by the easy exchange between the free water molecules and the molecules incorporated in the columns.

NMR data yielded some information about the order parameters S_{ij} of the DSCG–H_2O system. The order parameter, which is a second rank tensor, describes quantitatively the ordering in the system and is defined as follows:

$$S_{ij} = S(n_i n_j - {}^1/_3\delta_{ij}), \qquad (3)$$

where *S* is the scalar order parameter, n_i and n_j are the components of the director, and δ_{ij} is the Kronecker symbol.

It proved possible to calculate from the ^{17}O spectra of D_2O the principal components of the order parameter tensor for these molecules and to determine their temperature dependence.[80] It was found that the water molecules are well ordered and that the average parameter is about 0.5.

A detailed study[76] of the order parameter of the C–D bond has been carried out using DSCG containing deuterium in the chromonium rings and in the central CH group of the hydrocarbon bridge. The scalar order parameter S was calculated from the concentration dependence of the quadrupolar splitting in the ^2H spectrum. It increases linearly with increase in concentration in the range 4–29 wt.% from 0.76 to 0.97. These unusually high values are surprising, since the order parameter determined from the NMR spectra is a product of the order parameter of the molecules in the column and of the effective order parameter of the columns themselves. Nevertheless the value of S obtained correspond to those predicted by the Onsager theory.[87] Using its formal treatment and assuming that the diameter of the DSCG molecule is 26 Å, it is possible to estimate the length of the columns. It is about 2000 Å in the phase M and about 800 Å in the phase N.[76]

The order parameter in the nematic phase of the DSCG–H_2O system has also been investigated[84,88] by polarisation absorption spectroscopy.† Dichroic dyes such as indigo, carmine, eosin, Methyl Red, Congo Red, etc. were dissolved in the mesophase and the absorption spectra were measured in polarised light parallel and at right angles to the direction of a 20 kG magnetic field. It was found that S for the "guest" dye molecules varies from −0.2 to −0.005. The order parameter of the DSCG molecule as a whole was determined at the wavelength corresponding to the intrinsic absorption band. It proved to be −0.20. With increase in temperature, the order parameter diminishes as usual. It also decreases with decrease in the ionic strength of the solution.

In an interesting study[89] the order parameters were calculated from the intensities of individual IR absorption bands corresponding to particular bonds (Table 7). As was to be expected, all the parameters S are negative, which confirmed the perpendicular orientation of the DSCG molecules relative to the magnetic field. The average order parameter is −0.14, which agrees with the results of independent measurements.[84]

Spectroscopic data[89] also suggest that the oxygen atoms of the chromonium rings are linked by hydrogen bonds to water molecules. In addition it was found that the overlapping of the DSCG molecules in the nematic mesophase is much more marked than in the isotropic phase.

The 7,7-DSCG mesophases have also been investigated by X-ray diffraction.[81] The high-temperature phase R gives rise to three diffraction peaks corresponding to distances of 51.2, 25.1, and 32.1 Å at 27 °C. They are in proportions of $1:1/2:1/\sqrt{2}$ and correspond to the indices 1.0 : 1.1 : 2.0 of a two-dimensional square lattice. With decrease in temperature, the distances increase but their ratios do not change. The nematic phase produces only one peak corresponding to an index of 1.0. This peak, which does not undergo sharp changes in the transition $R \rightarrow N$, corresponds to distances between the columns of 60–70 Å. The three diffraction peaks of the phase M are in the ratios $1:1/\sqrt{3}:1/2$, which correspond to the hexagonal lattice. Immediately below the temperature of the transition from the phase N to the phase R, the hexagonal lattice parameter is about 46 Å, but it reaches 80 Å as the temperature is reduced.

Table 7. Order parameters for individual bonds in the nematic phase of the DSCG–H_2O system.[89]

Bond	Wavenumber, cm^{-1}	S
C=C	1482	−0.132
=C–H	1412	−0.127
CO_2^-	1364	−0.136
CO_2	1311	−0.149
C–O (ether)	1267	−0.110
C–O (in =C–O–C)	1128	−0.071
OH	1047	−0.102

The ^2H and ^{17}O NMR spectra of D_2O and the ^{23}Na NMR spectra of the same systems have been investigated. In the spectrum of phase R, there is no quadrupolar splitting, which indicates a disordered disposition of the water molecules. The usual quadrupolar splitting is observed in the spectra of the other mesophases. The quadrupolar splitting in the ^{23}Na spectrum is of a similar character and does not undergo sharp changes in the transition from the phase N to the phase S or M. This is explained by the fact that the distribution of Na^+ ions between two possible positions (see above) is independent of concentration. The study of the NMR spectra of the compound deuteriated in the chromonium ring made it possible to determine the order parameter of the C–D bond. It is independent of concentration but varies linearly with increase in temperature. Estimates have shown that the order parameter in the mesophases N and S is approximately unity, which indicates the almost complete ordering of the columns, although it does not rule out the free rotation of the molecular planes.

Detailed structural studies have made it possible to put forward the hypothesis of a relation between the liquid crystal nature of the anti-asthmatic drugs and their therapeutic properties.[15] If this relation is not fortuitous, three mechanisms are possible.

The therapeutic effect is associated with the formation of a chromonic mesophase on the surface of the lung.

The mesophase is not formed but the therapeutic effect is associated with a biologically active complex (a cyclic structure or a hollow column), which promotes the formation of the mesophase.

The mesophase is not formed but the therapeutic effect is due to the structure of the molecule itself, which is at the same time mesogenic.

Available knowledge is so far insufficient to reject *a priori* any of the three mechanisms indicated. However, the first is supported by the presence on the surface of the lung of a mesophase with a high phospholipid content. The breakdown of the liquid-crystal state of this layer leads to the breakdown of the tiny alveoli at the end of exhalation. It is therefore quite likely that the mesophases of anti-asthmatic drugs compensate for the deficiency of liquid crystal phospholipids.

As we have already stated, chromonic mesophases have a negative diamagnetic anisotropy. The geometry of the column permits the ready spontaneous formation of a planar texture. Reorientation in a magnetic field (the Fredericks transition) is usually observed in fields of 10–20 kG. It is accompanied by the appearance of interesting defects.

†The order parameter determined by this method is $S = (A_{||} - A_\perp)/(A_{||} + 2A_\perp)$, where $A_{||}$ and $A_\perp$ are the absorption intensities along and at right angles to the director respectively. Since $A_\perp > A_{||}$ for molecules with negative dichroism such as DSCG, it follows that $S < 0$ and amounts to −0.5 in the fully ordered state ($A_{||} = 0$).

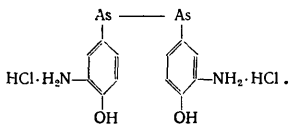
Thus, when an 18 kG magnetic field is applied to a thick (80–200 μm) planar DSCG specimen in the plane of the specimen and along the axes of the columns, a "bamboo" type of texture is formed (Fig. 10*e*). In the course of time, the "bamboo" sections grow and are obliterated.[79]

A periodic domain structure, the repeat step of which depends periodically on the magnetic strength, has been clearly observed on thin specimens (~20–40 μm).[90] This structure exhibits an interesting time variation.[91] The formation of a domain structure has a purely hydrodynamic cause—it arises as a result of the presence of a reverse flux accompanying the Fredericks transition.[79,90,91]

The addition of chiral admixtures converts the nematic DSCG mesophase to a cholesteric phase.[79] Various aminoacids, for example, alanine, proline, lysine, etc., at concentrations ranging from 1 to 36 wt.%, are used as the additives. Naturally the pitch of the helix of the cholesteric phase obtained depends on the concentration of the chiral additive. In all cases, the reciprocal of the pitch of the helix increases linearly with increasing concentration of the chiral additive.[79,92]

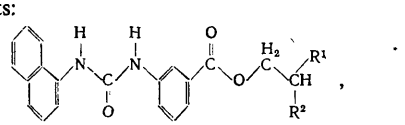
An interesting result was obtained in a study of the influence of the magnetic field on such induced cholesteric phases. After prolonged exposure to the field, the pitch of the helix diminishes, but not to zero. It falls to a finite value approximately equal to one-third of the initial pitch.[79]

Aqueous solutions of salvarsan and neosalvarsan—drugs active against syphilis, malaria, and recurrent fever—apparently form a chromonic mesophase.[5,93] Although direct structural studies have not been made, nevertheless the physical properties of these systems support indirectly this hypothesis. Firstly, the salvarsan molecule has a planar shape with polar hydrophilic groups at the end:

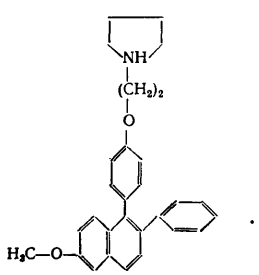


Secondly, the occurrence of polarisation in aqueous solutions indicates the formation of large aggregates. The third piece of evidence is provided by the presence of the nematic mesophase, which is optically monoaxial and negative, the negative side being in fact typical for chromonic mesophases.

Chromonic phases are formed in aqueous solutions and in heptane by *N*-1-naphthyl-*N'*-phenylenecarboxyalkylureas[94] which are used as antisunburn agents:



where R^1 and R^2 are various alkyl groups ranging from methyl to dodecyl. These compounds are chiral and form chromonic structures, which has been confirmed by the observation of the corresponding textures. Furthermore, more ordered mesophases, apparently hexagonal, have also been discovered:



Two mesophases are likewise formed by naphthoxidine hydrochloride,[95] eight molecules of which form a ring with the pyrrole groups on the periphery. The rings are in their turn packed in a chromonic column, which is an element of the superstructure.

Chromonic phases are apparently formed also by rivanol (6,9-diamino-2-ethoxyacridine lactate).[96] However, here further studies are necessary.

V. Conclusion

An independent branch of the field of study of lyotropic crystals, involving the investigation of the conditions governing the formation, structure, and properties of chromonic mesophases, has now been established. These phases differ from the classical lyotropic micellar liquid crystals but at the same time they have features in common with the latter. The amphiphilic nature of the molecules, their extended shape, and the presence of a long ($n > 8$) hydrocarbon "tail" are typical for micellar mesophases. Such construction ensures the formation, as a result of a balance between ionic and hydrophobic interactions, of anisotropic micelles, both normal (in water or in any polar solvent) and inverted (in non-polar solvents). The balance of forces is so fine that a change in the concentration of the amphiphilic substance alone is sufficient to entail a significant change in the form of the micelles, which change from spherical to discotic, biaxial, and cylindrical.

Molecules forming chromonic mesophases can be called amphiphilic only by way of a convention. They have the planar shape of a "plank" with small end groups which ensure its solubility in water. The principal cause of the formation of ordered structures is therefore in this instance the appearance of hydrogen bonds between the polar groups and water molecules. The hydrophobic interaction plays only a secondary role. However, micelles are formed, as in the classical lyotropic liquid crystals. Their role is assumed by columns—"coin stacks". The occurrence of a single leading interaction creates simpler structures—isotypical columns arise instead of a set of anisometric aggregates. Admittedly the packing of the molecules in the column depends on their chemical nature but this does not lead to a great variety. Structurally, chromonic mesophases are closer to columnar thermotropic liquid crystals than to micellar lyotropic mesophases. The principles of the molecular packing are identical although chromonic materials do not exhibit the wide variety of structures characteristic of columnar thermotropic mesophases.

The study of chromonic mesophases has continued at a high rate. Their practical importance is evident, because important substances such as dyes and medicinal drugs are the principal chromonic materials. However, much still remains to be done. In the first place, there are still very few data on the viscoelastic properties of these compounds. There is no information about their electrooptical and magnetooptical behaviour. There is no microscopic theory of the mesomorphic properties of these phases. Further studies will undoubtedly fill these gaps and will provide an answer to the principal question concerning the relation between the mesomorphic properties of chromonic phases and their structure.

References

1. P Gaubert *C.R. Seances Acad. Sci.*, 1916, **163** 392
2. P Gaubert *C.R. Seances Acad. Sci.*, 1933, **197** 1436
3. P Gaubert *C.R. Seances Acad. Sci.*, 1934, **198** 951
4. P Gaubert *C.R. Seances Acad. Sci.*, 1935, **200** 679
5. H Freundlich, R Stern, H Zocher *Biochem. Zeit.*, 1923, **138** 307
6. S Chandrasekhar, B K Sadashiva, K A Suresh, et al. *J. Phys. (France)*, 1979, **40** Suppl. C-3, 120
7. J Billard, B K Sadashiva *Pramana*, 1979, **13** 309
8. N Boden, R J Bushby, C Hardy *J. Phys. (Fr.) Letters*, 1985, **46** 325
9. B Kohne, K Praefoke, T Derz, et al. *Chimia*, 1986, **40** 171
10. N Boden, R J Bushby, C Hardy, et al. *Chem. Phys. Lett.*, 1986, **123** 359
11. N Boden, R J Bushby, L Ferris, et al. *Liquid Cryst.*, 1986, **1** 109
12. H Ringsdorf *XII International Liquid Crystal Conference. Program and Abstracts.* Freiburg, 1988, p. 113
13. J Wolff, K Wolf, J Koll, et al. BRD P. 3 149 129
14. J Koll, V Paulat, R Hörnle, et al. Europ. P. 0 029 958
15. T K Attwood, J E Lydon *Mol. Cryst. Liq. Cryst.*, 1984, **108** 349
16. J Dreyer US P. 2 400 877
17. J Dreyer *J. Phys. Colloid Chem.*, 1948, **52** 808
18. E Valco *Colloidal-Chemical Foundations of the Textile Technology* (Translated into Russian) Gizlegprom, Moscow–Leningrad, 1940, Vols. 1–2, 273 pp
19. S E Sheppard *Rev. Mod. Phys.*, 1942, **14** 303
20. R H Peters *Textile Chemistry*, Elsevier, Amsterdam, 1975, Vol. III, p. 581
21. B C Burdett *Aggregation Processes in Solution* (Edited by E Wynne-Jones, J Gormally), Elsevier, Amsterdam, 1983, p. 241
22. C Robinson *Trans. Faraday Soc.*, 1935, **31** 245, 277
23. C Robinson *Proc. Roy. Soc.*, 1935, **148A** 681
24. B Milicevic, G Evigenmann *Helv. Chim. Acta.*, 1964, **47** 1039
25. D J Blears, S S Danyluk *J. Am. Chem. Soc.*, 1966, **88** 1084
26. S R S Iyer, G S Singh *Kolloid Zeit. Zeit. Polym.*, 1970, **242** 1196
27. S R S Iyer, G S Singh *J. Soc. Dyers Colour*, 1973, **89** 128
28. E Coates *J. Soc. Dyers Colour*, 1969, **85** 355
29. M A Anisimov, I F Kazakova, A S Kurlyandskii, S A Pikin *Kristallografiya*, 1987, **32** 1100
30. E I Valko *Trans. Faraday Soc.*, 1935, **31** 230
31. E I Valko *J. Soc. Dyers. Colour*, 1939, **55** 173
32. E I Valko *J. Am. Chem. Soc.*, 1941, **63** 1433
33. S E Lenher, J E Smith *J. Am. Chem. Soc.*, 1935, **57** 497, 504
34. S E Lenher, J E Smith *J. Phys. Chem.*, 1936, **40** 1005
35. F H Holmes, H A Standing *Trans. Faraday Soc.*, 1945, **41** 542, 568
36. T Vickerstaff *Physical Chemistry of Dyeing*, Oliver and Boyd, London, 1954
37. R B McKay *Trans. Faraday Soc.*, 1965, **61** 374
38. A Datyner, A G Flowers, M T Paiethorpe *J. Colloid. Interface Sci.*, 1980, **74** 71
39. H P Frank *J. Colloid Sci.*, 1957, **12** 480
40. A Datyner, M T Paiethorpe *J. Colloid Interface Sci.*, 1980, **76** 557
41. G Scheibe *Angew. Chem.*, 1937, **50** 212
42. H Freundlich, C Schuster, H Zocher *Z. Physik. Chem.*, 1923, **105A** 118
43. C Robinson, H A Mills *Proc. Roy. Soc.*, 1931, **131A** 576, 596
44. G Scheibe, L Kandler, H Ecker *Naturwiss*, 1937, **25** 75
45. G Schiebe, L Kandler *Naturwiss*, 1938, **26** 412
46. G Scheibe *Angew Chem.*, 1939, **52** 631
47. S E Sheppard *Science*, 1941, **93** 42
48. L A Ignat'eva, L V Levshin, T D Osipova, et al. *Opt. Spektrosk.*, 1962, **13** 396
49. L V Levshin, T D Slavnova, Yu A Mittsel' *Zh. Prikl. Spektrosk.*, 1968, **8** 293
50. E Jelloy *Nature*, 1936, **138** 1009
51. V A Bykov, Yu A Bobrov, N A Ovchinnikova, *V Konferentsiya Sotsialisticheskikh Stran po Zhidkim Kristallam. Tezisy Dokladov. Odessa* (The V Conference of Socialist Countries on Liquid Crystals. Abstracts of Reports. Odessa), 1983, Vol. 2, Part 1, p. 217
52. V A Bykov, E V Generalova, L Ya Ignatov, et al. *Tezisy Dokladov VI Vsesoyuznoi Konferentsii 'Zhidkie Kristally i Ikh Prakticheskoe Ispol'zovanie'. Chernigov* (Abstracts of Reports at the VI All-Union Conference on 'Liquid Crystals and Their Practical Applications'. Chernigov), 1988.
53. F Brauner *Nord. Kemikermode Ford.*, 1939, **5** 207
54. T K Attwood, J E Lydon, F Jones *Liquid Cryst.*, 1986, **I** 499
55. T Imae, S Ikeda *Mol. Cryst. Liq. Cryst.*, 1983, **101** 155
56. N V Usol'tseva, V V Bykova, N M Kormilitsyn, et al. *Khimiya Zhidkikh Kristallov. Primenenie v Khromatografii. Tezisy Dokladov Oblastnoi Nauchnoi Konferentsii. Kuibyshev* (The Chemistry of Liquid Crystals. Applications in Chromatography. Abstracts of Reports at the Regional Scientific Conference. Kuibyshev), 1987, p. 33
57. N M Melankholin *Kristallografiya*, 1961, **6** 568
58. V A Bykov *Tezisy Dokladov V Vsesoyuznoi Konferentsii 'Zhidkie Kristally i Ikh Prakticheskoe Ispol'zovanie'. Ivanovo* (Abstracts of Reports at the V All-Union Conference on 'Liquid Crystals and Their Practical Applications'. Ivanovo), 1985, Vol. II, Book 1, p. 84
59. N V Anikifirova, Yu A Bobrov, V A Byov *Tezisy Dokladov VI Vsesoyuznoi Konferentsii 'Zhidkie Kristally i Ikh Prakticheskoe Ispol'zovanie'. Chernigov* (Abstracts of Reports at the VI All-Union Conference on 'Liquid Crystals and Their Practical Applications'. Chernigov), 1988, Vol. III, p. 441
60. S H Jury, R C Ernst *J. Phys. Colloid. Chem.*, 1949, **53** 609
61. R A Berg, B A Haxby *Mol. Cryst. Liq. Cryst.*, 1970, **12** 93
62. G W Gray, P A Winsor *Liquid Crystals and Plastic Crystals*, Halsted Press, Chichester, 1974, Vol. 2, p. 56
63. F Jones, D R Kent *Dyes and Pigments*, 1980, **1** 39
64. A S Sonin *Usp. Fiz. Nauk.*, 1987, **153** 273
65. D E Sadler, M D Shannon, P Tollin, et al. *Liquid Cryst.*, 1986, **1** 509
66. W Hoppe *Kolloid Z.*, 1942, **101** 300
67. N V Usol'tseva, V V Bykova, N M Kormilitsyn, et al. *Tezisy Dokladov V Vsesoyuznoi Konferentsii po Koordinatsionnoi i Fizicheskoi Khimii Porfirinov. Ivanovo* (Abstracts of Reports at the V All-Union Conference on the Coordination and Physical Chemistry of the Porphyrins. Ivanovo), 1988, p. 183
68. N V Usol'tseva, V V Bykova, G A Anan'eva, et al. *Kolloid. Zh.*, 1989 (in the press)
69. N V Usol'tseva, V V Bykova, G A Anan'eva, et al. *Tezisy Dokladov VI Vsesoyuznoi Konferentsii 'Zhidkie Kristally i Ikh Prakticheskoe Ispol'zovanie'. Chernigov* (Abstracts of Reports at the VI All-Union Conference on 'Liquid Crystals and Their Practical Applications'. Chernigov), 1988, Vol. III, p. 422

70. V A Bykov, T S Berzina, T A Ivanova, et al. *V Konferentsiya Sotsialisticheskikh Stran po Zhidkim Kristallam. Tezisy Dokladov. Odessa* (The V Conference of Socialist Countries on Liquid Crystals. Abstracts of Reports. Odessa), 1983, Vol. 2, Part 1, p. 219
71. I E Balaban, H King *J. Chem. Soc.*, 1927, 3068
72. J S G Cox, G D Woodard, W C McCrone *J. Pharm. Sci.*, 1971, **60** 1458
73. D Perahia, Z Luz, E J Wachtel, et al. *Liquid Cryst.*, 1987, **2** 473
74. N H Hartshorne, G D Woodard *Mol. Cryst. Liq. Cryst.*, 1973, **23** 343
75. H Lee, M M Labes *Mol. Cryst. Liq. Cryst.*, 1983, **91** 53
76. D Goldfarb, Z Luz, N Speilberg, H Zimmermann *Mol. Cryst. Liq. Cryst.*, 1985, **126** 225
77. J V Champion, G H Meeten *J. Pharm. Sci.*, 1973, **62** 1589
78. D Perahia, D Goldfarb, Z Luz *Mol. Cryst. Liq. Cryst.*, 1984, **108** 107
79. H Lee, M M Labes *Mol. Cryst. Liq. Cryst.*, 1982, **84** 137
80. D Goldfarb, M M Labes, Z Luz, R Poupko *Mol. Cryst. Liq. Cryst.*, 1982, **87** 259
81. D Perahia, Z Luz, E J Wachtel, H Zimmermann *Liquid Cryst.*, 1987, **2** 473
82. L J Yu, A Saupe *Mol. Cryst. Liq. Cryst.*, 1982, **80** 129
83. S Hamodrakas, A J Geddes, B Sheldrick *Pharm. Pharmac.*, 1974, **26** 54
84. B D Bostwick, M M Labes *Mol. Cryst. Liq. Cryst.*, 1987, **147** 179
85. J Lydon *Mol. Cryst. Liq. Cryst. Lett.*, 1980, **64** 19
86. N H Hartshorne, G D Woodard *Mol. Cryst. Liq. Cryst. Lett.*, 1981, **64** 153
87. P G de Gennes *The Physics of Liquid Crystals* (Translated into Russian), Izd. Mir, Moscow, 1977, 400 pp
88. M R Kuzma, V Skarda, M M Labes *J. Chem. Phys.*, 1984, **81** 2925
89. Y W Hui, M M Labes *J. Phys. Chem.*, 1986, **90** 4064
90. Y W Hui, M R Kuzma, M San Miguel, M M Labes *J. Chem. Phys*, 1985, **83** 288
91. J P McClymer, M M Labes *Mol. Cryst. Liq. Cryst.*, 1987, **144** 275
92. D Goldfarb, M E Moseley, M M Labes, Z Luz *Mol. Cryst. Liq. Cryst.*, 1982, **89** 119
93. H Zocher, V Birstein *Z. Phys. Chem.*, 1929, **142A** 126
94. U Hoppe *J. Soc. Cosmet. Chem.*, 1973, **24** 317
95. A R Mlodozeniec *J. Soc. Cosmet. Chem.*, 1978, **29** 659
96. V P Nazin *I Konferentsiya po Zhidkim Kristallam. Ivanovo* (The I Conference on Liquid Crystals. Ivanovo), 1972, p. 189

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The viscosity of nematic liquid crystals

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ABSTRACT. A simultaneous examination of data on the dynamic, kinematic, and rotational viscosities of nematic liquid crystals (NLC) belonging to 320 chemical classes has been carried out for the first time. The methods for the measurement of the viscosities of the NLC have been subjected to a comparative analysis and the limits of applicability of different procedures for the description of their temperature variation are discussed. The tables present data permitting the calculation with satisfactory accuracy of the viscosities of the majority of mesogenic substances at any temperature in the nematic range. The influence of the molecular structure of the NLC on the viscosities and on their temperature variation has been analysed and information is presented about the viscosities of the Soviet and foreign liquid crystal materials used in practice.

The bibliography includes 158 references.

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By virtue of their unique optical properties and low energy consumption, nematic liquid crystals (NLC) have now found wide scale applications in devices for the treatment and representation of information. One of the important characteristics of NLC, which determines the rapidity of their response in the working temperature range, is their viscosity. Both the dynamic viscosity η (or the kinematic viscosity ν), describing the flow of liquid in the nematic and isotropic phases, and the rotational viscosity γ_1, which has no analogue in isotropic liquids and is related to the dissipation of energy on reorientation of the NLC director (the director is a unit vector indicating the direction of the long axes of the NLC molecules), are measured for NLC. The communications by Benicewicz and Johnson[1] and de Gennes[2] are devoted to the viscosity of liquid crystals (LC) but the data presented there are too limited to permit a discussion not only of the relation between the viscosity and the molecular structure of NLC but also of the form of the temperature variation of the viscosity, the knowledge of which is essential for the development of LC materials with a satisfactory fast response at low temperature.

This review gives for the first time a systematic account of data concerning the relation between the chemical structure of NLC and their viscosity, the temperature variation of the viscosity of different NLC being considered from a single standpoint. The tabulated data are of interest for specialists dealing with liquids and may serve as a basis for specific investigations and the search for new nematic, smectic, polymeric, and lyotropic liquid crystals.

I. Methods for the measurement of the viscosities of nematic liquid crystals

Only the dynamic (η) or kinematic [$\nu = \eta/\rho$ (ρ is the density of the NLC)] viscosities are usually measured for many liquid crystals. However, in the present study attention is concentrated on the rotational viscosity γ_1, which determines the time of the electro-optical response. It has been shown[3,4] that there is a relation between the rotational viscosity γ_1 and the viscosity measured by capillary methods, described approximately by the relation

$$\gamma_1 \simeq a\eta + b, \tag{1}$$

$$\gamma_1 \simeq a(\eta_3 - \eta_2) + b, \tag{2}$$

where a and b are weakly temperature dependent coefficients and η_2 and η_3 are the Miesowicz viscosity coefficients.[2] These relations are confirmed by the simultaneous measurements of the viscosities γ_1 and η or η_2 and η_3 for a set of NLC belonging to different chemical classes.[4,5] For comparison, the tables indicate in a number of instances the values of γ_1 and η as well as the ratio γ_1/η.

Depending on the type of viscometer, the dynamic viscosity η (Ubbelohde viscometer) or the kinematic viscosity ν (Ostwald viscometer) is measured. Novel methods have been developed for the measurement of the rotational viscosity γ_1. They reduce to one of three types: the rotating magnetic field method, the dynamics of the Fredericks transition, and the spectrum of the light scattered by the thermal fluctuations of the director.

In the first method, the rotation of the magnetic field leads to the rotation of the NLC director, the second rotation occurring with a phase delay at sufficiently low angular velocities.[2,6] Having measured this delay, for example, with the aid of a torsional balance,[7] it is possible to determine the quantity γ_1/ρ or γ_1/χ_a (χ_a is the anisotropy of the diamagnetic permeability). The errors arising in this method of measurement have been studied in detail.[7] In order to measure γ_1 to within 0.1%, approximately 60 cm^3 specimens have been used,[4,7] which is by no means always possible especially in the study of new substances. The reduction of the volume of the specimen leads as a rule to an unduly low value of the measured quantity (compare, for example, the studies of Kneppe et al.[4] and Siedler et al.[8]).

An appreciably smaller amount of substances (less than 30 mg) is required in the measurement of γ_1 on the basis of the dynamics of the Fredericks transition. In this case the ratio γ_1/K_{22}[9] or η_S/K_{11}[10,11] is determined from the characteristic relaxation time (K_{11} and K_{22} are the elasticity coefficients of the NLC, $\eta_S = \gamma_1 - \alpha_3^2/\eta_2$ is the

viscosity describing the rate of relaxation of the transverse bending deformation, and α_3 is the Leslie viscosity coefficient). In the direct measurement of γ_1/K_{22}, one investigates the time variation of the location of the conoscopic figure formed when a convergent light beam is passed through a liquid crystal cell in a longitudinal magnetic field (the field is parallel to the supports but is at right angles to the director). Owing to the difficulty of determining the angle of rotation of the conoscopic figure and of K_{22}, this method has not come to be widely used. The method of measurement of η_S/K_{11} based on the optical[10] or capacitative[11] response of a planarly oriented cell after a transverse electric field has been switched off, has come to be more widely used. Since $|\alpha_3| \ll \gamma_1, \eta_1$,[12] the relation $\eta_S \simeq \gamma_1$ holds to within 1–2%, which is better than the accuracy of the measurement of η_S by this method (to within 7–10%). Simultaneously with γ_1, it is possible to measure in this cell the double refraction Δn and the elasticity coefficient K_{11} (when the dielectric anisotropy $\Delta\varepsilon$ is known). A method for the measurement of γ_1, based on the relaxation of the deformation of a specimen placed in a strong magnetic field (up to 0.8 T), has been described.[13] Its accuracy is to within 6%. It suffers from the disadvantage that the quantity χ_a has to be known.

The thermal fluctuations of the liquid crystal director lead to light scattering, which greatly exceeds that in isotropic liquids. The viscoelastic ratio γ_1/K_{22} or η_S/K_{11} can be determined from the half-width of the scattering spectrum and, knowing the intensity of the scattered light and of the refractive index of the NLC, the viscosity γ_1 or η_S itself can be determined.[2,14,15] Because of the need to view the light scattering at low angles where there is an appreciable contribution due to scattering by inhomogeneities in the orientation of the liquid crystal, the direct measurement of γ_1 is difficult or altogether impossible. The quantity η_S/K_{11} is therefore usually measured for the following geometry of the observation: the polarisation of the incident light is parallel to the director and perpendicular to the polarisation of the scattered light, while the scattering angle is 30–40°.[14] Although the corresponding method is fairly complex (the optical mixing spectroscopy and the correlation of single signals are needed), it has a significant advantage, namely the absence of are needed), it has a significant advantage, namely the absence of deformation of the specimen, which is important in the study of NLC with a strong transverse intermolecular interaction.

The tabulated γ_1 have been obtained using all the principal methods. It has been shown[16] that the results of the measurement of γ_1 by different methods agree well.

II. Temperature variation of the viscosities of nematic liquid crystals

The temperature variation of the viscosity of an isotropic liquid is usually described satisfactorily by the Arrhenius law:

$$\eta = a \exp(E/kT), \tag{3}$$

where a is a constant, E the activation energy, k the Boltzmann constant, and T the temperature. On the assumption that there is no intermolecular interaction, this relation is described by the Fulcher–Tammann formula:

$$\eta = b \exp[B/(T-T_0)], \tag{4}$$

where b and B are constants, $(T - T_0)/B$ is the fluctuation free volume, $T_0 \simeq T_g + 50$, and T_g is the glass point of the liquid. A dependence on the order parameter S is introduced into the preexponential factor in order to describe the variation of the viscosity γ_1 near the NLC–isotropic liquid transition temperature T_{NI}:

$$\gamma_1 = aS^x \exp(E/kT). \tag{5}$$

It has been shown[16] that $x = 1$ for liquid crystals with an elongated conjugation chain (biphenyls, phenylpyrimidines, phenyl benzoates, etc.), while $x = 2$ for liquid crystals whose molecules contain a fragment with saturated bonds (phenylcyclohexanes, phenylbicyclooctanes, etc.).

The limits of applicability of the activation and free volume models have been found.[17] The former is valid for all NLC with a small mesophase range (up to 40°) at temperatures $T > 20$ °C, while the latter is valid for NLC with a low activation energy ($E < 0.45$ eV = 4.95×10^3 Å) and also for NLC with an appreciable (above 60°) mesophase range extending to the region of reduced temperatures (as far as 0 °C and below). In the same study, it was shown that the viscosity γ_1 is determined by the molecular packing density, its temperature variation [the activation energy in Eqn. (5)] is determined by the intermolecular interaction energy, the order of magnitude of which is equal to that of the enthalpy of fusion of the NLC and is determined by the presence or absence of a fragment with saturated bonds (a cyclohexane or bicyclooctane fragment).

A theoretical description of the temperature variation of the rotational viscosity on the basis of a molecular-statistical approach, combining the characteristics of the activation and free volume models, has been proposed:[18]

$$\gamma_1(T, S) = gS^2 \exp[\varepsilon S/kT + \theta S^2/(T-T_0)], \tag{6}$$

where g is a weakly temperature dependent parameter, εS the height of the Maier–Saupe potential, θ a parameter determined by physical properties, and T_0 the temperature at which the motion of the director is frozen; in fitting the $\gamma_1(T, S)$ relation for any substance, the first or second term in the argument of the exponential function is neglected. The choice of the fitting procedure is determined by the width of the nematic range.

A comparative mathematical analysis of the suitability of different models for the description of the dependence of the rotational viscosity on temperature and the order parameter has been carried out.[16,17] The best agreement between the calculated curves and the experimental points and the highest correlation coefficients have been obtained for the majority of substances when the $\gamma_1(T)$ relation is described by an equation type (5). For certain cyclohexane and bicyclooctane derivatives, the smallest deviation was obtained when the results were fitted on the basis of the free volume model taking into account the order parameter S. Equations of type (6) as a rule give rise to a poorer agreement with experimental results although it has been noted[17] that the theory[18] makes it possible to explain the change in γ_1 in the homologous series of liquid crystal substances and the proportionality $E \propto T_{NI}$ for substances with a similar type of intermolecular interaction.

In most cases the experimental relations have therefore been fitted by curves of type (5) taking into account the specific molecular structure of the substance ($x = 1$ or 2). For a number of substances, the values of S were not available but the double refractions Δn were known, which made it possible to use analogous fitting procedures, because $\Delta n \propto S$.[2,16] In the absence of data making it possible to infer the temperature variation of the order parameter S, a simple equation of type (3) was fitted. For certain cyclohexane and bicyclooctane derivatives, a fitting procedure corresponding to the free volume model with allowance for the variation of S was employed.

Overall, in the tables an attempt has been made to analyse the temperature variations of the rotational viscosities of NLC belonging to different chemical classes using a single approach to their description. The relations were fitted on the basis of data presented in the tables or figures in the original publications. Only in certain cases (as a rule when the values of γ_1 or η were quoted at only one temperature) was an additional mathematical treatment of the original results not carried out.

III. Tables of the viscosities of nematic liquid crystals

The tables are constructed so that the values of γ_1 (or η and ν) can be obtained from the parameters listed in them at any temperature at which the given substance is nematic. Apart from specially stipulated cases, all the equations fitted were of the Arrhenius type:

$$\ln A = \ln A_0 + E/T. \qquad (a, b, c)$$

In equation (*a*) the letter A denotes the rotational viscosity γ_1 or its kinematic analogue γ_1/ρ (ρ is the density of the NLC) and also the dynamic viscosity η or the kinematic viscosity $\nu = \eta/\rho$. In the description of the temperature variation of the rotational viscosity by means of formula (*b*), the letter A denotes the ratio γ_1/S or $\gamma_1/\Delta n$ (account is taken of the proportionality $\Delta n \propto S$), whereas in the case where formula (*c*) is fitted A denotes the ratio γ_1/S^2 or $\gamma_1/(\Delta n)^2$. The viscosity is expressed in IS units: in 0.1 Pa s = 1 P (γ_1, η) or in 10^{-4} m^2 s^{-1} = 1 Stokes (γ_1/ρ, ν).

Table 1. The viscosities of nematic liquid crystals.

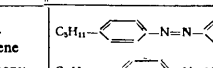
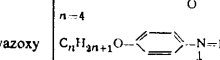
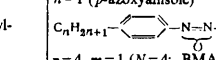
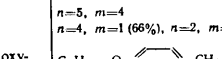
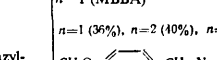
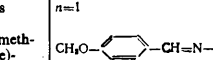
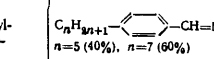
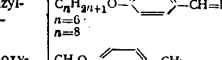
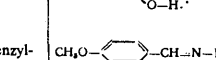
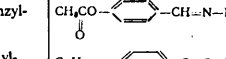
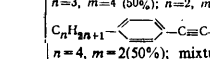
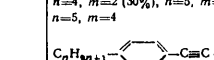
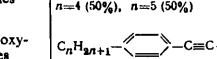
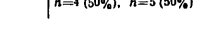
No. of compound	Name	Structural formula	Fitting formula	Viscosity[*1], 10^{-1} Pa s (γ_1, η), 10^{-4} m^2 s^{-1} (γ_1/ρ, ν)	ln A_0	E, 10^3 K	T^{*2}_{NI}, K	S or Δn	Refs.	Remarks
1	2	3	4	5	6	7	8	9	10	11
1	4-n-Butoxy-4'-n-pentylazobenzene		*a*	γ_1 (71.6° C)=0.37	—16.45	5.33	359.9		[3]	
2	4,4'-Di-n-alkylazoxybenzenes	 n=4	*b*	γ_1 (25° C)=0.48	—21.8	6.50	304.1	S (294.1 K)= =0.4956 [22]	[9]	see Table 2
3	4,4'-Di-n-alkoxyazoxy benzenes	 n=1 (*p*-azoxyanisole)	*a*	γ_1 (120° C)=0.070	—17.72	5.92	408.5	S (398.5 K) = =0.5784	[23]	see Table 3
4	4-Alkoxy-4'-alkyl-azoxybenzenes	 n=4, m=1 (N=4; BMAOB)	*b*	γ_1 (25° C)=1.89	—14.46	4.55	347.9	S (298.2 K)= =0.7182	[4]	n=5, m=1: T_g=198.7 K [26]
		n=5, m=4		γ_1 (25° C)=1.575			348	[24]	[25]	
		n=4, m=1 (66%), n=2, m=1 (34%)	*a*	γ_1 (40° C)=1.57	—14.01	4.53	376.5		[3]	
				η (20° C)=0.306			346		[27]	
5	4-n-Butyl(4'-alkoxybenzylidene)-anilines	 n=1 (MBBA)	*b*	γ_1 (25° C)=1.09	—18.92	5.82	318.3	S (308.3 K)= =0.54 [28]	[4]	see Table 4
		n=1 (36%), n=2 (40%), n=4 (24%)		η (20° C)=0.425			336		[27]	
6	(4'-Methoxybenzylidene)-4-aminophenyl acetates	 n=1	*b*	γ_1 (90° C)=0.394	—17.81	6.26	382.20	S(363.09 K)= =0.5954 [28]	[29]	see Table 5
7	4-But-1-enyl(4'-methoxybenzylidene)-aniline			η (133° C)=0.30			411.2		[30]	
8	(4'-n-Alkylbenzylidene)-4-cyano-anilines	 n=5 (40%), n=7 (60%)		γ_1 (25° C)=3.60, γ_1/η=5.36 at T=0.92 T_{NI}		5.36	343.9		[5]	$E=\partial\gamma_1/\partial\,(T^{-1})$ at T= =0.92 T_{NI}
9	(4'-n-Alkoxybenzylidene)-4-cyano-anilines	 n=6 n=8	*a*	γ_1 (60° C)=0.90	—15.05	5.05	373.1		[31]	
				γ_1 (88° C)=1.0			379		[32]	
10	4-Butyl-(4'-methoxysalicylidene)-aniline		*b*	γ_1 (44° C)=1.33	—22.37	7.349	338.15	S(0.95 T_{NI})= =0.60	[28]	
				γ_1 (T=0.95 T_{NI}) = =0.983						
11	Di-4-methoxybenzylideneazine		*a*	γ_1/ρ(174° C)=0.0444	—10.62	5.44	452		[33]	
12	Di-4-acetoxybenzylideneazine		*a*	γ_1/ρ (174° C)=0.107	—11.97	6.41	465		[33]	
13	4-n-Alkyl-4'-alkyltolanes	 n=3, m=4 (50%); n=2, m=5 (50%)							[27]	see compound 14
14	4-Alkoxy-4-n-alkyltolanes	 n=4, m=2(50%); mixture No. 13(50%);		η (20° C)=0.164			320	Δn (25° C)= =0.231	[27]	see Table 6
		n=4, m=2 (30%), n=5, m=1 (40%), n=5, m=2 (30%) n=5, m=4		η (20° C)=0.191			345	Δn (25° C)= =0.297	[27]	
			a	γ_1 (60° C)=0.48	—14.06	4.44	356.6		[3]	
15	4-n-Alkyl-4'-ethoxy-2'-methyltolanes	n=4 (50%), n=5 (50%)		η (20° C)=[0.329]			321	Δn (20° C)= =0.264	[34]	
16	4-n-Alkyl-4'-ethoxy-2'-fluorotolanes	n=4 (50%), n=5 (50%)		η (20° C)=[0.244]			331.5	Δn (20° C)= =0.278	[34]	

Table 1 (contd.)

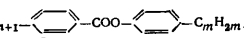
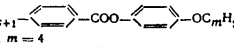
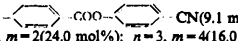
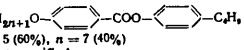
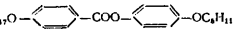
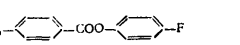
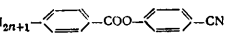
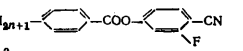
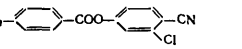
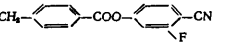
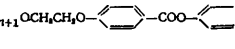
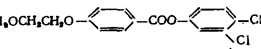
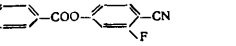
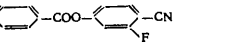
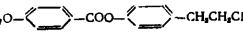
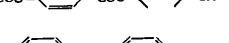
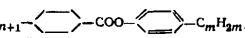
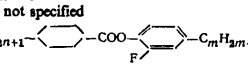
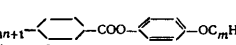
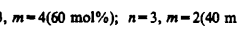
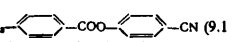
1	2	3	4	5	6	7	8	9	10	11
17	4-n-Alkylphenyl-4-n-alkylbenzoate	 $n=3$, $m=5$		η (20° C)=[0.23] η (25° C)=[0.19]			293		[35] [36]	
		n, m not specified		η (20° C)=0.46, η (0° C)=1.78			332	Δn=0.171	[37]	
18	4-n-Alkoxyphenyl-4-n-alkylbenzoates	 $n=5$, $m=4$	*a*	γ_1 (54.7° C)=0.38	−24.18	7.61			[3]	see Table 7
		$n=4$, $m=2$(45.45 mol%); $n=6$, $m=2$(45.45 mol%);	*b*	γ_1 (25° C)=2.20	−16.7	5.82	320.8	Δn (T= =0.95 T_{NI})= =0.126	[16, 39]	
		 $n=5$, $m=2$(24.0 mol%); $n=3$, $m=4$(16.0 mol%); $n=4$, $m=6$(60.1 mol%)	*a*	η (25° C)=0.38	−14.5	4.05	324.6		[38]	
19	4-Butylphenyl 4-n-alkoxybenzoate	 $n=5$ (60%), $n=7$ (40%)		ν (20° C)=0.85			331		[40]	
		n not specified		η (20° C)=(0.66)			343		[36]	
20	4-n-Pentyloxyphenyl 4-n-octyloxy benzoate			γ_1 (66.3° C)=0.953			357.5	S (339.5 K)= =0.6098 [24]	[7]	$\gamma_1(T)=1.994\cdot 10^9\cdot(1+T/357.65)^{0.2783}\cdot\exp[590.24/(T-214.0)]\sim\sim\rho S^2\exp[B/(T-T_0)]$
21	4-Fluorophenyl 4-butyl-benzoate			η (20° C)=[0.23]			[233]		[41]	
22	4-Cyanophenyl 4-alkylbenzoate	 $n=5$(40 mol%), $n=7$(60 mol%)		γ_1 (25° C)=4.10, $\gamma_1\eta$=5.21 at T=0.92 T_{NI}		6.48	329.4		[5]	$E=\partial\gamma_1/\partial(T^{-1})$ at T=0.92T_{NI} n=7: T_g=214 K [42]; n=2. n=4: T_g=219 K [26]
23	4-Cyano-3-fluoro-phenyl 4-alkyl-benzoate	 $n=3$		η (20° C)=[0.38]			[355]		[43]	$\Delta\varepsilon$=[45.5]
		$n=7$		γ_1 (25° C)=3.3			301.7		[44]	$\Delta\varepsilon$=49.7
24	3-Chloro-4-cyano-phenyl 4-propyl-benzoate			η (20° C)=[1.56]					[45]	$\Delta\varepsilon$=[41]
25	4-Cyano-3-fluoro-phenyl 4-(methoxy-methyl)benzoate			η (20° C)=[0.95]			(300.9)		[45]	$\Delta\varepsilon$=[60]
26	4-Cyano-3-fluoro-phenyl 4-(β-alkoxy-ethoxy)benzoate	 $n=2$		η (20° C)=[0.83]			[281.3]		[43]	$\Delta\varepsilon$=[48.9]
		$n=4$		η (20° C)=[1.08]			[259.9]			$\Delta\varepsilon$=[34.3]
27	3-Chloro-4-cyano-phenyl 4-(β-butoxy-ethoxy)benzoate			η (20° C)=[1.58]			[219.2]		[43]	$\Delta\varepsilon$=[30.8]
28	4-Cyano-3-fluoro-phenyl 4-fluoro-benzoate			η (20° C)=[0.42]			[285.3]		[46]	
29	4-Cyano-3-fluoro-phenyl 4-chloro-benzoate			η (20° C)=[0.68]			[306.3]		[46]	
30	4-(β-Cyanoethyl)-phenyl 4-n-octyl-oxybenzoate			ν (54° C)=0.79			331.2		[47]	
31	4-(Dicyanoethenyl)-phenyl 4-n-heptanoyl-oxybenzoate			ν (80° C)=0.63			375.2		[47]	
32	4-Nitrophenyl 4-n-octyloxybenzoate			γ_1 (69° C)=0.32					[48]	
33	4-Alkylphenyl 4-alkylcyclohexane-1-carboxylates	 $n=m=5$		ν (20° C)=0.13			320		[49]	
		n, m not specified		η (20° C)=(0.18)			313		[36]	
34	4-n-Alkyl-2-fluoro-phenyl 4-alkylcyclo-hexane-1-car-boxylates			η (20° C)=0.22			308		[36]	
35	4-Alkoxyphenyl 4-alkylcyclo-hexane-1-car-boxylates	 $n=4$, $m=2$	*a*	γ_1 (22° C)=1.20	−15.53	4.68	348.7		[50]	see Table 8 n=5, m=1: T_g=197 K [42]
		$n=3$, $m=4$(60 mol%); $n=3$, $m=2$(40 mol%)		γ_1 (25° C)=1.34		4.33	347.3		[5]	$E=\partial\gamma_1/\partial(T^{-1})$ at T= =0.92 T_{NI}
		$n=4$, $m=2$(45.45 mol%); $n=6$, $m=2$(45.45 mol%);	*c*	γ_1 (25° C)=1.34	−6.40	3.45	346.8	Δn (0.95 T_{NI})= =0 073	[16, 39]	
		 $(n+m)_{av}$=5.88 (in mixture)		η (25° C)=0.16					[51]	
		$(n+m)_{av}$=10.00 (in mixture)		η (25° C)=0.51					[51]	
		$n=5$, $m=1$		ν (20° C)=0.17			344		[49]	
		$n=3$, $m=2$		ν (20° C)=0.14			351		[49]	
		$n=4$, $m=2$		ν (20° C)=0.17			348		[49]	

Table 1 (contd.)

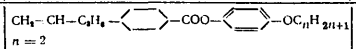
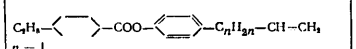
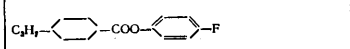
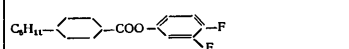
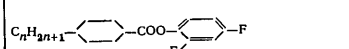
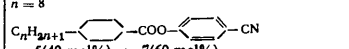
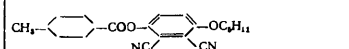
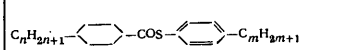
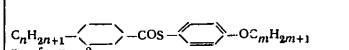
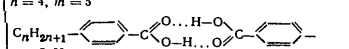
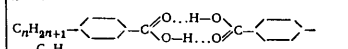
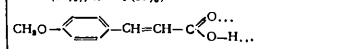
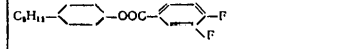
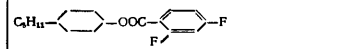
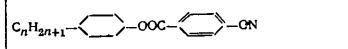
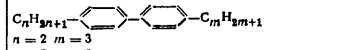
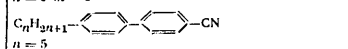
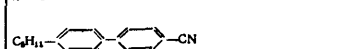
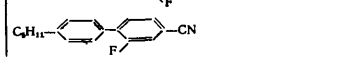
1	2	3	4	5	6	7	8	9	10	11
36	4-Alkoxyphenyl 4-(pent-1-enyl)-cyclohexane-1-carboxylates	 $n=2$ $n=3$	*a* *a*	γ_1 (22° C)=1.20 γ_1 (22° C)=1.08	−17.50 −18.94	5.27 5.67	331.5 318.0	Δn=0.065 Δn=0.061	[48] [48]	
37	4-Alkenylphenyl 4-ethylcyclohexane-1-carboxylates	 $n=1$ $n=2$		η (22° C)=0.225 γ_1 (22° C)=1.25 η (22° C)=0.315			353.2 334.6	Δn=0.062 Δn=0.068	[52] [52]	
38	4-Fluorophenyl 4-propylcyclohexane-1-carboxylate			η (20° C)=0.082					[53]	
39	3,4-Difluorophenyl 4-pentylcyclohexane-1-carboxylate			η (20° C)=[0.194]			(258)		[54]	ΔH_m=3520 K
40	2,4-Difluorophenyl 4-alkylcyclohexane-1-carboxylates	 $n=5$ $n=6$ $n=8$		η (20° C)=[0.17] η (20° C)=[0.22] η (20° C)=[0.22]			(282.0) (284.5) (291.7)		[55]	
41	4-Cyanophenyl 4-alkylcyclohexane-1-carboxylates	 $n=5$(40 mol%), $n=7$(60 mol%)		γ_1 (25° C)=2.69, γ_1/η=6.36 at $T=0.92\,T_{NI}$		4,43	353.4		[5]	$E=\partial\gamma_1/\partial\,(T^{-1})$ at $T=0.92\,T_{NI}$
		$n=5$		ν (50° C)=0.12			352.4		[47]	
42	1-Pentyloxy-2,3-dicyanophenyl 4-methylcyclohexane-1-carboxylate			η (20° C)=[1.5]			(329.4)		[56]	ΔH_m=3830 K
43	4-Alkylphenyl 4-alkylcyclohexane-1-thiolocarboxylate			η (25° C)=(0.37)					[35]	
44	4-Alkoxyphenyl 4-alkylcyclohexane-1-thiolocarboxylate	 $n=5$, $m=2$ $n=4$, $m=5$		η (25° C)=(0.20) η (25° C)=(0.35)					[35] [35]	
45	4-Alkylbenzoic acids	 $n=4$ (50%), $n=6$ (50%)	*b*	γ_1 (72° C)=0.36	−11.9	4.46	381.8	Δn (T=0.95 T_{NI})=0.120	[16, 57]	
		$n=5$	*a*	γ_1 (84° C)=0.53	−8.31	2.74	417.7		[3]	
46	4-Alkylcyclohexane-carboxylic acids	 $n=4$ (50%), $n=6$ (50%)		γ_1 (25° C)=1.85	−3.4	2.97	366.2	Δn (T=0.95 T_{NI})=0.042	[16, 57]	
			c	γ_1 (72° C)=0.33						
47	4-n-Methoxycinnamic acid		*a*	γ_1/ρ(173° C)=0.0956			447		[33]	
48	4-Pentylcyclohexyl 3,4-difluorobenzoate			η (20° C)=[0.70]			(267.2)		[58]	
49	4-Pentylcyclohexyl 2,4-difluorobenzoate			η (20° C)=[0.62]			(289.9)		[58]	
50	4-Alkylcyclohexyl 4-cyanobenzoates			η (25° C)=[0.30]			319.7		[59]	
51	4'-Alkyl-4-n-alkylbiphenyls	 $n=2$ $m=3$ $n=5$ $m=3$ $n=6$ $m=5$		η (20° C)=[0.20] η (20° C)=[0.12] η (20° C)=[0.38]			[284]		[60]	
52	4'-n-Alkyl-4-cyanobiphenyls	 $n=5$ $n=5$(40 mol%), $n=7$(60 mol%)	*b* *a* *a*	γ_1 (25° C)=0.82 γ_1 (25° C)=1.1 γ_1 (25° C)=1.1	−20.0 −17.1	5.84 6.34 5.64	308.2 312.2 312.2	Δn=0.178 Δn (T=307.2 K)=0.185	[16] [61] [16]	see Table 9 T_g=207 K [42]
				γ_1 (25° C)=1.02, γ_1/η=4.35 at $T=0.92\,T_{NI}$		5.58	312.6		[5]	$E=\partial\gamma_1/\partial\,(T^{-1})$ at $T=0.92\,T_{NI}$ $n=2$: T_g=202 K; $n=4$: T_g=206 K [26]
		$n=3$ (30%), $n=5$ (40%), $n=7$ (30%)		η (20° C)=0.34, η (0° C)=1.00			308.2		[62]	
		$n=5$		η (20° C)=[0.34], η (0° C)=[1.38]					[63]	
53	4-Cyano-3-fluoro-4'-n-pentylbiphenyl			η (20° C)=[0.39], η (0° C)=[1.68]			[273.2]		[63]	
54	4-Cyano-2-fluoro-4'-n-pentylbiphenyl			η (20° C)=[0.41], η (0° C)=[2.07]			294.9		[63]	

Table 1 (contd.)

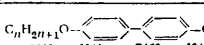
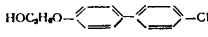
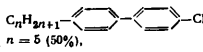
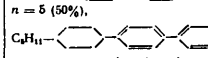
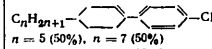
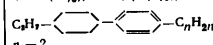
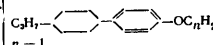
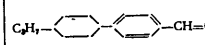
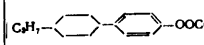
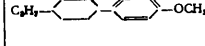
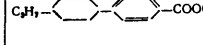
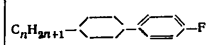
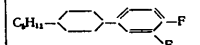
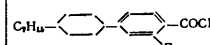
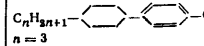
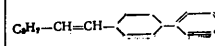
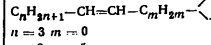
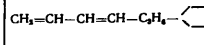
1	2	3	4	5	6	7	8	9	10	11
55	4'-n-Alkoxy-4-cyanobiphenyls	 $n = 5$(40 mol%), $n = 7$(60 mol%)	*b*	γ_1 (31° C)=2.22	—14.6	5.15	345.2	Δn (T = =0.95 T_{NI})= =0.177	[16]	see Table 10
				γ_1 (25° C)=3.71, γ_1/η = 3.97 at T=0.92 T_{NI}		5.71	344.8		[5]	$E=\partial\gamma_1/\partial\,(T^{-1})$ at T= =0.92 T_{NI}
		$n = 5$	*a*	γ_1 (49.3° C)=0.56		6.5	341.6		[3]	
				γ_1 (50° C)=0.27					[64]	$\gamma_1 \simeq -\alpha_2$
				ν (70° C)=0.18					[65]	
		$n = 8$		γ_1 (76° C)=0.20			342.2		[64]	$\gamma_1 \simeq -\alpha_2$
56	4'-(β-Alkoxyethyl)-4-cyanobiphenyl									
		$n = 1$		η (20° C)=[0.54]			[280.7]		[66]	
		$n = 2$		η (20° C)=[0.57]			[265]		[66]	
57	4-Cyano-4'-(3-hydroxypropoxy)-biphenyl			η (20° C)=[1.5]			386.8		[67]	$\Delta\varepsilon$=[18.4]
58	4'-Alkyl-4-biphenylyl-acetonitrile	 $n = 5$ (50%),		ν (20° C)=[0.46]			[379]		[68]	
										
59	1-(*p*-Cyanophenyl)-4-n-alkylcyclo-hexenes	 $n = 5$ (50%), $n = 7$ (50%)		η (25° C)=0.36			332		[69]	
		$n = 2$ (23%), $n = 5$ (38,5%), $n = 7$ (38,5%)		η (25° C)=0.25			321		[69]	
60	4-Alkyl-1-(4-n-propyl-cyclohexyl)-benzene									
		$n = 2$		ν (20° C)=0.04			(203.2)		[70]	T_g=159 K [42]
		$n = 3$		η (20° C)=[0.07]			[217]		[71]	$\mu_{\text{ethylbenzene}}$ = 0.37 D
		$n = 5$		η (20° C)=[0.10]			(241)		[34]	
61	4-Alkoxy-1-(4-n-propyl-cyclohexyl)-benzene									
		$n = 1$		ν (20° C)=0.06			(283.2)		[72]	
		$n = 2$		ν (20° C)=0.07			310.2		[70]	T_g=191 K [42]
				η (20° C)=[0.135]					[71]	
		$n = 4$		ν (20° C)=0.10					[49]	$\mu_{\text{ethoxybenzene}}$ = 1.28 D
62	4-(Prop-1-enyl)-1-(4-n-propylcyclo-hexyl)benzene			η (20° C)=[0.17]			358		[71]	$\mu_{\text{propenylbenzene}}$ = 0.71 D
63	4-(4'-Butanoyloxy-phenyl)-4-n-propyl cyclohexane			ν (20° C)=0.15			303		[49]	$\mu_{\text{phenyl acetate}}$ = 1.52 D
64	1-(3-Hydroxyethoxy)-4-(4-propylcyclo-hexyl)benzene			η (20° C)=[0.91]			354.6		[67]	
65	Methyl *p*-(4-n-propyl-cyclohexyl)-benzoate			η (20° C) = [0.54]			313		[71]	$\mu_{\text{methyl benzoate}}$ = 1.8 D
66	1-(4-n-Alkylcyclo hexyl)-4-fluoro-benzene	 $n = 3$		ν (20° C) = 0.05			(219.2)		[70]	$\mu_{\text{fluorobenzene}}$ = 1.46 D
		$n = 9$		ν (20° C) = [0.034]					[73]	
67	1-(3,4-Difluorophenyl) -4-pentylcyclo-hexane			η (20° C) = [0.07]			[219]		[74]	
68	2-Fluoro-4-(4'-heptyl-cyclohexyl)aceto-phenone			η (20° C) = [0.14]			[271]		[75]	
69	4-Alkyl-1-(4-cyano-phenyl)cyclo-hexane									see Tables 11 and 12
		$n = 3$		ν (20° C) = 0.20			318.2		[70]	T_g = 203 K [26]
		$n = 5$	*c*	γ_1 (25° C) = 0.97	—5.8	2.76	328.2	Δn (T = =0.95 T_{NI})= =0.149	[16]	$\mu_{\text{cyanobenzene}}$ = 4.0 D
70	4-(But-1-enyl)-1-(4-ethoxyphenyl)-cyclohexane			η (22° C) = 0.118			329.7	Δn = 0.085	[52]	
71	4-Alkenyl-1-(4-cyanophenyl)-cyclohexane									see Table 13
		$n = 3$ $m = 0$	*a*	γ_1 (22° C) = 1.34	—16.62	4.99	331.7	Δn = 0.116	[76]	
		$n = 0$ $m = 5$	*a*	γ_1 (22° C) = 0.99	—14.65	4.32	305.4	Δn = 0.086	[50]	
		$n = 0$ $m = 3$		γ_1 (22° C) = [0.20]		[7.84]	325.7	Δn (T = =315.7) = = [0.074]		ΔH_m = 3240 K, K_T = 2.3· ·10^{-12} H, T= = 315.7 K
72	1-(4-Cyanophenyl)-4-(hepta-4,6-dienyl)-cyclo-hexane			γ_1 (22° C) = [0.16]		[13.90]	[271.7]	Δn (T = = 261.7) = = [0.080]	[50]	ΔH_m = 3370 K, K_T = 2.5· ·10^{-12} H, T = = 261.7 K

Table 1 (contd.)

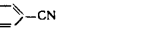
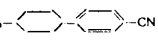
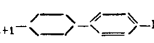
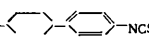
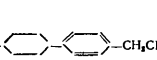
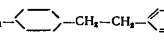
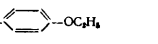
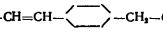
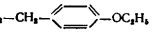
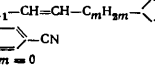
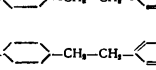
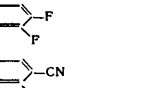
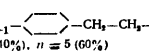
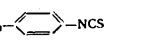
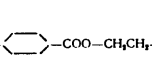
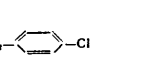
1	2	3	4	5	6	7	8	9	10	
73	4-Alkoxymethyl-1-(4-cyanophenyl)-cyclohexane	$C_nH_{2n+1}OCH_2$–  –CN $n = 1$ $n = 1$ (50%), $n = 2$ (25%), $n = 6$ (25%)		η (20° C) = [0.34] η (20° C) = [0.14]			302.4 [304]		[77]	there is a difference between the values of η due to the liquid crystal matrix
74	1-(4-Cyanophenyl)-4-(fluoropentyl)-cyclohexane	FC_5H_{10}–  –CN		γ_1 (22° C) = [0.92]		[7.61]	(307.0)	Δn (T = = 297.0) = = 0.078	[50]	$\Delta H_m = 3180$ K, $K_T = 3.3 \cdot 10^{-12}$ H, T = = 297.0 K
75	4-Alkyl-1-(4-isothiocyanatophenyl)-cyclohexane	C_nH_{2n+1}–  –NCS $n = 6$	a	η (20° C) = 0.128 γ_1 (22° C) = 0.83, η (22° C) = 0.162	−14.8	4.30	313 317.2	$\Delta n = 0.161$	[34] [78]	$\Delta\varepsilon = 8.9$ $\gamma_1/K_T = 9.1 \cdot 10^{-8}$ s m^{-2} $t_{off} = 41$ ms, $T = 22°$ C
		$n = 3$ (42.9%), $n = 6$ (57.1%) $n = 2$ (44.9%), $n = 6$ (55.1%)		η (20° C) = 0.21 η (20° C) = 0.135 η (20° C) = 0.21					[79] [80] [80]	$\Delta\varepsilon = 7.0$
76	4-Alkenyl-(4-isothiocyanatophenyl)-cyclohexane	C_nH_{2n+1}–CH=CH–C_mH_{2m}–  –NCS $n = 2$, $m = 2$	a	γ_1 (22° C) = 1.00, η (22° C) = 0.173	−16.33	4.82	310.4		[78]	$\gamma_1/K_T = 9.8 \cdot 10^{-8}$ s m^{-2} $t_{off} = 41$ ms, $T = 22°$ C
				γ_1 (22° C) = 0.97			309.1		[50]	$\gamma_1/K_T = 10.4 \cdot 10^{-8}$ s m^{-2} $T = 22°$ C
		$n = 2$, $m = 0$ (40%); $n = 4$, $m = 0$ (60%) $n = 0$, $m = 2$	a	γ_1 (22° C) = 0.50 γ_1 (22° C) = 0.51		5.40	296.1 316.2		[78] [50]	$\gamma_1/K_T = 5.3 \cdot 10^{-8}$ s m^{-2} $T = 22°$ C
		$n = 0$, $m = 4$		γ_1 (22° C) = 0.95			318.7		[50]	γ_1/K_T (22° C) = = 10.0 $\cdot 10^{-8}$ s m^{-2}
77	4-(4-Pentylcyclohexyl)-phenylacetonitrile	C_5H_{11}–  –CH_2CN		ν (20° C) = [0.52]			[297]		[68]	
78	2-(4-Ethoxyphenyl)-1-(4-n-pentylcyclohexyl)ethane	C_5H_{11}–  –CH_2–CH_2–  –OC_2H_5	a	γ_1 (22° C) = 0.79 η (22° C) = 0.120	−11.61	3.39	319.8	$\Delta n = 0.072$	[52]	
79	2-(4-Ethoxyphenyl)-1-[4-(pent-1-enyl)-cyclohexyl]-ethane	C_3H_7–CH=CH–  –CH_2–CH_2–  –OC_2H_5		η (22° C) = 0.118			317.1	$\Delta n = 0.087$	[52]	
80	1-(4-n-Alkylcyclohexyl)-2-(4-cyanophenyl)ethanes	C_nH_{2n+1}––CH_2–CH_2––CN $n = 5$	a	γ_1 (22° C) = 1.80, η (22° C) = 0.221		4.87	325.7		[76]	$\gamma_1/K_T = 1.22 \cdot 10^{-10}$ s m^{-2} $t_{off} = 43$ ms, $T = 22°$ C
		$n = 3$	a	η (20° C) = (0.195), η (0° C) = (0.44)		3.27	317.7		[81]	
		$n = 3$ (30%), $n = 5$ (40%), $n = 7$ (30%)		η (20° C) = 0.25, η (0° C) = 0.86			322.2		[65]	
81	1-(4-n-Alkenylcyclohexyl)-2-(4'-cyanophenyl)-ethanes	C_nH_{2n+1}–CH=CH–C_mH_{2m}–  –CH_2–CH_2––CN $n = 3$, $m = 0$	a	γ_1 (22° C) = 1.70, η (22° C) = 0.228	−15.60	4.76	319.9	Δn (T = = 309.9) = = 0.118	[76]	$\gamma_1/K_T = 1.21 \cdot 10^{-10}$ s m^{-2} $t_{off} = 38$ ms, $T = 22°$ C
		$n = 1$, $m = 0$ (60%); $n = 0$, $m = 2$ (40%)		γ_1 (22° C) = 2.15	−16.15	4.99	329.9	Δn (T = = 319.9) = = 0.122	[76]	$\gamma_1/K_T = 1.11 \cdot 10^{-10}$ s m^{-2} $t_{off} = 29$ ms, $T = 22°$ C
		$n = 0$, $m = 2$ (40%), CH_3–CH=CH–C_6H_4–  –CN (60%)		γ_1 (22° C) = 1.80			333.5	Δn (T = = 323.5) = = 0.125	[76]	$\gamma_1/K_T = 0.92 \cdot 10^{-10}$ s m^{-2} $t_{off} = 27$ ms, $T = 22°$ C
82	1-(3,4-Difluorophenyl)-2-(4-propylcyclohexyl)ethane	C_3H_7–  –CH_2–CH_2–  –F F		η (20° C) < [0.08]			[280.7]		[53]	
83	1-(4-Cyano-3-fluorophenyl)-2-(4-propylcyclohexyl)-ethane	C_3H_7–  –CH_2–CH_2–  –CN F		η (20° C) = [0.251]			(280.1)		[53]	$\Delta H_m = 1970$ K, $\Delta\varepsilon = 18.9$
84	1-(4-n-Alkylcyclohexyl)-2-(4-isothiocyanotophenyl)-ethanes	C_nH_{2n+1}–  –CH_2–CH_2–  –NCS $n = 3$ (40%), $n = 5$ (60%)	a	γ_1 (22° C) = 1.05, η (22° C) = 0.115		4.82	317.6	$\Delta n = 0.115$	[78]	$\gamma_1/K_T = 6.9 \cdot 10^{-8}$ s m^{-2} $t_{off} = 21$ ms, $T = 22°$ C
85	β-(4-Chlorophenyl)-ethyl 4-heptylcyclohexane-1-carboxylate	C_7H_{15}––COO–CH_2CH_2––Cl		η (20° C) = [0.11]			(241)		[82]	

Table 1 (contd.)

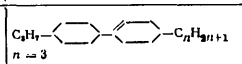
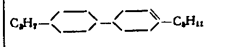
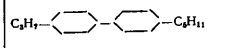
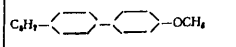
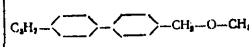
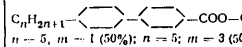
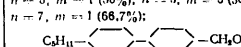
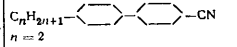
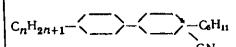
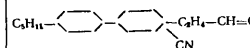
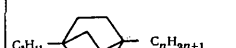
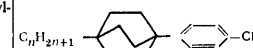
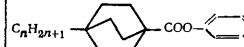
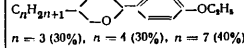
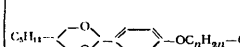
1	2	3	4	5	6	7	8	9	10	11
86	4-Alkyl-1-(4-propylcyclohexyl)cyclohex-1-ene			η (20° C) = [0.054] η (20° C) = [0.079] η (20° C) = [0.093]			285 300 312		[34]	
87	4-Pentyl-1-(4-propylcyclohexyl)cyclohex-3-ene			η (20° C) = [0.079]			295		[34]	
88	4-Pentyl-1-(4-propylcyclohexyl)-cyclohexane			η (20° C) = [0.065]			370		[34]	
89	4-Methoxy-1-(4-n-propylcyclohexyl)cyclohexane			ν (20° C) = (0.07)			290		[72]	
90	1-(4-Methoxymethylcyclohexyl)-4-propylcyclohexane			η (20° C) = [0.05]			324.2		[83]	
91	Alkyl 4-(4-n-alkylcyclohexyl)-cyclohexane-1-carboxylate	 $n = 5$, $m = 1$ (50%); $n = 5$; $m = 3$ (50%) $n = 7$, $m = 1$ (66.7%); 		η (20° C) = [0.14] η (20° C) = [0.07]			351 351		[84] [84]	
92	4-e-(4-Alkylcyclohexyl)-1-e-cyanocyclohexane	 $n = 2$ $n = 3$ $n = 4$ $n = 5$ $n = 7$		ν (20° C) = [0.65] ν (20° C) = [0.63] ν (20° C) = [0.68] ν (20° C) = [0.65] ν (20° C) = [0.75]			322 353 352 358 355		[49] [49, 40] [49] [49] [49]	
93	4-e-(4-Alkylcyclohexyl)-1-a-cyano-1-e-pentylcyclohexane			η (20° C) = 0.70			338		[40]	
94	1-e-(But-2-enyl)-1-a-cyano-4-e-(4-pentylcyclohexyl)-cyclohexane			γ_1 (22° C) = [1.58] η (22° C) = [0.50]		[6.62]	[325.8]		[52]	
95	1-Alkyl-4-pentylbicyclo[2.2.2]-octane									
		$n = 5$		η (20° C) = [0.077], η (0°) = [0.202]			[237]		[85]	
		$n = 7$		η (20° C) = [0.084], η (0°) = [0.222]			[243]		[85]	
96	1-Alkyl-4-cyanophenylbicyclo[2.2.2]-octanes									
		$n = 5$	a	γ_1 (60° C) = 0.48	−14.2	4,48	374.4		[3]	
		$n = 3$(40 mol%), $n = 5$(60 mol%)	c	γ_1 (25° C) = 2.96 γ_1 ($T = 0.95T_{NI}$) = =0.21	−11.3	3,60	369.7	Δn ($T = 0.95T_{NI}$) = =0.118	[16]	a more accurate fitting formula is $\ln[\gamma_1/(\Delta n)^2] = -6.40 + 0.743/(T - 198.8)$
		$n = 5$(40 mol%), $n = 7$(60 mol%) $n = 3$ (30%), $n = 5$ (40%), $n = 7$ (30%)	a	γ_1 (25° C) = (3.6) η (20° C) = 0.96		4,94	367.7 363.2		[61] [62]	
97	4-Alkylphenyl 4-alkylbicyclo[2.2.2]-octane-1-carboxylates		a	η (20° C) = (0.34)		1,73 $T = 20°$ C	333		[36]	
98	4-Alkoxyphenyl 4-alkylbicyclo[2.2.2]-octane-1-carboxylates		a	η (20° C) = (0.64)		1,33 $T = 20°$ C	368		[36]	
99	4-Alkyl-2-fluorophenyl 4-alkylbicyclo[2.2.2]-octane-1-carboxylates		a	η (20° C) = (0.44)		2,08 $T = 20°$ C	333		[36]	
100	5-Alkyl-2-(4-ethoxyphenyl)-1,3-dioxanes	 $n = 3$ (30%), $n = 4$ (30%), $n = 7$ (40%)		η (20° C) = 0.287			318		[27]	
101	2-(4-Butoxyphenyl)-5-(pent-1-en-3-yl)-1,3-dioxane		a	γ_1 (22° C) = [0.70]		[8.52]	308.4		[52]	
102	2-(4-Alkenyloxyphenyl)-5-pentyl-1,3-dioxanes	 $n = 1$ $n = 2$	a	γ_1 (22° C) = [1.30] γ_1 (22° C) = 1.18		[7.66]	295.2 274.1		[52] [52]	

Table 1 (contd.)

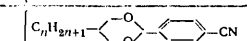
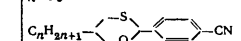
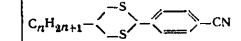
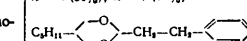
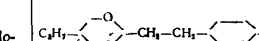
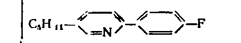
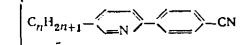
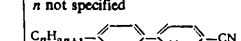
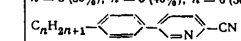
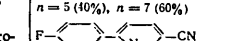
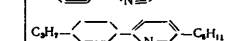
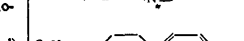
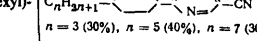
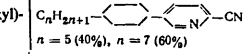
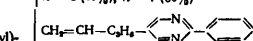
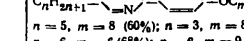
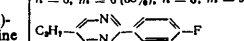
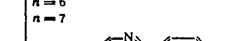
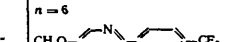
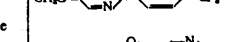
1	2	3	4	5	6	7	8	9	10	11
103	5-Alkyl-2-(4-cyanophenyl)-1,3-dioxanes									
		n = 5(40 mol%), n = 7(60 mol%)		γ_1 (25° C) = 1.34, γ_1/η = 5.59 at $T = 0.92T_{NI}$		3.10	323.0		[5]	$E = \partial\gamma_1/\partial(T^{-1})$ at $T = 0.92T_{NI}$
		n = 3 (30%), n = 5 (40%), n = 7 (30%)		η (20° C) = 0.41, η (0° C) = 1.48			318.2		[62]	
		n = 5		η (20° C) = [0.46]			(325)		[86]	
104	5-Alkyl-2-(4-cyanophenyl)-1,3-oxathianes									
		n = 4 (50%), n = 7 (50%)		η (20° C) = [0.54]			(288), n = 7		[87]	ΔH_m = 3650 K
105	5-Alkyl-2-(4-cyanophenyl)-1,3-dithiane									
		n = 4 (50%), n = 7 (50%)		η (20° C) = [0.74]					[88]	
106	5-Alkyl-2-[2-(4-cyanophenyl)ethyl]-1,3-dioxane			η (20° C) = [0.55]			(292)		[86]	
107	5-Propyl-2-[2-(4-propylcyclohexyl)ethyl]-1,3-dioxane			η (20° C) = [0.27]				Δn = 0.033	[89]	
108	5-(4-Fluorophenyl)-5-pentylpyridine			η (20° C) = [0.126]			[228.5]		[90]	
109	5-Alkyl-2-(4-cyanophenyl)pyridines									
		n = 5	b	γ_1 (25° C) = 1.28, γ_1 (T = = 0.95T_{NI}) = 1.03	−11.6	3.50	316.7	Δn (T = = 0.95T_{NI}) = = 0.176	[91]	
		n = 6	b	γ_1 (25° C) = 0.98, γ_1 (T = = 0.95T_{NI}) = 2.34	−18.9	5.75	305.7	Δn (T = = 0.95T_{NI}) = = 0.163	[91]	
		n = 7	b	γ_1 (25° C) = 2.15, γ_1 (T = = 0.95T_{NI}) = 1.47	−14.7	4.60	320.2	Δn (T = = 0.95T_{NI}) = = 0.272	[91]	
		n = 5(40 mol%), n = 7(60 mol%)	b	γ_1 (25° C) = 1.84	−16.0	5.40	317.4	Δn (T = = 0.95T_{NI}) = = 0.175	[16]	
		n not specified	a	γ_1 (25° C) = 1.46		6.38	317.4		[61]	
				η (20° C) = 0.496			314	Δn = 0.211	[34]	$\Delta\varepsilon$ = 22.9
110	2-(4-Alkylphenyl)-5-cyanopyridines									
		n = 3 (30%), n = 5 (40%), n = 6 (30%)	a	γ_1 (25° C) = 3.50		5.86	335.9		[92]	$\Delta\varepsilon$ = 7.3
111	5-(4-Alkylphenyl)-2-cyanopyridines									
		n = 5 (40%), n = 7 (60%)	a	γ_1 (25° C) = 2.20		5.74	322.4		[92]	$\Delta\varepsilon$ = 11.3
112	5-Cyano-2-(4-fluorophenyl)pyridine			η (20° C) = [0.25]			[313]		[90]	
113	5-n-Pentyl-2-(4-n-propylcyclohexyl)pyridine			η (20° C) = [0.104]			180		[90]	
114	2-(4-Alkylcyclohexyl)-5-cyanopyridines									
		n = 3 (30%), n = 5 (40%), n = 7 (30%)	a	γ_1 (25° C) = 1.40		5.63	330.5		[92]	$\Delta\varepsilon$ = 3.3
115	5-(4-Alkylcyclohexyl)-2-cyanopyridines									
		n = 5 (40%), n = 7 (60%)	a	γ_1 (25° C) = 1.78		5.57	331.2		[92]	$\Delta\varepsilon$ = 12.4
116	5-(Pent-4-enyl)-2-(4-pentylphenyl)-pyrimidine			η (22° C) = [0.30]			[243.8]		[52]	
117	5-Alkyl-2-(4-alkoxyphenyl)-pyrimidines									
		n = 5, m = 8 (60%); n = 3, m = 8 (40%)		η (20° C) = 0.40			338		[40]	
		n = 6, m = 6 (68%); n = 6, m = 9 (32%)		η (20° C) = 0.688			333		[27]	
118	2-(4-Fluorophenyl)-5-propylpyrimidine			η (20° C) = [0.087]			325.9		[93]	
119	5-Alkyl-2-(3,4-difluorophenyl)-pyrimidines								[94]	
		n = 2		η (20° C) = [0.138]						
		n = 3		η (20° C) = [0.158]						
		n = 4		η (20° C) = [0.174]						
		n = 5		η (20° C) = [0.185]						
		n = 6		η (20° C) = [0.196]						
		n = 7		η (20° C) = [0.301]						
120	5-Alkyl-2-(4-trifluoromethylphenyl)-pyrimidine								[95]	
		n = 2		η (20° C) = [0.11]				Δn = [0.07]		$\Delta\varepsilon$ = [37]
		n = 3		η (20° C) = [0.15]				Δn = [0.08]		$\Delta\varepsilon$ = [40]
		n = 4		η (20° C) = [0.24]			(305)	Δn = [0.07]		$\Delta\varepsilon$ = [31]
		n = 5		η (20° C) = [0.24]			(314)	Δn = [0.08]		$\Delta\varepsilon$ = [36]
		n = 6		η (20° C) = [0.29]			(303)	Δn = [0.07]		$\Delta\varepsilon$ = [25]
121	5-Methoxy-2-(4-trifluoromethylphenyl)pyrimidine			η (20° C) = [0.41]				Δn = [0.06]	[95]	$\Delta\varepsilon$ = [35]
122	5-n-Alkyl-2-(2-n-pentyl-5-pyrimidinyl)-1,3-dioxanes									
		n = 3		η (20° C) = [0.13]			(338)	Δn = [0.03]	[96]	$\Delta\varepsilon$ = [13]
		n = 5		η (20° C) = [0.13]			370	Δn = [0.03]	[96]	$\Delta\varepsilon$ = [8]

Table 1 (contd.)

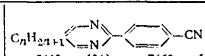
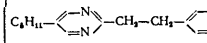
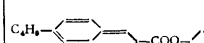
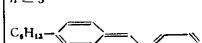
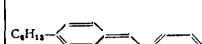
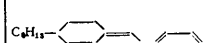
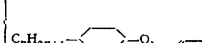
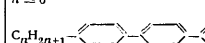
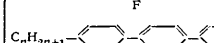
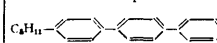
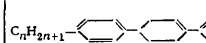
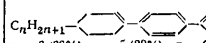
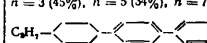
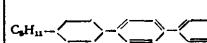
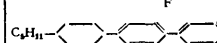
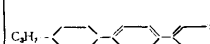
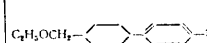
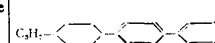
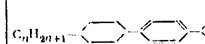
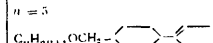
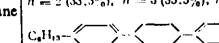
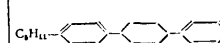
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123	5-Alkyl-2-(4-cyanophenyl)-pyrimidines									
		n = 5(40 mol%), n = 7(60 mol%)	*b*	γ_1 (25° C) = 1.91	−14.9	5.11	324.4	Δn (T = =0.95T_{NI})= = 0.177	[16]	T_g = 215 K [42]
			b	γ_1 (25° C) = 2.01		5.64	324.2		[5]	$E = \partial\gamma_1/\partial\,(T^{-1})$ at T= =0.92T_{NI}
		n = 7		η (25° C) = [0.50]			(324)		[86]	n = 5: T_g = = 214 K [26],
		n not specified		η (20° C) = 0.528			319	Δn = 0.195	[34]	$\Delta\varepsilon$ = 23.6
124	2-[2-(4-Cyanophenyl)-ethyl]-5-pentyl-pyrimidine			η (20° C) = [0.56]			[262]		[86]	
125	4-n-Alkylcyclo-hexyl 6-n-butyl-2-naph-thoates									
		n = 3	*a*	η (25° C) = (1.60)	−15.67	4.81	349.2		[97]	
		n = 4	*a*	η (25° C) = (1.85)	−15.73	4.87	342.2			
		n = 5	*a*	η (25° C) = (1.80)	−15.96	4.93	350.2			
126	2-(4-Cyanophenyl)-6-n-hexylnaph-thalene		*a*	η (20° C) = (1.76), η (70° C) = 0.15, η (80° C) = 0.11		2.05	390.2		[98]	
127	2-(4-Cyanophenyl)-6-n-hexyl-5,6-dihy-dronaphthalene		*a*	η (20° C) = (4.10), η (70° C) = 0.285		2.24	352.9		[98]	
128	2-(4-Cyanophenyl)-6-n-hexyl-5,6,7,8-tetrahydro-naphthalene		*a*	η (80° C) = 0.166			375.6		[98]	
129	6-Alkyl-2-hexyl-phenyl-*trans*-1,3-dioxadecalins									
		n = 5		η (20° C) = [1.26]			367.2		[99]	ΔH_m = 4909 K
		n = 6		η (20° C) = [1.27]			361.3			ΔH_m = 3983 K
130	4'-Alkyl-1-(4-alkyl-phenyl)-2-fluoro-biphenyl			η (20° C) = [0.40], η (0° C) = [1.15]			414		[100]	
131	4'-Alkoxy-1-(4-alkyl-phenyl)-2-fluoro-biphenyl			η (20° C) = [0.75], η (0° C) = [3.00]			453		[100]	
132	4-Cyano-4''-pentyl-terphenyl			η (20° C) = [0.82]			[546]		[101]	
133	1-[4-(4-Alkylphenyl)-cyclohex-1-enyl]-4-fluoro-benzene						(347)		[102]	
		n = 3 (50%), n = 4 (50%)		η (20° C) = [0.16]			[317]			
134	4-n-Alkyl-1-(4'-cyano-4-biphenylyl)-cyclohexenes									
		n = 3 (38%), n = 5 (29%), n = 6 (16%), n = 7 (12%)		η (25° C) = 0.35			333		[68]	
		n = 3 (45%), n = 5 (34%), n = 7 (16%), n = 6 (5.3%)		η (25° C) = 0.35			334		[68]	
135	4-Ethyl-4'-(4-n-propyl-cyclohexyl)-biphenyl			ν (20° C) = (0.20)			437.2		[70]	
				η (20° C) = (0.336)			438		[27]	
136	4-Ethyl-2'-fluoro-4'-(4-pentylcyclo-hexyl)biphenyl			ν (20° C) = (0.27)			380.2		[70]	
137	4-Ethyl-2,2'-difluoro-4'-(4-pentyl-cyclohexyl)-biphenyl			ν (20° C) = (0.42)			315.2		[70]	
138	4-Methoxy-4'-(4-n-propylcyclo-hexyl)biphenyl			ν (20° C) = (0.70)			438.2		[70]	
139	4-Ethoxymethyl-1-(4'-methyl-4-bi-phenylyl)cyclohexane			η (20° C) = (0.43)			412.7		[103]	
140	4-Fluoro-4'-(4-n-propylcyclo-hexyl)biphenyl			ν (20° C) = (0.24)			426.2		[70]	
141	4'-(4-n-Alkylcyclo-hexyl)-4-cyano-biphenyl									
		n = 3		ν (20° C) = (0.90)			495.2		[70]	
		n = 5		η (20° C) = [1.08]			[563]		[104]	
142	4-Alkoxymethyl-1-(4'-cyano-4-bi-phenylyl)cyclohexane									
		n = 2 (33.3%), n = 3 (33.3%), n = 5 (33.3%)		η (20° C) = [0.55]			453		[76]	
143	1-(4-Fluorophenyl)-4-(4-hexylphenyl)-cyclohexane			η (20° C) = [0.19]			[316]		[102]	
144	1-(4-Cyanophenyl)-4-(4-pentylphenyl)-cyclohexane			η (20° C) = [0.48]			[474]		[104]	

Table 1 (contd.)

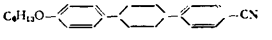
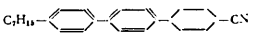
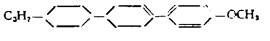
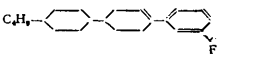
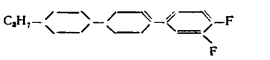
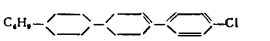
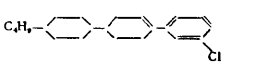
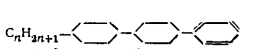
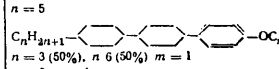
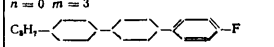
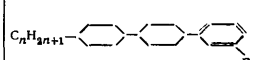
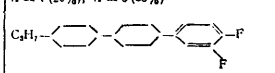
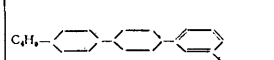
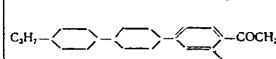
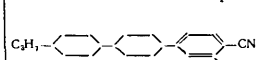
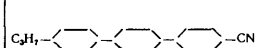
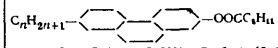
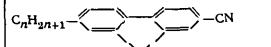
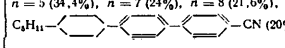
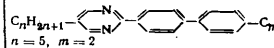
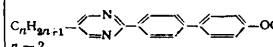
1	2	3	4	5	6	7	8	9	10	11
145	1-(4-Cyanophenyl)-4-(4-hexyloxyphenyl)cyclohexane			η (20° C) = [0.25]			[477]		[104]	
146	4-(4-Cyanocyclohexyl)-4′-n-heptylbiphenyl			η (20° C) = [0.26]			[522]		[104]	
147	1-[4-(4-Propylcyclohexyl)cyclohex-1-enyl]-4-methoxybenzene			η (20° C) = [0.23]			475.4		[105]	
148	1-[4-(4-Butylcyclohexyl)cyclohex-1-enyl]-3-fluorobenzene			η (20° C) = [0.23]			364		[102]	
149	1,2-Difluoro-4-[4-(4-propylcyclohexyl)cyclohex-1-enyl]benzene			η (20° C) = [0.27]			388.2		[102]	
150	1-[4-(4-Butylcyclohexyl)cyclohex-1-enyl]-4-chlorobenzene			η (20° C) = [0.29]			456.6		[102]	
151	1-[4-(4-Butylcyclohexyl)cyclohex-1-enyl]-3-chlorobenzene			η (20° C) = [0.47]			340.7		[102]	
152	[4-(4-Alkylcyclohexyl)cyclohexyl]-benzene	 $n = 5$ (50%), $n = 7$ (50%) $n = 5$		η (20° C) = [0.23] η (20° C) = [0.23]			379.3 385.0		[105] [105]	
153	4-Alkoxy-1-[4-(4-alkylcyclohexyl)cyclohexyl]-benzene	 $n = 3$ (50%), n 6 (50%) $m = 1$ $n = 0$ $m = 1$ $n = 0$ $m = 3$		η (20° C) = [0.23] η (20° C) = [0.30] η (20° C) = [0.38]			479		[105] [105] [105]	
154	4-Fluoro-1-[4-(4-propylcyclohexyl)cyclohexyl]-benzene			η (20° C) = [0.11]			431.7		[102]	
155	1-[4′-(4-Alkylcyclohexyl)cyclohexyl]-3-fluorobenzene	 $n = 4$ (20%), $n = 6$ (80%)		η (20° C) = [0.23]			360.8		[102]	
156	1,2-Difluoro-4-[4-(4-propylcyclohexyl)cyclohexyl]-benzene			η (20° C) = [0.23] η (20° C) = [0.21]			397.3 391		[102] [53]	
157	1-[4-(4-Butylcyclohexyl)cyclohexyl]-4-chlorobenzene			η (20° C) = [0.30]			455.2		[102]	
158	1-[4-(4-Butylcyclohexyl)cyclohexyl]-3-chlorobenzene			η (20° C) = [0.69]			313		[102]	
159	2-Fluoro-4-[4-(4-propylcyclohexyl)cyclohexyl]-acetophenone			η (20° C) = [0.36]					[74]	
160	4-Cyano-3-fluoro-1-[4-(4-propylcyclohexyl)cyclohexyl]-benzene			η (20° C) = [0.547] η (20° C) = [0.44]			480.8		[53] [74]	
161	4-Cyano-4″-propyl-*p*-tercyclohexyl			η (20° C) = [1.00]			[488]		[106]	
162	7α-Alkyl-2β-hexanoyloxyperhydrophenanthrenes	 $n = 4$ (18%), 5 (17%), 6 (23%), 7 (20%), 10 (22%)		ν (20° C) = 0.41			348	$\Delta n = 0.05$	[107]	$\Delta\varepsilon = -0.5$
163	2-Alkyl-7-cyanofluorene	 $n = 5$ (34.4%), $n = 7$ (24%), $n = 8$ (21.6%),  (20%)		ν (20° C) = 3.25			335—340	$\Delta n = 0.208$	[108]	
164	5-Alkyl-2-(4′-alkyl-4-biphenylyl)-pyrimidines	 $n = 5$, $m = 2$ $n = 6$, $m = 2$ $n = 2$, $m = 3$ $n = 5$, $m = 5$ $n = 3$, $m = 7$		η (20° C) = [0.32] η (20° C) = [0.27] η (20° C) = [0.28] η (20° C) = [0.35] η (20° C) = [0.29]			440 428 452 446 441	$\Delta n = [0.27]$ $\Delta n = [0.30]$ $\Delta n = [0.30]$	[101]	$\Delta\varepsilon = [9.2]$ $\Delta\varepsilon = [7.9]$ $\Delta\varepsilon = [11.2]$
165	5-Alkyl-2-(4′-propoxy-4-biphenylyl)-pyrimidines	 $n = 2$ $n = 6$ $n = 7$		η (20° C) = [0.56] η (20° C) = [0.54] η (20° C) = [0.47]			478 462 464		[101]	

Table 1 (contd.)

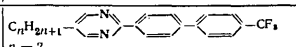
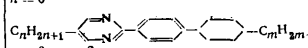
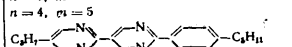
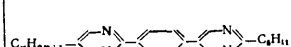
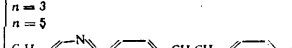
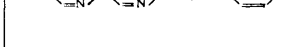
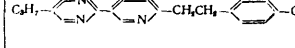
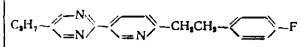
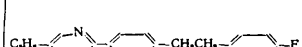
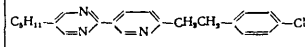
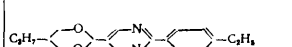
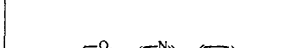
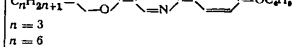
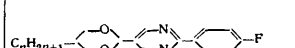
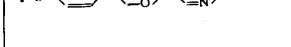
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166	5-Alkyl-2-[4'-trifluoromethyl-4-biphenylyl]-pyrimidines								[95]	
		$n = 2$		η (20° C) = [0.33]			527	Δn = [0.20]		$\Delta\varepsilon$ = [43]
		$n = 3$		η (20° C) = [0.38]			513	Δn = [0.22]		$\Delta\varepsilon$ = [41]
		$n = 4$		η (20° C) = [0.43]			503	Δn = [0.19]		$\Delta\varepsilon$ = [32]
		$n = 5$		η (20° C) = [0.40]			501	Δn = [0.20]		$\Delta\varepsilon$ = [34]
		$n = 6$		η (20° C) = [0.52]			495	Δn = [0.19]		$\Delta\varepsilon$ = [29]
167	5-Alkyl-2-[4-(4-alkylcyclohexyl)-phenyl]-pyrimidines								[101]	
		$n = 3$, $m = 2$		η (20° C) = [0.30]			446	Δn = [0.19]		$\Delta\varepsilon$ = [6.5]
		$n = 4$, $m = 2$		η (20° C) = [0.48]			426			
		$n = 5$, $m = 2$		η (20° C) = [0.26]			435			
		$n = 2$, $m = 3$		η (20° C) = [0.27]			457	Δn = [0.21]		$\Delta\varepsilon$ = [6.5]
		$n = 6$, $m = 3$		η (20° C) = [0.41]			443			
		$n = 5$, $m = 4$		η (20° C) = [0.30]			446			
		$n = 4$, $m = 5$		η (20° C) = [0.33]			448			
168	2(n-Pentylphenyl)-5'-propyl-5,2'-bipyrimidine			η (20° C) = [0.57]			[488]	Δn = [0.30]	[109]	$\Delta\varepsilon$ = [32]
169	5-Alkyl-2-[4-(2-pentyl-5-pyrimidinyl)-phenyl]-pyrimidine								[110]	
		$n = 3$		η (20° C) = [1.16]			[546]		[110]	
		$n = 5$		η (20° C) = [3.0]			[546]	Δn = [0.27]	[110]	$\Delta\varepsilon$ = [27]
170	2-[β-(4-Ethylphenyl)-ethyl]-5-(5-propyl-2-pyrimidinyl)-pyridine			η (20° C) = [0.24]			[371]	Δn = [0.20]	[111]	$\Delta\varepsilon$ = [16]
171	2-[β-(4-Methoxyphenyl)ethyl]-5-(5-propyl-2-pyrimidinyl)pyridine			η (20° C) = [0.31]			[423]	Δn = [0.25]	[111]	$\Delta\varepsilon$ = [20]
172	2-[β-(4-Fluorophenyl)-ethyl]-5-(5-propyl-2-pyrimidinyl)-pyridine			η (20° C) = [0.38]			[355]	Δn = [0.19]	[111]	$\Delta\varepsilon$ = [46]
173	2-[β-(3,4-Difluorophenyl)ethyl]-5-(5-propyl-2-pyrimidinyl)-pyridine			η (20° C) = [0.48]			[333]	Δn = [0.19]	[111]	$\Delta\varepsilon$ = [34]
174	2-[β-(4-Cyanophenyl)-ethyl]-5-(5-pentyl-2-pyrimidinyl)-pyridine			η (20° C) = [1.23]			[449]	Δn = [0.33]	[111]	$\Delta\varepsilon$ = [61]
175	2-[2-(4-Ethylphenyl)-5-pyrimidinyl]-5-n-propyl-1,3-dioxane			η (20° C) = [0.30]			458	Δn = [0.20]	[95]	$\Delta\varepsilon$ = [15]
176	5-n-Alkyl-2-[2-(4-butoxyphenyl)-5-pyrimidinyl]-1,3-dioxane									
		$n = 3$		η (20° C) = [0.34]			491	Δn = [0.19]	[95]	$\Delta\varepsilon$ = [21]
		$n = 6$		η (20° C) = [0.33]			476	Δn = [0.16]	[95]	$\Delta\varepsilon$ = [17]
177	2-[2-(4-Fluorophenyl)-5-pyrimidinyl]-5-n-propyl-1,3-dioxane			η (20° C) = [0.20]			446	Δn = [0.12]	[95]	$\Delta\varepsilon$ = [23]
178	5-n-Alkyl-2-[2-(3,4-difluorophenyl)-5-pyrimidinyl]-1,3-dioxane									
		$n = 3$		η (20° C) = [0.38]			425	Δn = [0.23]	[95]	$\Delta\varepsilon$ = [28]
		$n = 5$		η (20° C) = [0.40]			419	Δn = [0.22]	[95]	$\Delta\varepsilon$ = [26]
179	2-[2-(4-Pentylcyclohexyl)-5-pyrimidinyl]-5-n-propyl-1,3-dioxane			η (20° C) = [0.27]			438	Δn = [0.12]	[95]	$\Delta\varepsilon$ = [21]
180	5-(4-n-Octylphenyl)-2-(2-pentyl-5-pyrimidinyl)-1,3-dioxane			η (20° C) = [0.43]			429	Δn = [0.10]	[95]	$\Delta\varepsilon$ = [16]
181	5-(4-n-Pentylcyclohexyl)-2-(2-pentyl-5-pyrimidinyl)-1,3-dioxane			η (20° C) = [0.28]			390	Δn = [0.08]	[95]	$\Delta\varepsilon$ = [18]
182	5-(1-Butyl-4-piperidinyl)-2-(4-cyanophenyl)-1,3-dioxane			η (25° C) = (1.54)			442		[112]	$\Delta\varepsilon$ (82° C) = = +12
183	1-[5-(n-Alkylphenyl)-2-pyrimidinyl]-4-cyanocyclohexane									
		$n = 5$ (40%), $n = 7$ (60%)	*a*	η (60° C) = 0.840		[4.50]	438		[113]	T_m = 336 K, $\Delta\varepsilon$ (60° C) = = 19.80

Table 1 (contd.)

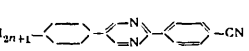
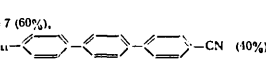
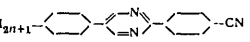
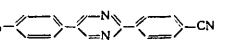
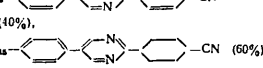
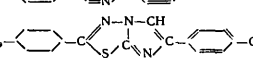
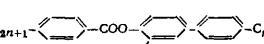
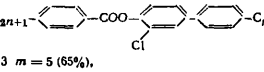
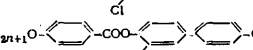
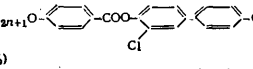
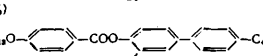
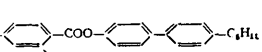
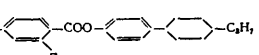
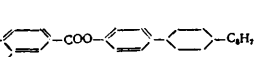
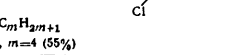
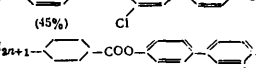
1	2	3	4	5	6	7	8	9	10	11
184	4-[5-(4-n-Alkylcyclohexyl)-2-pyrimidinyl]-benzonitrile	 $n = 5$ (10%), $n = 7$ (60%)	*a*	η (60° C) = 0.306		[3.45]	495		[113]	T_m = 340 K, Δε (60° C) = = 17.20
		$n = 7$ (60%),  (40%)	*a*	η (60° C) = 0.286			492		[113]	T_m = 317 K, Δε (60° C) = = 15.26
185	4-[5-(4-n-Alkylcyclohexyl)-2-pyrimidinyl]-cyclohexane-carbonitrile	 $n = 5$ (10%), $n = 7$ (60%)	*a*	η (60° C) = 0.385		[3.81]	471		[113]	T_m = 330 K, Δε (60° C) = = 16.30
186	4-[5-(4-n-Butylphenyl)-2-pyrimidinyl]-benzonirtile	 186 (40%),  (60%)	*a*	η (60° C) = 0.385		[1.39]	501		[113]	T_m = 359 K, Δε (60° C) = = 19.20
		186 (60%), (40%)	*a*	η (60° C) = 0.550			509		[113]	T_m = 343 K, Δε (60° C) = = 22.90
187	2-(4-Butylcyclohexyl)-6-(4-cyanophenyl)-imidazo-[2,1-*b*]-1,3,4-thia-diazole			γ_1 (25° C) = [5.6] γ_1 (60° C) = [0.46]		[10.0]	>551 (decom-poses)		[114]	T_m = 445 K
188	4-(4-Alkylphenyl)-2-chloro-phenyl 4-alkyl-benzoates	 $n = 3$ $m = 5$ (65%),  (35%)		η (50° C) = 0.30			398		[115]	
189	4-(4-Alkylphenyl)-2-chloro-phenyl 4-alkoxy-benzoates	 (85%)  (15%)		η (50° C) = 0.65			373		[115]	
190	4-(4-n-Butyl-phenyl)-2-cyanophenyl 4-(4-n-hexyloxyl)-benzoate			η (20° C) = [4.6]			[407]		[116]	Δε = [−4.3]
191	4'-Pentyl-4-biphenylyl 2,4-difluoro-benzoate			η (20° C) = [0.42]			429.9		[117]	Δε = [+2.7]
192	4-(4-Propyl-cyclo-hexyl)phenyl 2,4-difluoro-benzoate			η (20° C) = [0.42]			435.5		[117]	
193	4-(4-Propyl-cyclo-hexyl)phenyl 3,4-difluoro-benzoate			η (20° C) = [0.40]			417.7		[117]	
194	4-(4-Pentyl-phenyl)-cyclohexyl 3,4-difluoro-benzoate			η (20° C) = [0.43]			421.0		[117]	
195	4-(4-Alkylphenyl)-2-chlorophenyl 4-alkylcyclo-hexane-1-carboxy-lates	 n=3, m=4 (55%)  (45%)		η (20° C) = [0.32]			414		[115]	
196	3',4'-Difluoro-4-biphenylyl 4-alkylcyclo hexane-1-carboxylates	 n=3 n=5		η (20° C) = [0.34] η (20° C) = [0.46]			416.8		[118] [118]	
197	4-(4-Propylcyclo-hexyl)cyclo-hexyl 3,4-difluoro-benzoate			η (20° C) = [0.66]			[560]		[117]	
198	4-(4-Butylcyclo-hexyl)cyclohexyl 3-chloro-4-fluoro-benzoate			η (20° C) = [0.89]			399.5		[117]	

Table 1 (contd.)

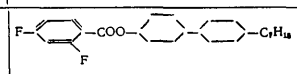
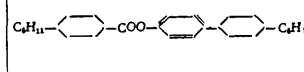
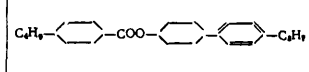
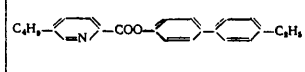
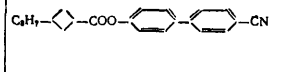
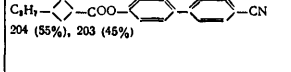
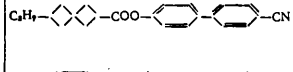
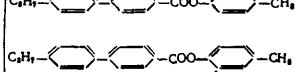
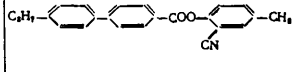
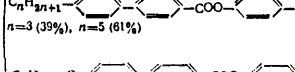
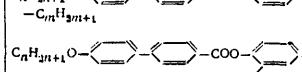
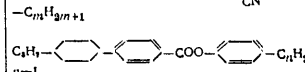
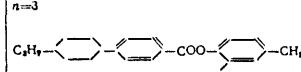
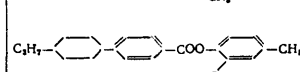
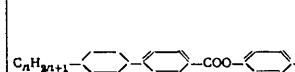
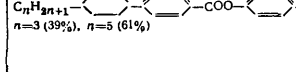
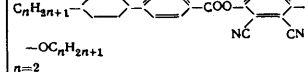
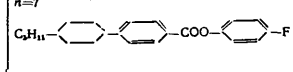
1	2	3	4	5	6	7	8	9	10	11
199	4-(4-Heptylcyclohexyl)-cyclohexyl 2,4-difluorobenzoate			η (20° C) = [0.32]			442.6		[117]	
200	4-(4-Propylcyclohexyl)phenyl 4-pentylcyclohexane-1-carboxylate			η (20° C) = (0.40)			466		[70]	
201	4-(4-Propylphenyl)-cyclohexyl 4-butylcyclohexane-1-carboxylate			η (25° C) = [0.3]					[35]	
202	5-Butyl-2-pyridyl 4'-ethylbiphenyl-4-carboxylate			η (20° C) = [10.5]					[119]	ΔH_m = 2323 K
203	*cis*-4'-Cyano-4-biphenylyl 3-n-propylcyclobutane-1-carboxylate			η (20° C) = [1.33]			336.2		[120]	
204	*trans*-4'-Cyano-4-biphenylyl 3-n-propylcyclobutane-1-carboxylate	 204 (55%), 203 (45%)		η (20° C) = [0.74] η (20° C) = [1.00]			414.7 374.3		[120] [120]	
205	4'-Cyano-4-biphenylyl 3-n-propylspiro-[3,3]heptane-1-carboxylate			η (20° C) = [1.70]			428.0		[120]	
206	4-Methylphenyl 4'-propylbiphenyl-4-carboxylate			η (20° C) = [0.81]			472		[35]	ΔH_m = 3660 K
207	3-Cyano-4-methyl phenyl 4'-propyl-biphenyl-4-carboxylate			η (25° C) = [2.00]					[35]	
208	4-Ethoxyphenyl 4'-alkylbiphenyl-4-carboxylate	 n=3 (39%), n=5 (61%)		η (25° C) = [1.02]			500		[35]	ΔH_m = 3500 K
209	4-Alkylphenyl 4'-alkoxybiphenyl-4-carboxylate			η (25° C) = [1.60]					[35]	
210	4-n-Alkyl-2-cyanophenyl 4'-alkoxybiphenyl-4-carboxylate			η (25° C) = [3.10]					[35]	
211	4-Alkylphenyl 4-(4-propylcyclohexyl)-benzoates	 n=1 n=3		η (20° C) = [0.69] ν (20° C) = [0.60]			461 459		[35] [49]	ΔH_m = 2940 K
212	2,4-Dimethylphenyl 4-(4-propylcyclohexyl)-benzoate			η (25° C) = [1.44]			391		[35]	ΔH_m = 2610 K
213	2-Bromo-4-methylphenyl 4-(4-propylcyclohexyl)-benzoate			η (25° C) = [2.02]			392		[35]	ΔH_m=3590 K
214	4-Alkyl-2-cyanophenyl 4-(4-alkylcyclohexyl)-benzoate	 n=3/m=1 n=5/m=4		η (25° C) = [1.77] η (20° C) = [1.0]					[35] [56]	
215	4-Ethoxyphenyl 4-(4-alkylcyclohexyl)-benzoate	 n=3 (39%), n=5 (61%)		η (25° C) = [0.94]			492		[35]	ΔH_m = 3220 K
216	4-n-Alkoxy-2,3-dicyanophenyl 4-(4-alkylcyclohexyl)-benzoates	 n=2 n=7		η (20° C) = [2.1] η (20° C) = [1.8]			(377.2) (408.7)		[56] [56]	ΔH_m = 3220 K ΔH_m = 4580 K
217	4-Fluorophenyl 4-(4-pentylcyclohexyl)-benzoate			η (20° C) = [0.60]			[435]		[41]	

Table 1 (contd.)

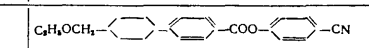
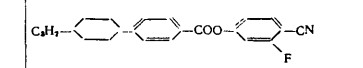
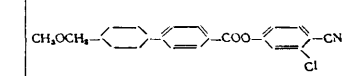
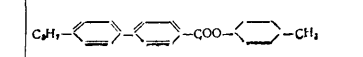
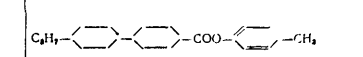
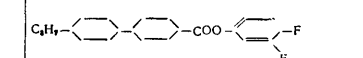
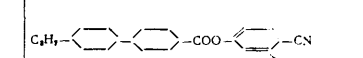
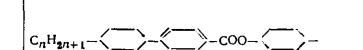
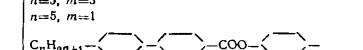
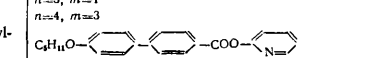
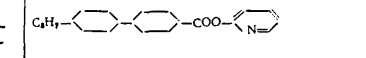
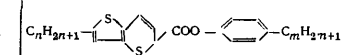
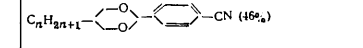
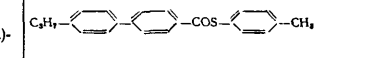
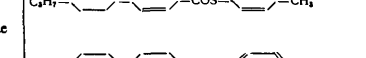
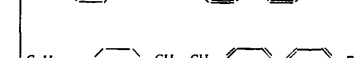
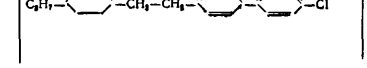
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218	4-Cyanophenyl 4-(4-ethoxymethylcyclohexyl)benzoate			η (20° C) = [1.28]			477		[121]	
219	4-Cyano-3-fluorophenyl 4-(4-propylcyclohexyl)benzoate			η (20° C) = [1.4]					[44]	
220	4-Cyano-3-chlorophenyl 4-(4-methoxymethylcyclohexyl)benzoate			η (20° C) = [1.88]			410		[44, 121]	
221	4-Methylcyclohexyl 4'-propylbiphenyl-4-carboxylate			η (20° C) = [0.30]			399		[35]	ΔH_{mi} = 2460 K
222	4-Methylphenyl 4-(4-propylcyclohexyl)cyclohexane-1-carboxylate			η (20° C) = [0.16]			477		[35]	ΔH_m = 2990 K
223	3,4-Difluorophenyl 4-(4-propylcyclohexyl)cyclohexane-1-carboxylate			η (20° C) = [0.31]			426.2		[53]	
224	4-Cyano-3-fluorophenyl 4-(propylcyclohexyl)-cyclohexane-1-carboxylate			η (20° C) = [0.621]			484.2		[53]	
225	4-Alkylcyclohexyl 4-(4-alkylcyclohexyl)-benzoates	 n=2, m=3 n=3, m=3 n=4, m=3 n=5, m=3 n=5, m=1		η (20° C) = [1.30] η (20° C) = [1.30] η (20° C) = [1.29] ν (20° C) = [1.19] η (20° C) = [0.77]			406 433 423 427 402		[53] [53] [53] [70] [35]	ΔH_m = 3200 K
226	4-Alkylcyclohexyl 4-(4-alkylcyclohexyl)-cyclohexane-1-carboxylates	 n=3, m=1 n=4, m=3		η (20° C) = [0.19] ν (20° C) = [0.50]			428 457		[35] [49]	ΔH_m = 3890 K
227	2-Pyridyl 4'-n-pentyloxybiphenyl-4-carboxylate			η (25° C) = [1.95]			387		[35]	ΔH_m = 1840 K
228	2-Pyridyl 4-(4-n-propylcyclohexyl)cyclohexane-1-carboxylate			η (25° C) = [0.37]			391		[35]	ΔH_m = 4290 K
229	4-Alkylphenyl 2-alkyl-5*H*-thieno-[3,2-*b*]thiine-5-carboxylate	 n=3 (18%), n=5 (18%), n=7 (18%),  (46%)		ν (20° C) = [0,31]			335		[122]	
230	4-Methylphenyl 4-(4-propylphenyl)-thiobenzoate			η (25° C) = [0,79]			508		[35]	ΔH_m = 3080 K
231	4-Methylphenyl 4-(4-propylcyclohexyl)thiobenzoate			η (25° C) = [0,62]			497		[35]	ΔH_m = 2380 K
232	[4-(4-Propylcyclohexyl)cyclohexyl]-(4-cyano-3-fluorophenoxy)-methane			η (20° C) = [0,871]			429.5		[53]	
233	1-(4-Biphenylyl)-2-(4-propylcyclohexyl)ethane			η (20° C) = [0,22]					[123]	μ_{C-H} = 1.46 D r^3_H = 1.7 Å^3
234	1-Alkylcyclohexyl-2-(4'-fluoro-4-biphenylyl)-ethane	 n=2 n=3 n=4 n=5		η (20° C) = [0,245] η (20° C) = [0,25] η (20° C) = [0,36] η (20° C) = [0,315]					[123]	μ_{C-F} = 1.48 D, r^3_F = 2.5 Å^3
235	1-(4'-Chloro-4-biphenylyl)-2-(propylcyclohexyl)ethane			η (20° C) = [0,49]					[123]	μ_{C-Cl} = 1.56 D, r^3_{Cl} = 5.9 Å^3

Table 1 (contd.)

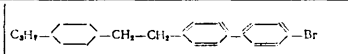
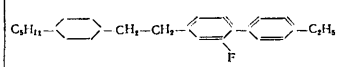
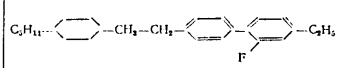
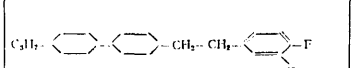
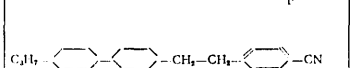
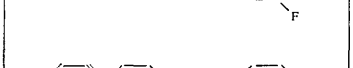
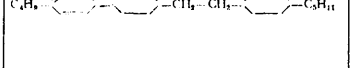
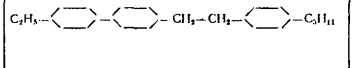
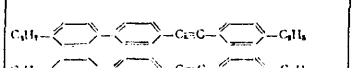
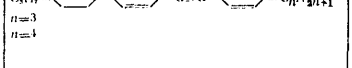
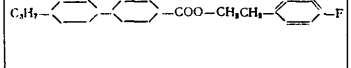
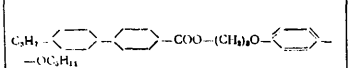
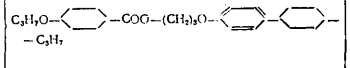
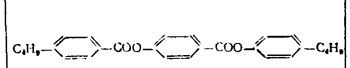
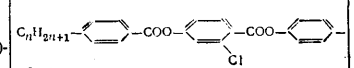
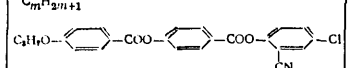
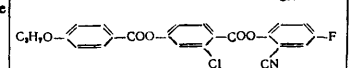
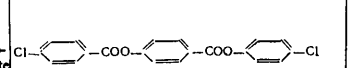
1	2	3	4	5	6	7	8	9	10	11
236	1-(4′-Bromo-4-biphenylyl)-2-(propylcyclohexyl)ethane			η (20° C) = [0.60]					[123]	μ_{C-Br} = 1.59 D, r^3_{Br} = 7.5 Å^3
237	1-(4′-Ethyl-2-fluoro-4-biphenylyl)-2-(4-pentylcyclohexyl)ethane			ν (20° C) = [0.24]			377.7		[124]	
238	1-(4′-Ethyl-2′-fluoro-4-biphenylyl)-2-(4-pentylcyclohexyl)ethane			ν (20° C) = [0.215]			376.2		[124]	
239	1-(3,4-Difluorophenyl)-2-[4-(4-propylcyclohexyl)cyclohexyl]-ethane			η (20° C) = [0.19]			391.2		[53]	ΔH_m = 3050 K
240	1-(4-Cyano-3-fluorophenyl)-2-[4-(4-propylcyclohexyl)cyclohexyl]-ethane			η (20° C) = [0.461]			446.1		[53]	
241	1-[4-(4-Butylphenyl)-cyclohexyl]-2-(4-pentylcyclohexyl)-ethane			η (25° C) = [1.03]			(456)		[125]	
242	1-[4-(4-Ethylcyclohexyl)cyclohexyl]-2-(4-pentylcyclohexyl)-ethane			η (25° C) = [0.71]			442		[125]	
243	4′-Ethyl-4-(4-propylphenyl)tolane			η (20° C) = [0.74]			[482]	Δn = [0.344]	[126]	
244	4′-Alkyl-4-(4-propylcyclohexyl)tolane	 n=3 n=4		η (20° C) = [0.31] η (20° C) = (0.479)			[465] 474	Δn = [0.309] Δn (25° C) = =0.253	[126] [27]	
245	β-(4-Fluorophenyl)-ethyl 4-(4-propylcyclohexyl)-cyclohexane-1-carboxylate			η (20° C) = [0.19]			356.7		[81]	
246	3-(4-Pentyloxyphenoxy)-1-propyl-4-(4-propylcyclohexyl)cyclohexane-1-carboxylate			η (20° C) = [0.88]			(348.7)		[127]	
247	3-[4-(4-Propylcyclohexyl)phenoxy]-1-propyl 4-propoxycyclohexane-1-carboxylate			η (20° C) = [0.45]			(339.5)		[127]	
248	4-n-Butylphenyl 4-(4-n-butylbenzoyloxy)benzoate		*a*	γ_1 (138° C) = 0.80	−0.8	3.95	452		[23]	
249	4-Alkylphenyl 4-(4-alkylbenzoyloxy)-2-chlorobenzoate			η (20° C) = (8)			420		[131]	
250	4-Chloro-2-cyanophenyl 4-(4-propoxybenzoyloxy)benzoate			η (20° C) = [1.36]			[241]		[129]	
251	2-Cyano-4-fluorophenyl 2-chloro-4-(4-propoxybenzoyloxy)-benzoate			η (20° C) = [1.30]			(372.5)		[129]	
252	Chlorophenyl 4-(4-chlorobenzoyloxy)benzoate		*a*	γ_1 (138° C) = 0.23	−10.8	3.83	513		[23]	
253	2-Cyano-4-fluorophenyl 4-(4-hexylcyclohexane-1-carbonyloxy)benzoate			η (20° C) = [1.31]			396.0		[129]	
254	2-Cyano-4-fluorophenyl 2-fluoro-4-(4-propylcyclohexane-1-carbonyloxy)benzoate			η (20° C) = [0.87]			392.2		[129]	

Table 1 (contd.)

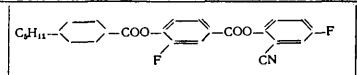
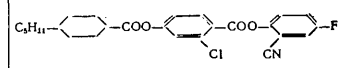
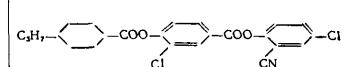
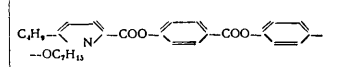
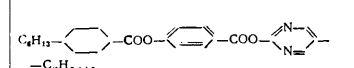
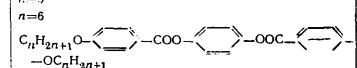
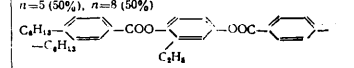
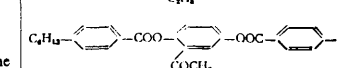
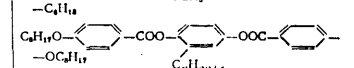
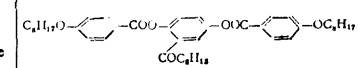
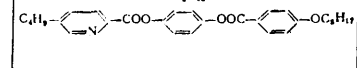
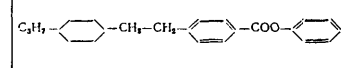
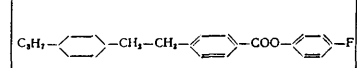
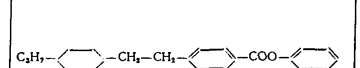
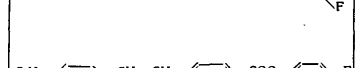
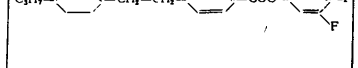
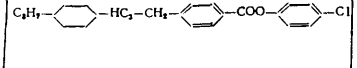
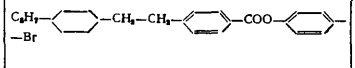
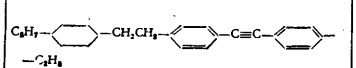
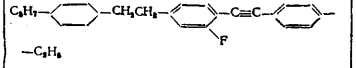
1	2	3	4	5	6	7	8	9	10	11
255	2-Cyano-4-fluorophenyl 3-fluoro-4-(4-pentylcyclohexane-1-carbonyloxy)benzoate			η (20° C) = [1.18]			407.2		[129]	
256	2-Cyano-4-fluorophenyl 2-chloro-4-(4-pentylcyclohexane-1-carbonyloxy)benzoate			η (20° C) = [1.72]			[308]		[129]	
257	4-Chloro-2-cyanophenyl 3-chloro-4-(4-propylcyclohexane-1-carbonyloxy)benzoate			η (20° C) = [1.50]					[129]	
258	4-Heptyloxyphenyl 4-(5-butylpyridine-2-carbonyloxy)-benzoate			η (20° C) = [5.6]			434		[119]	ΔH_m = 2190 K
259	5-Alkyl-2-pyrimidinyl 4-(4-hexylcyclohexane-1-carbonyloxy)benzoate									
	n=5			η (20° C) = [1.38]			398.5		[130]	
	n=6			η (20° C) = [1.14]			[411]		[130]	
260	1,4-Bis(4-n-alkoxybenzoyloxy)-benzenes			ν (87° C) = 1.26			357		[132]	
	n=5 (50%), n=8 (50%)									
261	2-Ethyl-1,4-bis-(4-n-hexylbenzoyloxy)benzene		*a*	γ_1 (45° C) = 1.09		6.43	348.7		[133]	
			a	ν (25° C) = 2.83					[134]	
262	2-Acetyl-1,4-bis-(4-n-hexylbenzoyloxy)benzene			ν (25° C) = 6.61			360.1		[134]	
263	2-Alkyl-1,4-bis-(4-n-octyloxybenzoyloxy)-benzene									
	n=7			ν (87° C) = 6.42			352		[135]	
				ν (25° C) = 9.6						
	n=8			ν (80° C) = 0.87			350		[128]	
264	2-Heptanoyl-1,4-bis-(4-n-octyloxybenzoyloxy)benzene			ν (87° C) = 6,8			354		[135]	
265	4-(5-Butylpyridyl-2-carbonyloxy)-1-(4-octyloxybenzoyloxy)-benzene			η (20° C) = [5.5]			450		[119]	ΔH_m = 3454 K
266	Phenyl 4-[β-(4-n-propylcyclohexyl)-ethyl]-benzoate			η (20° C) = [0.19]					[136]	
				η (20° C) = [0.26]					[54]	
267	4-Fluorophenyl 4-[β-(4-n-propylcyclohexyl)-ethyl]-benzoate			η (20° C) = [0.2]					[136]	
				η (20° C) = [0.27]					[54]	
268	3-Fluorophenyl 4-[β-(4-n-propylcyclohexyl)-ethyl]-benzoate			η (20° C) = [0.27]					[54]	
269	3,4-Difluorophenyl 4-[β-(4-n-propylcyclohexyl)-ethyl]-benzoate			η (20° C) = [0.104]			405		[54]	ΔH_m = 3760 K
				η (20° C) = [0.30]					[54]	
270	4-Chlorophenyl 4-[β-(4-n-propylcyclohexyl)-ethyl]-benzoate			η (20° C) = [0.27]					[136]	
271	4-Bromophenyl 4-[β-(4-n-propylcyclohexyl)-ethyl]-benzoate			η (20° C) = [0.31]					[136]	
272	4-Ethyl-4'-(4-propylcyclohexylethyl)-tolane			η (20° C) = [0.056]			435.0	Δn = [0.332]	[126]	
273	4-Ethyl-2'-fluoro-4'-(4-propylcyclohexylethyl)-tolane			η (20° C) = [0.14]			423.0	Δn = [0.314]	[126]	
274	Methoxybenzylidene-4-aminoazobenzene		*a*	γ_1/ρ(174° C) = 0.043	−9.81	5.06	453		[33]	

Table 1 (contd.)

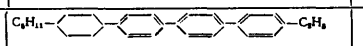
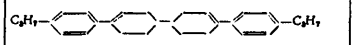
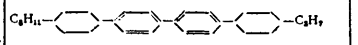
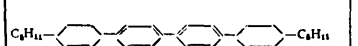
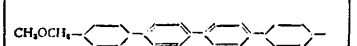
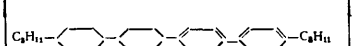
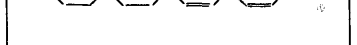
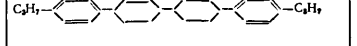
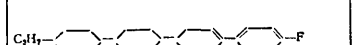
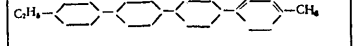
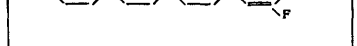
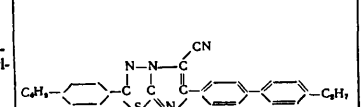
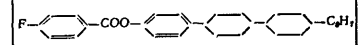
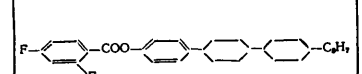
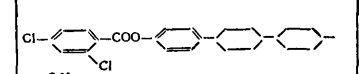
1	2	3	4	5	6	7	8	9	10	11
275	1-Ethyl-4″-(4-pentylcyclohexyl)-terphenyl			η (20° C) = [0.82]			[584]		[137]	
276	4,4′-Bis(4-propylphenyl)-2,3,5,2′,3′,6′-hexahydrobiphenyl			η (20° C) = [2.2]			532		[137]	
277	4-(4-n-Propylcyclohexyl)-4′-(4-n-pentylcyclohexyl)-biphenyl			η (20° C) = (0.42)			584		[70]	
278	2′-Fluoro-4,4′-bis-(4-n-pentylcyclohexyl)biphenyl			η (20° C) = [0.08] [0.50]			[628] [622]		[138]	in the matrix comprising phenylcyclohexanes in a matrix comprising biphenyls
279	4-(4-Propylcyclohexyl)-4′-(4-methoxymethylcyclohexyl)-biphenyl			η (20° C) = [3.7]			553		[103]	
280	4-Pentyl-4′-(4′-pentyl-4-bicyclohexylyl)-biphenyl			η (20° C) = [2.0]			[662]		[137]	
281	4-Cyano-4′-(4′propyl-4-bicyclohexylyl)-biphenyl			η (20° C) = [1.01]			[653]		[139]	
282	4,4′-Bis(4-propylphenyl)bicyclohexyl			η (20° C) = [0.83]			[501]		[137]	
283	4′-(4′-Ethyl-4-bicyclohexylyl)-2′,3′,4′,5′-tetrahydro-4-methylbiphenyl			η (20° C) = [0.81]			457		[137]	
284	4′-(4′-Propyl-4-bicyclohexylyl)-4-fluoro-2′,3′,4′,5′-tetrahydrobiphenyl			η (20° C) = [0.24]			452		[140]	
285	4″-Ethyl-4-(4-methylphenyl)-*p*-tercyclohexyl			η (20° C) = [0.81]			466		[137]	
286	4-(Fluorophenyl)-4″-propyl-*p*-tercyclohexyl			η (20° C) = [0.24]			452		[140]	
287	4″-Butyl-4-(3,4-difluorophenyl)-*p*-tercyclohexyl			η (20° C) = [1.36]			472		[140]	
288	4″-Butyl-4-(4-cyanophenyl)-*p*-tercyclohexyl			η (20° C) = [1.36]					[140]	
289	1-(4′-Propyl-4-bicyclohexylyl)-4-(4-ethylcyclohexyl)-benzene			η (20° C) = [2.5]			[541]		[137]	
290	2-(4-Butylcyclohexyl)-5-cyano-6-(4′-propyl-n-biphenylyl)-imidazo[2,1-*b*]-1,3,4-thiadiazole			γ_1(60° C) = [2.9]		[6.87]	>566		[141]	decomposes at T>566 K
291	4-(4′-Propyl-4-bicyclohexylyl)-phenyl 4-fluorobenzoate			η (20° C) = [3.2]			[850]		[142]	
292	4-(4′-Propyl-4-bicyclohexylyl)-phenyl 2,4-difluorobenzoate			η (20° C) = [0.83]			[610]		[117]	
293	4-(4′-Propyl-bicyclohexylyl)-phenyl 2,4-dichlorobenzoate			η (20° C) = [3.2]			[584]		[142]	

Table 1 (contd.)

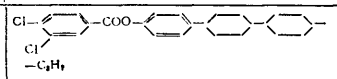
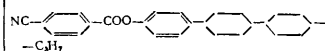
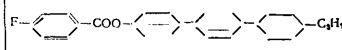
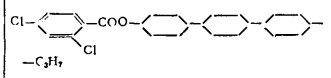
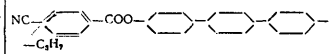
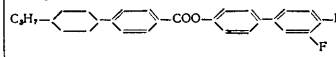
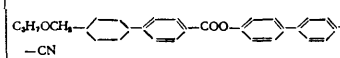
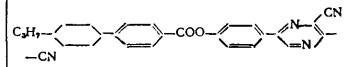
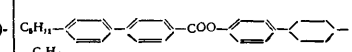
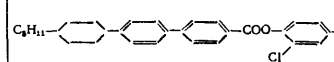
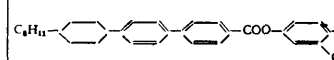
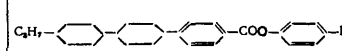
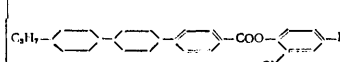
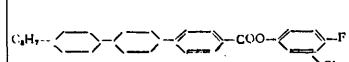
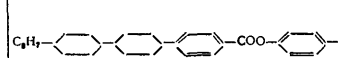
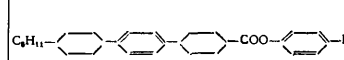
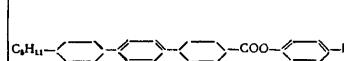
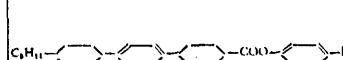
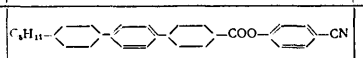
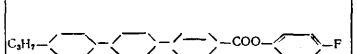
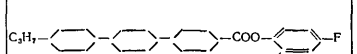
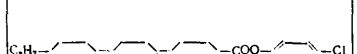
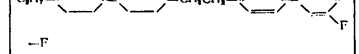
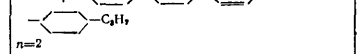
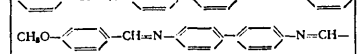
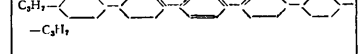
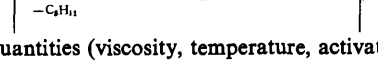
1	2	3	4	5	6	7	8	9	10	11
294	4-(4'-Propyl-n-bicyclohexylyl)-phenyl 3,4-dichlorobenzoate			η (20° C) = [2.6]			[584]		[142]	
295	4-(4'-Propyl-4-bicyclohexylyl)-phenyl 4-cyanobenzoate			η (20° C) = [5.8]			[940]		[142]	
296	4''-Propyl-4-octahydro-*p*-terphenylyl 4-fluorobenzoate			η (20° C) = [1.9]			[570]		[142]	
297	4''-Propyl-4-octahydro-*p*-terphenylyl 2,4-dichlorobenzoate			η (20° C) = [2.6]			[584]		[142]	
298	4''-Propyl-4-octahydro-*p*-terphenylyl 4-cyanobenzoate			η (20° C) = [3.2]			[659]		[142]	
299	3',4'-Difluoro-4-biphenylyl 4(4-propylcyclohexyl)benzoate			η (20° C) = [1.12]			553,5		[118]	
300	4'-Cyano-4-biphenylyl 4-(4-propoxymethylcyclohexyl)-benzoate			η (20° C) = [1.82]			[584]		[121]	
301	4-(2,3-Dicyano-5-pyrazinyl)phenyl 4-(4-propylcyclohexyl)benzoate			η (20° C) = [0.78]			546		[143]	
302	4-(4-Propylcyclohexyl)-phenyl 4'-pentylbiphenyl-4-carboxylate			η (20° C) = [9.4]					[144]	
303	2-Chloro-4-fluorophenyl 4'-(4-pentyl cyclohexyl)-biphenyl-4-carboxylate			η (20° C) = [0.20]			552.8		[142]	in a matrix comprising biphenyls (compounds in a matrix comprising phenylcyclohexanes)
304	3-Chloro-4-fluorophenyl 4'-(4-pentylcyclohexyl)-biphenyl-4-carboxylate			η (20° C) = [1.29]			528.8		[142]	
305	4-Fluorophenyl 4-(4'-propyl-4-bicyclohexylyl)-benzoate			η (20° C) = [0.77]			[770]		[142]	
306	2-Chloro-4-fluorophenyl 4-(4'-propyl-4-bicyclohexylyl)-benzoate			η (20° C) = [0.64]			504.2		[142]	
307	3-Chloro-4-fluorophenyl 4-(4'-propyl-4-bicyclohexylyl)-benzoate			η (20° C) = [1.29]			515.5		[142]	
308	4-Cyanophenyl 4-(4'-propyl-4-bicyclohexylyl)-benzoate			η (20° C) = [2.9]			[850]		[142]	
309	4-Fluorophenyl 4-[(4-pentylcyclohexyl)phenyl]-cyclohexane-1-carboxylate			η (20° C) = [0.39]			[770]		[142]	
310	2-Chloro-4-fluorophenyl 4-[(4-pentylcyclohexyl)phenyl]-cyclohexane-1-carboxylate			η (20° C) = [0.39]			511.0		[142]	
311	3-Chloro-4-fluorophenyl 4-[(4-pentylcyclohexyl)phenyl]-cyclohexane-1-carboxylate			η (20° C) = [0.30]			495.4		[142]	

Table 1 (contd.)

1	2	3	4	5	6	7	8	9	10	11
312	4-Cyanophenyl 4-[(4-pentylcyclohexyl)phenyl]-cyclohexane-1-carboxylate			η (20° C) = [0.64]			511.0		[142]	
313	4-Fluorophenyl 4''-propyloctadecahydro-*p*-terphenyl-4-carboxylate			η (20° C) = [0.23]					[142]	
314	2-Chloro-4-fluorophenyl 4''-propyloctadecahydro-*p*-terphenyl-4-carboxylate			η (20° C) = [0.64]			532.9		[142]	
315	2,4-Dichlorophenyl 4''-propyloctadecahydro-*p*-terphenyl-4-carboxylate			η (20° C) = [0.64]			538.5		[142]	
316	4-Cyanophenyl 4''-propyloctadecahydro-*p*-terphenyl-4-carboxylate			η (20° C) = [1.29]			[850]		[142]	
317	3-[4-(4-Propylcyclohexyl)-phenoxy]propyl 4'-propylbicyclohexyl-4-carboxylate			η (20° C) = [0.78]			427		[127]	
318	1-(3',4'-Difluoro-4-biphenylyl)-2-(4'-propyl-4-bicyclohexylyl)-ethane			η (20° C) = [0.280]					[53]	
319	1-[4-(4'-Alkyl-4-bicyclohexylyl)-phenyl]-2-(4-propylcyclohexyl)ethane									
		$n=2$		η (20° C) = [0.55]			525.3		[145]	
		$n=3$		η (20° C) = [0.63]			517.6		[145]	
320	Dibenzylidenebenzidine		*a*	γ_1/ρ (259° C) = = 0.1350	−2.09	2.50	558		[33]	
321	Di-4-methoxybenzylidenebenzidine		*a*	γ_1/ρ (256.3° C) = =0.0243	−11.32	6.53	530		[33]	
322	1,4-Bis[4-(4-(propylcyclohexyl)-cyclohex-1-enyl]benzene			η (20° C) = [15.8]					[137]	
323	1,4-Bis-(4'-pentyl-4-bicyclohexylyl)-benzene			η (20° C) = [5.9]			[927]		[137]	

Remarks. The physical quantities (viscosity, temperature, activation energy, and double refraction), obtained by extrapolating the concentration variations of these quantities in the mixtures, are quoted in square brackets throughout the table.

*[1]The viscosities obtained by extrapolating their temperature variation are given in round brackets.

*[2]The temperatures of the "isotropic liquid—nematic liquid crystal" monotropic transition are given in round brackets.

*[3]The order parameter S or the double refraction Δn are quoted (also for reference), depending on the approximation formula used, taking into account the proportionality of the temperature variations of these physical quantities.

The order in which the liquid crystal substances have been arranged in terms of chemical classes approximately corresponds to the order adopted in the familiar Demus Tables for liquid crystals.[19] For substances belonging to one chemical class, for example, Schiff bases, the relative positions are determined by the polarity of the substituent (alkyl, alkoxy-, acyloxy-, cinnamate, CN, etc. groups). For representatives of a single chemical class which are members of a homologous series, the values of γ_1 or η are indicated at one or several temperatures at which these homologues exhibit mesogenic properties and also for the same temperature difference $\Delta T = T_{NI} - T$ or at the same reduced temperature, for example $T = 0.95T_{NI}$. The values of S or Δn are also listed for the same temperature difference. The temperature variation of the order parameter S is similar for different substances and can be described approximately by the formula

$$S \simeq S_0(1 - T/T^*)^{\beta}, \qquad (7)$$

where $T^* \simeq T_{NI} + (0.2-0.7)$, $\beta \simeq 0.18 \pm 0.02$, and $S_0 = 1.1-1.4$.[2,20,21]

Table 2. The viscosities of 4,4'-di-n-alkylazoxybenzenes C_nH_{2n+1}—⟨⟩—N=N(→O)—⟨⟩—C_nH_{2n+1}.

n	γ_1				T_{NI}	Fitting formula	ln A_0	E	S (ΔT=10° C) [22]	Refs.
	25° C	30° C	64° C	ΔT = 10° C						
4	0.476	0.15	—	0.67	304.1	*b*	—21.8	6.50	0.4956	[9]
	0.59			0.79	304	*a*	—21.6	6.27		[23]
5	—	0.948	0.168	0.28	339.8	*b*	—13.65	4.26	0.5918	[9]
	0.94	0.83			340.8	*a*	—13.13	3.90		[3]
6	—	0.783	—	0.38	326.4	*b*	—15.52	4.76	0.6105	[9]
		1.56		0.54	327	*a*	—22.4	6.96		[23]
7	—	—	0.291	0.36	343.3	*b*	—17.18	5.50	0.7041	[9]
8	—	—	0.388		339.4					[9]

Table 3. The viscosities of 4,4'-di-n-alkoxyazoxybenzenes [fitting formula *d*: $\ln(\gamma_1/S^2) = \ln A_0 + BS^2/(T - T_0)$]

$C_nH_{2n+1}O$—⟨⟩—N=N(→O)—⟨⟩—OC_nH_{2n+1} (Fig. 1).

n	γ_1		T_{NI}	Fitting formula	ln A_0	B, E, K	T_0	S (ΔT=10 °C) (Ref.21)	Refs.
	120° C	ΔT=10° C							
1	0.076	0.068	408.5	*d*	—1.711	10.41	336	0.5784	[18]
	0.064			*a*	—17.0	5600			[31]
	0.088			*a*	—17.68	7790			[33]
	0.068								[146]
	0.70	0.059		*a*	—17.72	5920			[23]
2	(0.39)	0.114	440.7	*d*	—1.455	10.61	386	0.6708	[18]
	(0.17)			*a*	—10.13	5029			[33]
3	0.10	0.152	396.8	*d*	—1.181	10.97	364	0.6330	[18]
4	0.18	0.136	409.9	*d*	—2.446	29.37	345	0.6706	[18]
5	0.10	0.182	396.4	*d*	—1.199	58.31	316	0.6427	[18]
6	0.16	0.174	402.3	*d*	—1.438	77.60	313	0.6810	[18]
7	0.205	0.295	397.4		—0.762	13.52	357.5	0.7118	[18]

Table 4. The viscosities of 4-alkoxybenzylidenebutylanilines

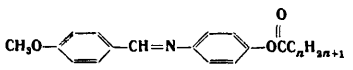
$C_nH_{2n+1}O$—⟨⟩—CH=N—⟨⟩—C_4H_9.

n	γ_1				T_{NI}	Fitting formula	ln A_0	E	S (ΔT=10° C)	Refs.	Remarks
	25° C	44° C	57.4° C	ΔT=10° C							
1	1.09	0.192		0.552	318.3	*a*		5.78		[4]	
						b	—18.92	5.82	0.54 [28]	[4]	
	0.89				317.5			6.63		[5]	$E = \partial\gamma_1/\partial(T^{-1})$, $T = 0.92\,T_{NI}$
	0.96									[2]	
	0.98				319.6	*a*	—18.38	5.48		[3]	
	1.06				317.5			6.05		[13]	$E = \partial\gamma_1/\partial(T^{-1})$, $T = 0.92\,T_{NI}$
	0.85					*a*		5.69		[31]	
	0.75					*a*	—19.0	5.57		[23]	
		0.25								[48]	
2	—	0.781	0.45	0.229	352.5	*b*		4.78		[124]	
3		0.66	0.27		332.0	*a*	—21.0	6.53		[3]	
4			0.49		348.4					[3]	
		0.44	0.21	0.26						[141]	$\ln(\gamma_1/S^2) = -0.041 + 0.105\,S^2/(T-280)$
5			0.55		342.8					[3]	

For homologous series of certain substances, more detailed information about the viscosity and other physicochemical properties is given in Tables 2–13. The values of γ_1 and/or η, taken from different literature sources and treated by different procedures, are presented for certain substances. The results of the treatment based on the activation and free volume models are presented simultaneously for some of the substances. In a number of instances, the glass point T_g is indicated, which makes it possible to infer the value of γ_1 at low temperatures. In some cases, a general (alkyl, alkoxy-groups) rather than specific substitution is indicated and the values

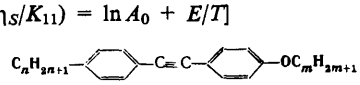
of γ_1 or η presented make it possible to infer only approximately the influence of molecular structure on the viscosity. Some of the results were obtained in studies of the properties not of individual substances but of mixtures of compounds referring to a single chemical class, which made it possible to extend greatly the range of existence of the mesophase while retaining a specific chemical structure. It has been shown[17] that, for the majority of NLC, the activation energy for rotational viscosity E is equal to or only 1.5–2 times greater than the enthalpy of fusion ΔH_m. The values of ΔH_m have therefore been listed for a number of substances making it possible to estimate the temperature variation of the viscosity.

Table 5. The viscosities of 4-anisilidene-4′-aminophenyl acetates[29] (fitting formula *b*)



n	γ_1		T_{NI}	$\ln A_0$	E	S ($T=0.95T_{NI}$) (Ref.28)
	90° C	$T=0.95\ T_{NI}$				
1	0.394	0.398	382.20	−17.81	6.26	0.5954
2	0.305	0.285	384.02	−17.14	5.96	0.5577
3	0.313	0.270	385.77	−14.58	5.03	0.6254
4	0.257	0.388	373.65	−15.31	5.28	0.6042
5	0.328	0.419	377.56	−17.44	6.12	0.6386
9	0.342	0.782	370.25	−23.71	8.42	0.6434

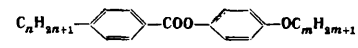
Table 6. The viscosities of 4-n-alkoxy-4′-n-alkyltolanes[148] [fitting formula: $\ln(\eta_S/K_{11}) = \ln A_0 + E/T$]



n	m	η_S/K_{11}		T_{NI}	E
		60° C	70° C		
4	2	0.45	0.33	353	1.08
5	2	0.40	0.355	353	1.08
6	2	0.47	0.405	349	1.16
8	2	0.53	0.45	352	1.16

The activation energy E and the enthalpy of fusion ΔH_m are quoted in Kelvin degrees to facilitate the use of the tables. All the temperatures are expressed in Kelvin degrees. The NLC clarification temperatures T_{NI}, listed in round brackets, indicate the monotropic isotropic liquid–nematic phase transition observed when the NLC is supercooled; the virtual isotropic liquid–nematic phase transition temperatures, calculated from the concentration variations of T_{NI} in NLC mixtures, are indicated in square brackets. In some cases, the anisotropies of the dielectric constant $\Delta\varepsilon$, the dipole moments μ expressed in Debyes (1 D = 10^{-18} CGSE units), the viscoelastic ratios γ_1/K_T, where $K_T = K_{11} + 1/4(K_{33} - 2K_{22})$ is the elasticity coefficient for the deformation in the twist-cell, as well as the times when the electrooptical response of the twist-effect t_{off} is switched off, which are of interest as regards practical applications, are indicated in the remarks. The cubes of the van der Waals radii r of the hydrogen, fluorine, chlorine, and bromine atoms are given in the 'remarks' for halogeno-derivatives. The relation between the parameters given in the 'remarks' and the viscosity of the NLC is discussed in Section IV.

Table 7. The viscosities of 4-alkoxyphenyl 4-n-alkylbenzoates[38] (Fig. 2) (fitting formula: $\ln\eta = \ln\eta_0 + E/T$)



No. of mixture	Mixture of composition*	$(n+m)_{av}$	L_{mol}^{av}**	η (25° C)	T_{NI}	$\ln\eta_0$	E
1	n=1, m=1 (11.2); n=3, m=2 (22.2); n=5, m=2 (28.3); n=1, m=4 (19.1); n=3, m=4 (19.2)	5.61	20.39	0.325	330.9	−15.6	4.32
2	n=1, m=1 (7.3); n=3, m=2 (14.8); n=5, m=2 (18.0); n=1, m=4 (11.9); n=3, m=4 (11.7); n=6, m=4 (36.4)	7.21	22.37	0.36	325.6	−15.2	4.23
3	Mixture 1 (50%), Mixture 6 (50%)	8.20	23.36	0.37	328.9	−15.8	4.42
4	n=5, m=2 (24.0); n=3, m=4 (16.0); n=4, m=6 (60.1)	8.82	24.31	0.38	324.6	−14.5	4.05
5	n=3, m=4 (12.0); n=6, m=4 (37.5); n=5, m=6 (50.4)	10.12	25.95	0.39	328.2	−14.4	4.02
6	n=3, m=6 (24.9); n=5, m=6 (33.1); n=3, m=8 (21.3); n=6, m=8 (20.7)	11.50	27.14	0.44	329.5	−15.1	4.27

*The contents of the mixture components in molar percentages are indicated in brackets.

**L_{mol}^{av} is the average length of the molecules in the mixture expressed in angstroms.

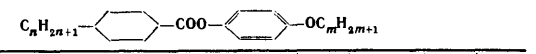
IV. Relation between the molecular structure of nematic liquid crystals and their viscosity

We shall trace the variation of the viscosities of NLC (rotational or dynamic) and their activation energies as the geometrical structure of the molecule and the distribution of electron density within it are varied, namely with increase in the length of the alkyl chain in the homologous series, with increase in the dipole moment of the molecular skeleton or of the connecting bridge, and after the introduction of heteroatoms or lateral substituents. We shall also attempt to indicate the causes of these changes.

In a homologous series with alkyl substituents, an even-odd correlation is observed for the values of γ_1 and η—in the even homologues the viscosity is greater than in the odd ones. The viscosities at the same remove from the nematic liquid crystal–isotropic liquid transition temperature and not viscosities at the same absolute temperature are compared for different homologues. Such variation of the viscosity with increase in the number of the homologue has been observed for dialkylazoxybenzenes (Table 2), cyanobiphenyls (Table 9), cyanophenylcyclohexanes (Table 11),

cyanobicyclohexanes (compound 92),† and cyanophenylpyridines (109). For tricyclic compounds, the even–odd alternation of the viscosity is much less pronounced, which has been confirmed by alkylcyclohexyl esters of alkylcyclohexylbenzoic acids (225). In the series with alkoxy- and acyloxy-substituents [dialkoxyazoxybenzenes (Table 3), alkoxycyanobiphenyls (Table 10), phenyl acetate derivatives (Table 5), and alkoxybenzylidenebutylanilines (Table 4)], the opposite situation obtains—the viscosity is greater for the odd homologues. Such variation of the viscosity in the homologous series is associated with the characteristic features of the molecular packing, which has been confirmed by theoretical calculations[18] (Fig. 1). As the alkyl chain is lengthened, the viscosity generally speaking increases, which can be seen particularly clearly in relation to alkoxyphenyl esters of alkylbenzoic and alkylcyclohexanecarboxylic acids (Tables 7 and 8, Fig. 2). If the molecular skeleton contains two benzene rings, the viscosity increases linearly with increase in the length f of the molecule. For Demus esters, where one benzene ring has been replaced by a cyclohexane fragment, the viscosity increases exponentially with increase in the length of the molecule. This suggests that, with increase in the contribution by repulsion forces, the free volume necessary for the migration and reorientation of the NLC molecules diminishes appreciably. For this reason, in the development of liquid crystal materials for matrix screens, where a greater steepness of the voltage-contrast characteristic (VCC) is required, phenyl benzoates with a long alkyl chain are preferred. They are not only characterised by a lower elasticity coefficient ratio K_{33}/K_{11}, ensuring a greater steepness of the VCC, but they also have a lower viscosity compared with that of Demus esters. The examples quoted above permit the conclusion that the activation energy for viscosity depends only slightly on the number of the homologue.

Table 8. The viscosities of 4-alkoxyphenyl 4-alkylcyclohexanecarboxylates[51] (Fig. 2) [fitting formula: $\ln\eta = \ln\eta_0 + B(T - T_0)$]



No. of mixture	Mixture composition*	$(n+m)_{av}$	L_{mol}^{av}**	$\eta_{(25°C)}$	T_{NI}	$\ln\eta_0$	B	T_0
1	$n=5$, $m=1$ (49.7); $n=3$, $m=2$ (31.1); $n=5$, $m=2$ (19.2)	5.88	21.00	0.16	349.3	—4 94	203.9	233.0
2	$n=5$, $m=1$ (39.4); $n=5$, $m=2$ (13.5); $n=4$, $m=4$ (47.0)	7.07	22.70	0.205	344.8	—5.03	246.6	226.3
3	$n=5$, $m=1$ (28.3); $n=4$, $m=4$ (35.8); $n=5$, $m=6$ (35.9)	8.51	24.43	0.27	346.4	—6.03	442.0	204.4
4	$n=4$, $m=4$ (48.3); $n=5$, $m=6$ (51.7)	9.55	25.68	0.42	348.0	—5.86	385.6	220.1
5	$n=4$, $m=6$ (100)	10.00	26.15	0.51	343.2	—5.60	316.5	233.9

*The mixture components expressed in molar percentages are indicated in brackets.

**L_{mol}^{av} is the average length of the molecules in the mixture expressed in angstroms

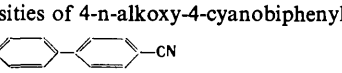
The influence of the increase in the polarisability of the substituent will be examined in relation to the alkenyl derivatives of phenylcyclohexanes (Table 13). The increase in the distance of the group containing a double bond from the molecular skeleton increases the polarisability of the solvent, which can be seen from the increase in the values of Δn, and also increases the rotational viscosity compared with pentylphenylcyclohexane. Nevertheless, the practical value for alkenyl derivatives is high, since they have shorter twist-effect switch-over times owing to the smaller viscoelastic ratio. By comparing the viscosities of a series of substances (compounds 5–8), we also see that an increase in the polarisability of the substituents (alkyl, acetoxy-, cinnamoyloxy-, and cyano-groups) leads to an increase in viscosity (see also Figs. 3 and 4).

Table 9. The viscosities of 4-n-alkyl-4′-cyanobiphenyls [fitting formula *b*: $\ln(\gamma_1/\Delta n) = \ln A_0 + E/T$; *e*: $\ln(\gamma_1/S^2) = \ln A_0 + ES/T$]



n	γ_1 25° C	γ_1 $\Delta T = 5$ K	T_{NI}	Fitting formula	$\ln A_0$	E	S ($\Delta T = 5$ K)	Refs.
5	0.82							[4]
	0.82		308.2	*b*	—20.0	5.84		[16]
	0.76	0.55	308.4	*e*	—0.095	0.88	0.5326	[8]
6	0.56	0.65	302.1	*e*	0.389	0.82	0.4928	[8]
			303.1			5.41		[3]
7		0.48	315.9	*e*	—1.402	1.65	0.5416	[8]
8	1.11		313.7	*b*	—15.8	5.31		[4. 16]
	($T = 34°$ C)	0.72	313.6	*e*	0.329	0.63	0.5585	[8]
9		0.48	322.6					[8]

Table 10. The kinematic viscosities of 4-n-alkoxy-4-cyanobiphenyls[65]



n	3	4	5	6	7	8	9
ν (70 °C), S	0.15	0 085	0.18	0.12	0.10	0.155	0.12 (80° C)
T_{NI}	347.7	351.2	312.2	330.2	327.2	327.7	337.2

A quantitative relation between the viscosities η and the bulk and dipole moment of the substituent has been obtained for halogenoderivatives of propylcyclohexylbiphenylylethane (compounds 233 to 236). On successive replacement of the hydrogen atom by F, Cl, and Br atoms, $\ln\eta$ increases in proportion to the dipole moment of the bond between the carbon and halogen atoms or in proportion to the cube of the van der Waals radius of the substituent (Fig. 5). Bearing in mind that the halogen substituent is rigidly bound to the molecular skeleton, this result can be interpreted also from the standpoint of the influence of the dipole moment of the molecular skeleton on the viscosity (the dipole moments of molecules or their fragments were taken from the papers of Minkin and co-workers[151,152] or calculated in accordance with their procedures). The correlation between the dipole moments of substituents rigidly attached to the molecular skeleton and the dynamic or kinetic viscosity of the NLC can be seen also in relation to the bicyclic and tricyclic derivatives of phenylcyclohexane (compounds, 60, 61, 66, 69 and 135, 138, 140, 141). We may note that alkylphenylalkylcyclohexanes (compounds 60) have the smallest viscosities among the known NLC and also the smallest

†The numbers of the compounds in Table 1 are indicated in brackets.

glass points T_g = 159 K, as a result of which they are used as the main components in the development of liquid crystal materials with a fast response at low (down to −60 °C) temperatures.

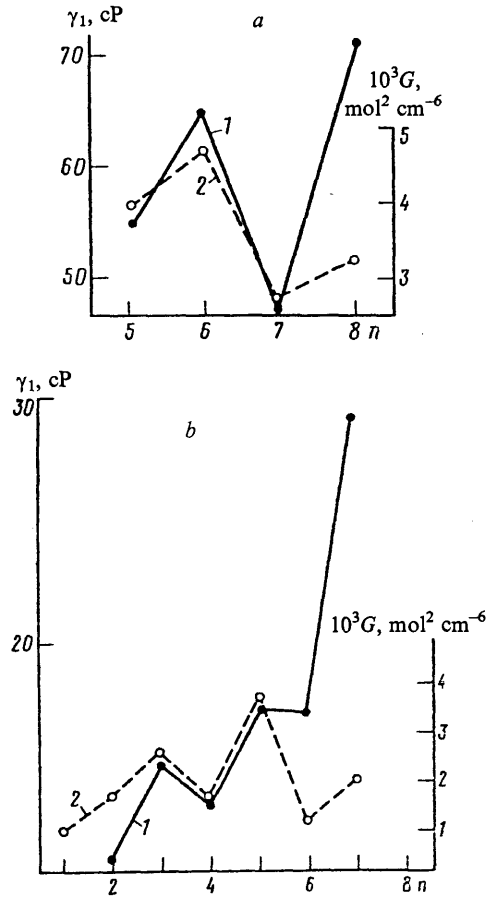


Figure 1. Correlation between the odd-even variation of the rotational viscosity γ_1 (line *1*) and the parameter G (line *2*) characterising molecular packing for alkylcyanobiphenyls (52) ($\Delta T = T_{NI} - T$ = 5 °C) (*a*) and dialkoxyazoxybenzenes (line *3*) (ΔT = 10 °C) (*b*). $G = [V_N(V^a - V_N)]^{-1}$, where V_N is the molar volume in the nematic phase and V^a is the molar volume in the nematic phase extrapolated from the isotropic phase.[18]

The influence of the dipole moment of the bridge connecting the benzene rings on the rotational viscosity and its activation energy can be examined with the aid of Table 14. The tabulated data not only confirm the correlation established between the dipole moment of the molecular skeleton and the viscosity of the NLC but also permit the claim that the distribution of electron density within the molecule influences significantly also the activation energy, which characterises the intermolecular interaction energy.

Table 15 presents the viscosity and dielectric characteristics of the NLC whose molecules contain a heterocyclic fragment. Although the dipole moments of the heterocycles themselves are almost the same, their introduction into the NLC molecule alters significantly the dipole moment of the latter, which has an appreciable effect on the anisotropy of the dielectric constant Δε; furthermore, a correlation is again observed between Δε and γ_1. The quantities γ_1 and E are influenced also by the positions of the heteroatoms (see the data for phenylpyridines—compounds 110, 111, 114, and 115 in Table 1). It can be seen in relation to dioxane, oxathiane, and dithiane derivatives (103–105) that the replacement of one and then the second oxygen atoms in the dioxan fragment by sulphur atoms increases the viscosity.

Table 11. The kinematic viscosities of 1-alkyl-4-(4-cyanophenyl)-cyclohexanes[150]

C_nH_{2n+1}—⟨⟩—⟨⟩—CN

n	1	2	3	4	5	6
ν (20 °C), S	0.18	0.19	0.18	0.22	0.21	0.28
n	7	8	9	10	11	12
ν (20 °C), S	0.265	0.33	0.325	0.40	0.40	0.47

Note. The values of ν were obtained by extrapolating their temperature variation.

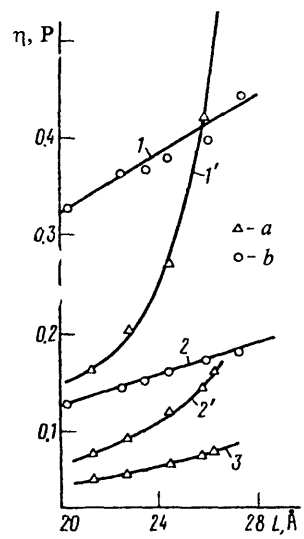


Figure 2. Dependence of the dynamic viscosity η on the average length of the molecule L in mixtures of phenylbenzoates (18) (*b*) and cyclohexyl benzoates (35) (*a*) at different temperatures (°C): (1) and (1′) 25; (2) and (2′) 45; (3) 65.

The close relation between the viscosity and the anisotropy of the dielectric constant is indicated by Fig. 6, where the viscosities of more than 80 materials produced by the Swiss firm Hoffmann-La Roche are plotted along the ordinate axis against the values of Δε for the same materials along the abscissa axis. The statistical mean

Table 12. The rotational and dynamic viscosities of 1-alkyl-4-(4-cyanophenyl)cyclohexanes [fitting formula *a*: $\ln\gamma_1 = \ln A_0 + E/T$; *b*: $\ln[\gamma_1/(\Delta n)^2] = \ln A_0 + E/T$; *f*: $\ln[\gamma_1/(\Delta n)^2] = \ln A_0 + E/(T - T_0)$]

C_nH_{2n+1}—⟨⟩—⟨⟩—CN

n	γ_1		η (20° C)	T_{NI}	Fitting formula	$\ln A_0$	*E*	Δn ($T = 0.95T_{NI}$)	T_0	Refs.	Remarks
	25° C	$T = 0.95T_{NI}$									
3			0.193							[149]	
5	0.97		0.210	328.2	*b*	—5.8	2.76	0.149		[16, 149]	
					f				247.4	[16]	more accurate fitting formula
	1.28 (22° C)				*a*		4.87			[76]	
	0.80			328.2	*a*		4.48			[3]	
7	1.40	0.69	0.268	330.2	*b*	—10.05	3.25	0.102		[16, 149]	
	1.09				*f*	—5.52	0.529		207.8	[16]	more accurate fitting formula

straight line is described by the equation $\eta = 0.105 + 0.02\,\Delta\varepsilon$ and virtually all the $\eta(\Delta\varepsilon)$ points fit between the two straight lines $\eta_{max} = 0.22 + 0.02\,\Delta\varepsilon$ and $\eta_{min} = 0.055 + 0.02\,\Delta\varepsilon$.

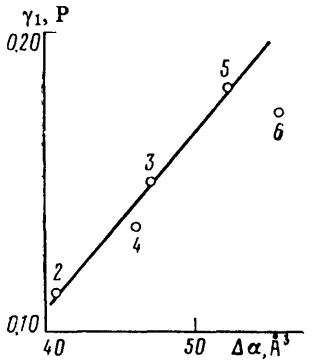


Figure 3. Dependence of the rotational viscosity γ_1 of dialkoxyazoxybenzenes ($C_nH_{2n+1}O$—⟨⟩—N=N(O)—⟨⟩—OC_nH_{2n+1}) on the anisotropy of the polarisability of the molecule. The numerals represent the numbers of the homologues.

Table 16 is a compilation of data for polar compounds without heterocyclic fragments. The replacement of the CN groups by NCS diminishes the viscosity of the liquid crystal, although the twist-effect switch-over times remain the same. The introduction of the ethane bridge instead of a single bond or the replacement of the alkyl group by an alkenyl group with the double bond remote from the cyclohexane fragment did not alter t_{off} either, although both these factors increase appreciably the viscosity of the NLC. On the other hand, the combination of two factors acting in opposite directions—the introduction of the thiocyanoto-group and of the ethane bridge—leads to an appreciable decrease in γ_1 and t_{off} (apparently as a consequence of the less dense molecular packing and the absence of a dipole moment in the bridge).

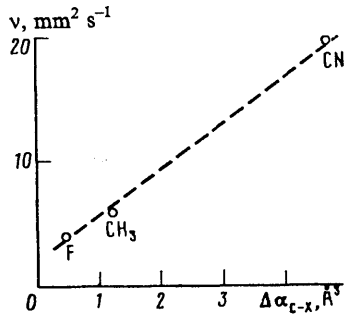
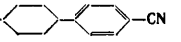
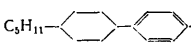
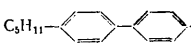


Figure 4. Dependence of the kinematic viscosity ν of phenylcyclohexane derivatives (C_3H_7—⟨⟩—⟨⟩—X) on the anisotropy of the polarisability of the C—X bond, where X = F, CH_3, or CN.

Although the substitution of a hydrogen atom by a fluorine atom is actually referred to as isogeometrical,[153] the increase in the electronegativity of the molecule occurring thereupon diminishes the thermal stability of the mesophase and increases the coefficient of internal friction, which can be seen in relation to the fluorinated derivatives of the alkylphenyl esters of alkylcyclohexanecarboxylic acids (compounds 34), tolanes (16), biphenyls (53, 54), and biphenylcyclohexanes (136, 137). However, the simultaneous introduction of fluorine in the *meta*- and *para*-positions promotes a significant decrease in viscosity. Thus the difluorophenyl derivatives of bicyclohexylethane (239 and 318) have almost the lowest viscosities among the tricyclic and tetracyclic substances respectively. It is also

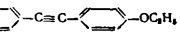
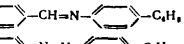
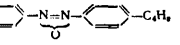
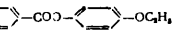
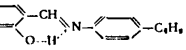
Table 13. The viscosities of 1-alkenyl-4-(4-cyanophenyl)cyclohexanes[50,78] (fitting formula: $\ln\gamma_1 = \ln\gamma_0 + E/T$)

C_nH_{2n+1}—CH=CH—C_mH_{2m}—  —CN

n, m	γ_1 (22° C)	η (22° C)	γ_1/K_T (22 °C), 10^{-10} s m^{-2}	T_{NI}	ln γ_0	E	Δn ($\Delta T = 10°$ C)	t_{off} (22 °C), ms
$n = 3$, $m = 0$	1.34	0.221	1.11	331.7	—16.62	4.99	0.116	40
$n = 3$, $m = 0$ (60%); $n = 2$, $m = 0$ (40%)	1.21	0.228	1.23	325.4	—16.32	4.87	0.117	42
$n = 3$, $m = 0$ (60%); $n = 0$, $m = 2$ (40%)	1.19	0.209	1.15	324.1	—16.33	4.87	0.115	37
$n = 1$, $m = 2$ (60%); $n = 0$, $m = 2$ (40%)	1.50	0.190	0.83	338.4	—15.73	4.76	0.127	32
$n = 3$, $m = 0$ (60%); $n = 0$, $m = 3$ (40%)	0.97	0.278	1.59	308.3	—20.10	5.92	0.105	67
$n = 0$, $m = 5$	0.99		2.02	305.4	—14.65	4.32	0.086	
C_5H_{11}—  —CN	1.28	0.215	1.14	328.1	—16.67	4.99	0.099	43
C_5H_{11}—  —CN	1.01	0.263	1.18	308.1	—21.24	6.27	0.178	55

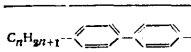
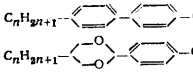
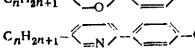
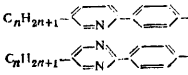
noteworthy that compounds containing the CN group in the *para*-position and fluorine in the *meta*-position have a higher positive value of $\Delta\varepsilon$ than the analogous compounds without fluorine. For example, $\Delta\varepsilon = +12$ for cyanophenyl heptylbenzoate, while $\Delta\varepsilon = +49.7$ (22, 23) for the analogous 4-cyano-3-fluorophenyl ester, which is associated with the fact that the fluorine atom prevents the dimerisation of the polar molecules leading to the partial cancelling of their dipole moments. This property makes it possible to reduce significantly the threshold potential of the electrooptical effect. Substances with fluorine or chlorine in the terminal position (compound 66 is an analogue) are frequently introduced into the liquid crystals in order to reduce their viscosity.[154]

Table 14. The influence of the dipole moment μ of the skeleton of a molecule having a bridging fragment on the rotational viscosity γ_1 and the activation energy E.

Compound	γ_1, P (25 °C)	E (10^3 K)	μ, D
C_4H_9—  —OC_5H_9	(0.9)	3.6	0—0.3
CH_3O—  —C_4H_9	1.09	5.82	1.57
CH_3O—  —C_4H_9	1.57	4.55	1.70
C_4H_9—  —OC_5H_9	2.20	5.11	1.90
CH_3O—  —C_4H_9	(6)	7.35	2.39

The sulphur atom is less electronegative than the oxygen atom and the substitution of oxygen by sulphur in the COO ester bridge therefore tends to increase the thermal stability of the mesophase and to increase slightly the viscosity, which can be seen from a comparison of the alkoxyphenyl and alkoxythiophenyl esters of alkylcyclohexanecarboxylic acids (35, 44) and methylphenyl and methylthiophenyl esters of propylbiphenylcarboxylic and propylcyclohexylbenzoic acids (compounds 206 and 230, 211 and 231).

Table 15. The influence of a heterocyclic fragment having a dipole moment μ on the anisotropy of the dielectric constant $\Delta\varepsilon$ and the rotational viscosity γ_1.

Compound	γ_1, P (25 °C)	μ, D	$\Delta\varepsilon$ ($\Delta T = 10$ K)
C_nH_{2n+1}—  —CN	1.02	~0	11.73
C_nH_{2n+1}—  —CN	1.34	2.14÷2.55	13.30
C_nH_{2n+1}—  —CN	1.84	2.11—2.20	16.60
C_nH_{2n+1}—  —CN	2.01	2.0÷2.42	19.72

When liquid crystals are selected for the observation of the dynamic scattering effect or in order to obtain a low frequency of the inversion of the sign of the anisotropy of the dielectric constant, substances with a large transverse dipole moment, usually with one or two lateral CN groups, are used. On comparing the viscosities of 4-methylphenyl 4'-propylbiphenyl-4-carboxylate and 3-cyano-4-methylphenyl 4'-propylbiphenyl-4-carboxylate (compounds 206 and 207), the analogous propylcyclohexyl derivatives (211, 214), as well as the 4-ethoxyphenyl 4'-alkylcyclohexylbenzoate and the analogous 2,3-dicyanophenyl benzoate (215, 216), we see that the increase in

viscosity (by a factor of 2.2–2.5 compared with the viscosities of substances without lateral groups) is independent of the number of CN groups. The less polar methyl group increases the viscosity to a lesser extent (compound 212). By increasing the length of the alkyl chains along the long molecular axis, it is in general possible to reduce to a minimum the increase in viscosity caused by the introduction of the CN group (see the data for compound 214, where the viscosities of two derivatives of 3-cyanophenyl benzoate with overall lengths of the alkyl chains equivalent respectively to 4 and 9 methyl groups are compared). Evidently the presence of lateral cyano-groups in bicyclic compounds affects the viscosity to a greater extent (35, 42).

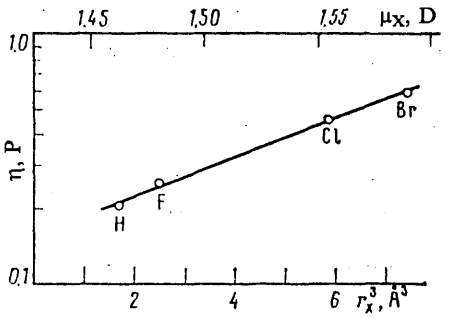


Figure 5. Dependence of the dynamic viscosity η of halogeno-derivatives on the van der Waals radius of the substituent (r_X) and the C–X bond dipole moment (μ_X).

The introduction of lateral alkyl and alkoxy-groups in the *meta*-position as in bisalkyl(or alkoxy)benzoyloxybenzenes (compounds 260–264) leads to an appreciable increase in the viscosity of the NLC for purely geometrical reasons, alkoxy- and acyloxy-groups giving rise to a greater increase in viscosity than alkyl groups. The viscosity of derivatives of bicyclooctane (compounds 96–99) is high mainly because of geometrical reasons—as a consequence of the denser molecular packing due to the presence of bulky fragment. We may note yet again that this does not affect the character of the intermolecular interaction and the activation energy for phenylbicyclooctanes is just as low as for phenylcyclohexanes. The influence of molecular packing on the rotational viscosity of bicyclic polar compounds is illustrated in Fig. 7.

In order to enhance the amplitude modulation of light using the dynamic light scattering effect or phase modulation in conjunction with *S*- and *B*-effects in image transformation problems in defectoscopy a high double refraction Δn is needed. Tolane derivatives (compounds 13–16, 243, 244, 272, 273) have a low viscosity combined with a high value of Δn. It is seen from Table 6 that tolane derivatives have a low activation energy for the viscoelastic ratio, which is the reason for the weak temperature dependence of the electrooptical response switch-over times.

The influence of the form of the skeletal fragment and also of the position of the substituent in the *cis*- and *trans*-position can be observed in relation to derivatives of spiro[3.3]heptane (compound 205), *cis*- and *trans*-cyclobutanes (203, 204), bicyclohexanes (88–94), and cyclohexylcyclohexenes (86, 87). In relation to derivatives of cyclohexene (134, cf. with 132, 141; 276, cf. with 282) and naphthalene (compounds 126–128), we see that the hydrogenation of the bonds in the molecular skeleton does not always reduce the

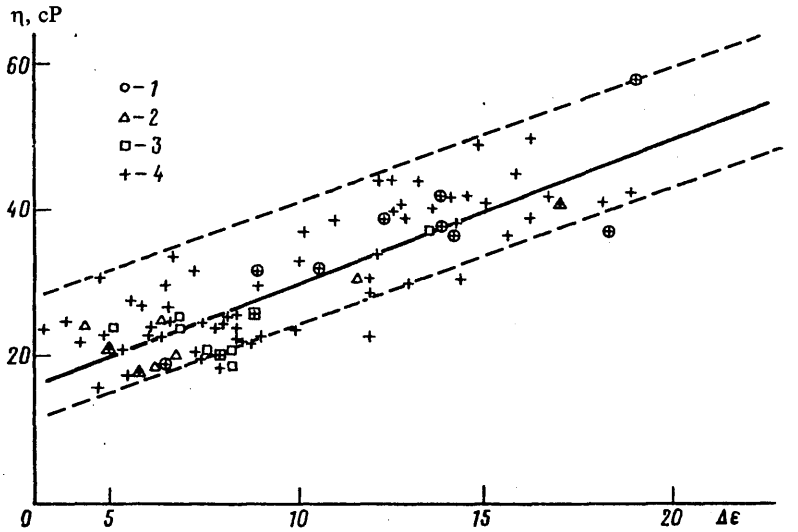


Figure 6. Dependence of the viscosity η of Hoffmann-La Roche liquid crystals on the anisotropy of the dielectric constant Δε: continuous line—averaging with respect to all the liquid crystals; dashed lines—η_{max} and η_{min} (see text); (*1*) liquid crystals with 1 : 4 multiplexity; (*2*) liquid crystals for TPT-matrices; (*3*) liquid crystals for the supertwist-effect; (*4*) remaining liquid crystals.

viscosity. Analysis of the data for this group of substances reveals a very small viscosity of the methyl ether of propylbicyclohexylmethanol (90) combined with a fairly high clarification temperature. The unusual structure of their side chain is responsible for this property.

Table 16. The rotational viscosities (γ_1), activation energies (E), and times at which the twist-effect is switched off (t_{off}) for bicyclic polar compounds.

Compound	γ_1, P	E (10^4 K)	t_{off}, ms
C_5H_{11}–⟨⟩–⟨⟩–CN	1.28	4.87	43
C_5H_{11}–⟨⟩–⟨⟩–NCS	0.83	4.30	41
CH_3–CH=CH–C_6H_4–⟨⟩–⟨⟩–CN,	1.50	4.76	32
CH_2–CH–C_6H_4–⟨⟩–⟨⟩–CN			
C_2H_5–CH=CH–C_6H_4–⟨⟩–⟨⟩–NCS	1.00	4.82	32
C_5H_{11}–⟨⟩–CH_2–CH_2–⟨⟩–CN	1.80	4.87	43
CH_3–CH=CH–⟨⟩–CH_2–CH_2–⟨⟩–CN,	2.15	4.99	29
CH_2=CH–C_6H_4–⟨⟩–CH_2–CH_2–⟨⟩–CN			
C_3H_7/C_6H_{13}–⟨⟩–CH_2–CH_2–⟨⟩–NCS	1.05	4.82	21
C_5H_{11}/C_7H_{15}–⟨⟩–COO–⟨⟩–CN	2.69	4.43	29
C_5H_{11}–⟨⟩–⟨⟩–CN	1.01	6.27	55
C_4H_{11}/C_7H_{15}–⟨⟩–CH=N–⟨⟩–CN	3.60	5.36	39
C_5H_{11}/C_7H_{15}–⟨⟩–COO–⟨⟩–CN	4.10	6.48	70

The higher viscosity of the polar cyclohexylcyclohexane derivative (92) combined with a higher clarification temperature compared with the phenylcyclohexane analogue (69) suggests a denser packing of the bicyclohexane molecules, despite the fact that repulsion forces play the main role in the formation of the mesophase in these substances. A similar increase in viscosity and in activation energy can be seen also in the tricyclic derivatives of pyrimidine (183 and 185) having a cyclohexane fragment next to the CN group. At the same time, the lower values of T_{NI} for these compounds compared with the benzonitrile analogue (184) show that in such cases the molecule is apparently non-linear. Among substances consisting of tricyclic polar molecules, alkylcyclohexylpyrimidinylbenzonitrile (184) is optimal as regards viscosity and temperature for the preparation of liquid crystal materials.

The molecular shape and hence the viscosity and thermal stability of the test substance depend to a large extent on the atom of the –COO– bridge group to which the cyclohexane fragment is linked, which is clearly confirmed by many examples [compare the viscosities of the cyanophenyl esters of alkylcyclohexanecarboxylic acids and alkylcyclohexyl esters of cyanobenzoic acids (39 and 48, 40 and 49), alkylcyclohexyl alkylcyclohexylbenzoate and alkylcyclohexylphenyl alkylcyclohexanecarboxylate (200 and 225), the alkylphenyl and alkylcyclohexyl esters of alkylphenylbenzoic acids (206 and 221), and the analogous esters of alkylbicyclohexanecarboxylic acids (222 and 226)]. The comparison shows that substances with the C_nH_{2n+1}–⟨⟩–O– fragment have a lower viscosity and lower clarification temperature compared with substances having the C_nH_{2n+1}–⟨⟩–O– fragment. Among tricyclic non-polar compounds, methylphenyl propylbicyclohexanecarboxylate has the lowest viscosity and a fairly high clarification temperature, which makes it promising for practical application. A lower viscosity of alkoxy-compounds with –COO– bridges is achieved when the benzene ring is located between two oxygen atoms [compared with data for alkoxyphenyl akylbenzoates and alkylphenyl alkoxybenzoates (18 and 19) and also for alkoxyphenyl akylbiphenylcarboxylates and alkylphenyl alkoxybiphenylcarboxylates (208 and 209)].

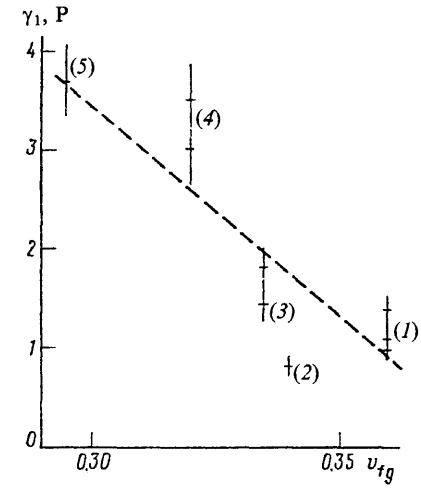


Figure 7. Relation between the rotational viscosity γ_1 of bicyclic polar compounds and the geometrical free volume $v_{fg} = 1 - k_p$, where k_p is the molecular packing coefficient determined from density measurements:

(*1*) – C_nH_{2n+1}–⟨⟩–⟨⟩–CN, (*2*) – C_nH_{2n+1}–⟨⟩–⟨⟩–CN,

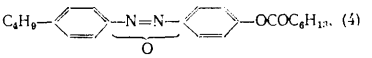
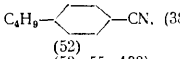
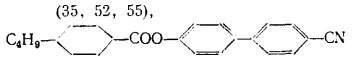
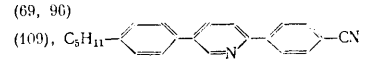
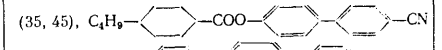
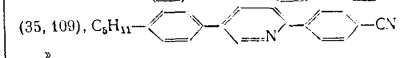
(*3*) – C_nH_{2n+1}–⟨N⟩–⟨⟩–CN, (*4*) – C_nH_{2n+1}–⟨⟩–⟨⟩–CN,

(*5*) – $C_nH_{2n+1}O$–⟨⟩–⟨⟩–CN

By way of principal conclusion, we emphasise that the viscosity of NLC is determined by the following molecular characteristics: the size and shape of the molecule, the polarisability of the substituents, and the dipole moment of the molecular skeleton. The tables can serve as a guide for the specific synthesis of new substances and the selection of existing compounds for the creation of liquid crystal materials with a specified fast response. We may note that the viscosities of liquid crystals in mixtures are not always additive. The properties of mixtures of NLC and liquid crystal materials have been

described[133,155–158] and constitute the subject of a separate study. For reference purposes, Table 17 presents the kinematic viscosities of various Soviet and foreign materials.

Table 17. The kinematic viscosities of Soviet and foreign liquid crystal materials.[156–158]

Designation	Compound •	$10^3\ \nu$, S (20 °C)
LC-440	 (4)	37.07
LC-616	LC-440, (22)	41.8
LC-654	»	51.4
LC-805	(38)	51.96
LC-910	 (38)	30
LC-609	(52)	32.31
LC-807	(52, 55, 132)	69.58
E7 (BDH, England)	(52, 132)	44
LC-1282	(35, 52, 55), 	52
LC-1289	ditto	41
LC-1290	»	43
P-52 (Chisso, Japan)		40
SP-706C (DNT, Japan)		32.13
E-202, 210 (BDH)		24.7
LC-1350	(35, 61, 69, 138, 143)	22
LC-1351	ditto	19
LC-1390	(60, 61, 69, 135, 143)	24.45
LC-1391	ditto	21.30
NP-1565 (Merck, FRG)	»	19
ZLI-1957/5 (Merck, FRG)		18
ZLI-2471 (Merck, FRG)		17
ZLI-2081		14
RO-3652		η = 16 cP (T = 22° C)
RO-2915 (Hoffmann–La Roche, Switzerland)		η = 22 cP (T = 22° C)
LC-1133	(69, 96)	36.7
LC-1144	(109), 	78.3
LC-1281	(35, 45), 	32
LC-1283	(35, 109), 	66
LC-1285	»	58
LC-999	LC-440, (42, 246)	36.4
LC-1000	(18, 42, 246)	62.1

*The numbers of the compounds in Table 1 are indicated in round brackets.

References

1. B C Benicewicz, J F Johnson *Mol. Cryst. Liquid Cryst.*, 1981, **65** 111
2. P G de Gennes *The Physics of Liquid Crystals* (Translated into Russian), Izd. Mir, Moscow, 1982, 152 pp
3. F-J Bock, H Kneppe, F Schneider *Liquid Cryst.*, 1986, **1** 239
4. H Kneppe, F Schneider, N K Sharma *J. Chem. Phys.*, 1982, **77** 3203
5. P R Gerber, M Schadt *Z. Naturforsch. A.*, 1982, **37** 179
6. V N Tsvetkov *Zh. Eksp. Teor., Fiz.*, 1939, **9** 602
7. H Kneppe, F Schneider *J. Phys. E. Sci. Instrum.*, 1983, **16** 512
8. L T S Siedler, A J Hyde, R A Pethrick, F M Leslie *Mol. Cryst. Liquid Cryst.*, 1983, **90** 255
9. J W Van Dijk, W W Beens, W H De Jeu *J. Chem. Phys.*, 1983, **79** 3888
10. V G Chigrinov, M F Grebenkin *Kristallografiya*, 1975, **20** 1240
11. Hp Schad *J. Appl. Phys.*, 1983, **54** 4994
12. W Helfrich *J. Chem. Phys.*, 1972, **56** 3187
13. P R Gerber *Appl. Phys.*, 1981, **A26** 139
14. S A Ivanov, V Yu Vetrov *Kristallografiya*, 1982, **27** 1014
15. J P Van der Meulen, R J J Zijlstra *J. Phys. (Paris)*, 1984, **45** 1347
16. V V Belyaev, S A Ivanov, M F Grebenkin *Kristallografiya*, 1985, **30** 1160
17. V V Belyaev, M F Grebyonkin, S A Ivanov *6th Liquid Crystal Conference of Socialist Countries, Abstracts, Halle, DDR*, 1985, p. 82
18. A C Diogo, A F Martins *Mol. Cryst. Liquid Cryst.*, 1981, **66** 133
19. D Demus, H Demus, H Zaschke *Flussige Kristalle in Tabellen I.* VEB Deutscher Verlag Grundstoffindustrie, Leipzig, 1976; D Demus, H. Zaschke *Flussige Kristalle in Tabellen. II*, VEB Deutscher Verlag Grundstoffindustrie, Leipzig,, 1984.
20. V M Aver'yanov, V A Zhuikov, V F Shabanov, P V Adomenas *Kristallografiya*, 1982, **27** 333
21. E G Hanson, Y R Shen *Mol. Cryst. Liquid Cryst.*, 1976, **36** 193
22. W H De Jeu, W A P Claassen *J. Chem. Phys.*, 1978, **63** 102
23. L Bata, A Buka, G Molnar *Mol. Cryst. Liquid Cryst.*, 1977, **38** 155
24. H Kneppe, V Reifenrath, F Schneider *Chem. Phys. Lett.*, 1982, **87** 59
25. W W Beens, W H De Jeu *J. Phys. (Paris)*, 1983, **44** 129
26. A Mukoh, H Abe, T Kitamura *Mol. Cryst. Liquid Cryst.*, 1983, **94** 155
27. H Takatsu, K Takeuchi, Y Tanaka, M Sasaki *Mol. Cryst. Liquid. Cryst.*, 1986, **141** 279
28. F Leenhouts, W H De Jeu, A J Dekker *J. Phys. (Paris)*, 1979, **40** 989
29. J P Van der Meulen, R J J Zijlstra *J. Phys. (Paris)*, 1984, **45** 1347
30. D H McQueen, V K Singhal *J. Phys. D; Appl. Phys.*, 1974, **7** 1983
31. S Meiboom, R G Hewit *Phys. Rev. Lett.*, 1973, **30** 261
32. M G Kim, S Park, M Cooper Sr, S V Letcher *Mol. Cryst. Liq. Cryst.*, 1976, **36** 143
33. W Zwetkoff, A Sosnovsky *Acta Physicochim. URSS*, 1943, **18** 358; C K Yun *Phys. Lett. A*, 1973, **43** 369
34. DIC Recent Liquid Crystal, Materials Produced by the Dai Nippon (Japan) Company, 1988
35. J D Margerum, S-M Wong, J E Jensen, et al. *Mol. Cryst. Liquid Cryst.*, 1985, **122** 97
36. J Constant, E P Raynes *Mol. Cryst. Liquid Cryst.*, 1981, **70** 105
37. B.P. 3695 (US P. 4462924); *Chem. Abs.*, 1980, **93** 58293j
38. J D Margerum, J E Jensen, A M Lackner *Mol. Cryst. Liquid Cryst.*, 1981, **68** 137
39. V V Belyaev, A A Gerasimov, M F Grebenkin, L N Lisetskii *Zh. Eksp. Teor. Fiz.*, 1984, **86** 955
40. R Eidenschink *Chem. in unserer Zeit*, 1984, **5** 168
41. US P. 4430498; *Chem. Abs.*, 1982, **96** 199323t
42. H Schad, H P Zeller *Phys. Rev. A*, 1982, **26** 2940
43. US P. 4454193; *Chem. Abs.*, 1984, **101** 156450g

44. H Schad, S M Kelly *J. Chem. Phys.*, 1984, **81** 1514
45. Europ. P. 155 792; *Chem. Abs.*, 1986, **104** 120167x
46. Japanese P. 61/030 565; *Chem. Abs.*, 1986, **105** 106322H
47. D Demus, H Zaschke *Mol. Cryst. Liquid Cryst.*, 1981, **63** 129
48. S G Polushin, T A Rotinyan, M A Agafonov *V Vsesoyuznaya Nauchnaya Konferentsiya 'Zhidkie Kristally i Ikh Prakticheskoe Ispol'zovanie': Tezisy Dokladov. Ivanovo* (The V All-Union Scientific Conference on 'Liquid Crystals and Their Practical Applications': Abstracts of Reports. Ivanovo), 1985, Vol. 1, Books 1 and 2, p. 12
49. E Merck (FRG) *Publicity Leaflet*, 1988
50. R Buchecker, M Schadt *Mol. Cryst. Liquid Cryst.*, 1987, **149** 359
51. J D Margerum, S-M Wong, A M Lackner, J E Jensen *Mol. Cryst. Liquid Cryst.*, 1981, **68** 157
52. M Schadt, R Buchecker, F Leenhouts, et al. *Mol. Cryst. Liquid Cryst.*, 1986, **139** 1
53. Y Goto, S Sugimori, T Ogawa *Proceedings of the 6th International Display Research Conference 'Japan Display'*, Tokyo, 1986, p. 324
54. H Takatsu, K Takeuchi, H Sato *Mol. Cryst. Liq. Cryst.*, 1984, **112** 165
55. BRD P. 3 317 921; *Chem. Abs.*, 1984, **100** 148628q
56. T Inukai, K Furukawa, H Inoue, K Terashima *Mol. Cryst. Liquid Cryst.*, 1983, **94** 109
57. V V Belyaev, M F Grebenkin, L N Lisetskii *Zh. Fiz. Khim.*, 1988, **62** 3087 [English translation in *Russ. J. Phys. Chem.*, 1988(11)]
58. Europ. P. 87 102; *Chem. Abs.*, 1984, **100** 15416x
59. BRD P. 3 029 378; *Chem. Abs.*, 1981, **94** 217673x
60. BRD P. 2 548 360; *Chem. Abs.*, 1977, **87** 46607c
61. V V Belyaev, M F Grebenkin *Kristallografiya*, 1983, **28** 1003
62. M J Bradshaw, D G McDonnel, E P Raynes *Mol. Cryst. Liquid Cryst.*, 1981, **70** 289
63. D G McDonnel, E P Raynes, R A Smith *Mol. Cryst. Liquid Cryst.*, 1985, **123** 169
64. A G Chmielewski *Mol. Cryst. Liquid Cryst.*, 1986, **132** 339
65. J Constant, E P Raynes *Mol. Cryst. Liquid Cryst.*, 1980, **62** 115
66. BRD P. 3 216 281; *Chem. Abs.*, 1983, **98** 135314z
67. Europ. P. 171 794; *Chem. Abs.*, 1986, **105** 143704e
68. BRD P. 3 151 367; *Chem. Abs.*, 1983, **99** 149641m
69. US P. 4 211 666; *Chem. Abs.*, 1980, **92** 41593p
70. R Eidenschink *Mol. Cryst. Liquid Cryst.*, 1983, **94** 119
71. H Takatsu, K Takeuchi *Mol. Cryst. Liquid Cryst.*, 1986, **138** 231
72. R Eidenschink *Mol. Cryst. Liquid Cryst.*, 1985, **123** 57
73. Europ. P. 14 840; *Chem. Abs.*, 1981, **94** 121064y
74. Europ. P. 194 879; *Chem. Abs.*, 1987, **106** 186647b
75. Europ. P. 119 756; *Chem. Abs.*, 1985, **102** 24260k
76. M Schadt, M Petrzilka, P Gerber, A Villiger *Mol. Cryst. Liquid Cryst.*, 1985, **122** 241; M Schadt, M Petrzilka *Proc. SID*, 1985, **26** 117
77. US P. 4 468 340; *Chem. Abs.*, 1983, **99** 149639s
78. M Schadt, R Buckecker, A Villiger, et al. *IEEE Transactions on Electron Devices*, 1986, **ED-33** 1187
79. R Dabrowski, J Dziaduszek *Mol. Cryst. Liquid Cryst. Lett.*, **1984, 102** 155
80. R Dabrowski, J Dziaduszek, T Szezučiński *Mol. Cryst. Liquid Cryst.*, 1985, **124** 241
81. N Carr, G W Gray, D G McDonnel *Mol. Cryst. Liquid Cryst.*, 1983, **97** 13
82. Japanese P. 60/215 652; *Chem. Abs.*, 1986, **105** 162746m
83. BRD P. 3 420 110; *Chem. Abs.*, 1985, **103** 14653x
84. Europ. P. 90 548; *Chem. Abs.*, 1984, **100** 59667j
85. H M Abdullah, G W Gray, K J Toyne *Mol. Cryst. Liquid Cryst.*, 1985, **124** 105
86. B M Andrews, G W Gray, M J Bradshaw *Mol. Cryst. Liquid Cryst.*, 1985, **123** 257
87. Y Haramoto, H Kamogawa *Mol. Cryst. Liquid Cryst.*, 1985, **131** 210
88. Y Haramoto, H Kamogawa *Mol. Cryst. Liquid Cryst.*, 1985, **131** 101
89. B.P. 8 400 665 (US P. 4 698 176); *Chem. Abs.*, 1986, **104** 139427
90. Europ. P. 194 153; *Chem. Abs.*, 1987, **106** 93752s
91. M F Grebyonkin, V F Petrov, V V Belyaev, et al. *Mol. Cryst. Liquid Cryst.*, 1985, **129** 245
92. M F Grebenkin, A V Ivashchenko *Zhidkokristallicheskie Materialy* (Liquid Crystal Materials), Izd. Khimiya, Moscow, 1989
93. Europ P. 123 907; *Chem. Abs.*, 1985, **102** 141028b
94. US P. 4 640 795; *Chem. Abs.*, 1987, **106** 129480t
95. Europ. P. 193 191; *Chem. Abs.*, 1987, **106** 41728u
96. Japanese P. 62/010 083; *Chem. Abs.*, 1987, **107** 68350x
97. H-J Deutscher, W Schäfer, M Keil, et al. *Z. Chem.*, 1984, **24** 406
98. G W Gray, D Lacey *Mol. Cryst. Liquid Cryst.*, 1983, **99** 123
99. DDR P. 227 721; *Chem. Abs.*, 1986, **105** 143703d
100. L K M Chan, G W Gray, D Lacey *Mol. Cryst. Liquid Cryst.*, 1985, **123** 185
101. Japanese P. 59/039 876; *Chem. Abs.*, 1984, **101** 171276c
102. BRD P. 3 139 130; *Chem. Abs.*, 1982, **97** 109680a
103. Europ. P. 96 850; *Chem. Abs.*, 1984, **100** 148629r
104. BRD P. 2 701 591; *Chem. Abs.*, 1978, **89** 215805e
105. US P. 4 422 951; *Chem. Abs.*, 1983, **98** 98883m
106. Japanese P. 59/161 348; *Chem. Abs.*, 1985, **102** 112938t
107. BRD P. 3 148 448; *Chem. Abs.*, 1981, **94** 183325k
108. I R Davison, D Muriel Hall *Mol. Cryst. Liquid Cryst.*, 1985, **129** 17
109. US P. 4 603 485
110. US P. 4 640 796; *Chem. Abs.*, 1985, **105** 181666b
111. Japanese P. 61/280 489; *Chem. Abs.*, 1987, **107** 124744t
112. DDR P. 226 891; *Chem. Abs.*, 1986, **104** 216675h
113. A Villiger, A Boller, M Schadt *Z. Naturforsch B*, 1979, **34** 1535
114. S I Torgova, A G Abolin, L A Karamysheva, A V Ivashchenko *Zh. Org. Khim.*, 1988, **24** 192
115. US P. 4 390 467; *Chem. Abs.*, 1984, **101** 101302j
116. BRD P. 2 613 293; *Chem. Abs.*, 1977, **87** 37448v
117. Europ. P. 202 514; *Chem. Abs.*, 1987, **106** 186669k
118. Europ. P. 61/207 359; *Chem. Abs.*, 1987, **106** 205733v
119. BRD P. 3 510 795; *Chem. Abs.*, 1986, **104** 79323e
120. L K M Chan, R A Gemmel, G W Gray, et al. *Mol. Cryst. Liquid Cryst.*, 1987, **147** 113
121. Europ. P. 94 198; *Chem. Abs.*, 1984, **100** 112368r
122. BRD P. 3 342 631; *Chem. Abs.*, 1985, **103** 186953m
123. H Takatsu, K Takeuchi, H Sato *Mol. Cryst. Liquid Cryst.*, 1984, **108** 157
124. P Balkwill, D Bishop, A Pearson, I Sage *Mol. Cryst. Liquid Cryst.*, 1985, **123** 1
125. DDR P. 260 127 (BRD P. 3 427 119); *Chem. Abs.*, 1986, **104** 120173w
126. Europ. P. 255 700; *Chem. Abs.*, 1988, **109** 102368n
127. Japanese P. 61/151 150; *Chem. Abs.*, 1987, **106** 205364a

128. US P. 4 519 936
129. Europ. P. 152 014; *Chem. Abs.*, 1986, **104** 177856a
130. Japanese P. 60/078 972; *Chem. Abs.*, 1985, **103** 105003b
131. M G Clark, J Harrison *Appl. Phys.*, 1973, **47** 13
132. H Kresse, D Demus, S Wrobel, et al. *Acta Phys. Polon.*, 1980, **A57** 699
133. H Kneppe, F Schneider *Mol. Cryst. Liquid Cryst.*, 1983, **97** 219
134. A Hauser, R Rettig, C Selbmann, et al. *Cryst. Res. Technol.*, 1984, **19** 261
135. H Kresse, M Keil, W Weissflog *Cryst. Res. Technol.*, 1983, **18** 563
136. H Takatsu, K Takeuchi *Mol. Cryst. Liquid Cryst.*, 1983, **100** 345
137. Europ. P. 84 974; *Chem. Abs.*, 1984, **100** 15786t
138. BRD P. 3 117 152; *Chem. Abs.*, 1983, **98** 106943y
139. BRD P. 3 223 637; *Chem. Abs.*, 1983, **98** 225350n
140. Europ. P. 99 099; *Chem. Abs.*, 1984, **100** 191435m
141. S I Torgova, A G Abolin, K V Roitman, et al. *Zh. Org. Khim.*, 1988, **24** 199
142. Europ. P. 90 671; *Chem. Abs.*, 1984, **100** 148624k
143. US P. 4 592 857
144. US P. 4 617 141; *Chem. Abs.*, 1984, **100** 148629r
145. Japanese P. 61/158 937; *Chem. Abs.*, 1987, **106** 205373c
146. H Gasparoux, J Prost *J. Phys. (Paris)*, 1971, **32** 953
147. O Ya Shmelev, V A Balandin *V Vsesoyuznaya Nauchnaya Konferentsiya 'Zhidkie Kristally i Ikh Prakticheskoe Ispol'zovanie': Tezisy Dokladov. Ivanovo* (The V All-Union Scientific Conference on 'Liquid Crystals and Their Practical Applications': Abstracts of Reports. Ivanovo), 1985, Vol. 2, Books 1 and 2, p. 9
148. S A Ivanov, V Yu Vetrov, P Adomenas, R Sirutkaitis *V Konferentsiya Sotsialiticheskikh Stran po ZhK: Tezisy Dokladov. Odessa* (The V Conference of Socialist Countries on Liquid Crystals: Abstracts of Reports. Odessa), 1983, p. 17
149. L Pohl, R Eidenschink, G Krause, D Erdmann *Phys. Lett.*, 1977, **60A** 421
150. L Pohl, R Weber, R Eidenschink *XI Freiburgerarbeitstagung*, Freiburg, 1979
151. V I Minkin, O A Osipov, Yu A Zhdanov *Dipol'nye Momenty v Organicheskoi Khimii* (Dipole Moments in Organic Chemistry), Izd. Khimiya, Leningrad, 1968
152. O A Osipov, V I Minkin, A D Garnovskii *Spravochnik po Dipol'nym Momentam* (Handbook of Dipole Moments), Izd. Vys. Shkola, Moscow, 1971
153. G W Gray *Mol. Cryst. Liquid Cryst. Lett.*, 1985, **124** 89
154. BRD P. 3 136 624; *Chem. Abs.*, 1983, **99** 70370p
155. V V Belyaev, M F Grebenkin *Kristallografiya*, 1984, **29** 815
156. V V Belyaev, M F Grebenkin, E I Kovshev, G G Slashcheva *III Nauchno-Tekhnicheskii Seminar 'Opticheskie Svoistva Zhidkikh Kristallov i Ikh Primenenie': Tezisy Dokladov. Leningrad* (The III Science and Engineering Seminar on the 'Optical Properties of Liquid Crystals and Their Applications': Abstracts of Reports. Leningrad), 1983, p. 51
157. V F Petrov, M F Grebenkin, V V Belyaev, A V Ivashchenko *III Nauchno-Tekhnicheskii Seminar 'Opticheskie Svoistva Zhidkikh Kristallov i Ikh Primenenie': Tezisy Dokladov. Leningrad* (The III Science and Engineering Seminar on the 'Optical Properties of Liquid Crystals and Their Applications': Abstracts of Reports. Leningrad), 1983, p. 49
158. L M Blinov, E I Kovshev, V V Titov *Mol. Cryst. Liquid Cryst.*, 1981, **70** 267

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Acetylenic ethers and their analogues

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ABSTRACT. The latest data on the chemistry of acetylenic ethers, sulphides, selenides, and tellurides are considered: their methods of synthesis, physical properties, and reactivities in relation to various reagents. The principal applications of these compounds in fine organic synthesis are indicated.

The bibliography includes 455 references.

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I. Introduction

The vigorous development of the chemistry of acetylenic ethers and their sulphur, selenium, and tellurium analogues is associated with the high reactivity of these compounds, which makes them irreplaceable synthons in the specific synthesis of many classes of organic compounds. The principles of the chemistry of acetylenic ethers and sulphides have been examined in an exhaustive review.[1] It has been established that the regioselectivity of the addition of electrophiles and nucleophiles to acetylenic ethers can be predicted with a high degree of probability on the basis of the concept of the existence of a strong +M effect of the alkoxy-group. The mode of addition of electrophiles to acetylenic sulphides is determined by the same effect. On the other hand, the modes of addition of nucleophiles to acetylenic ethers and sulphides are different:

$$RC{\equiv}COR \xrightarrow{\overline{Nu}} R\bar{C}{=}C(Nu)OR,$$
$$RC{\equiv}CSR \xrightarrow{\overline{Nu}} RC(Nu){=}\bar{C}SR.$$

Numerous studies of the regioselectivity of the addition of various reagents to acetylenic chalcogenides, studies undertaken to determine the characteristic features of their electronic structure, and studies involving attempts to predict the regioselectivities from the standpoint of the structure–reactivity concept were published subsequently. However, the fragmentary character of the existing new reviews[2–6] precludes the assessment of the state of the problem as a whole.

The aim of the present review is the analysis of the current state of the chemistry of acetylenic ethers and their analogues and also the principal directions of its development.

II. Methods of synthesis

During the last 20 years, the existing methods of synthesis of acetylenic ethers and their analogues have been significantly improved and new procedures have been developed. The following general methods have been developed further: dehydrohalogenation of halogen-containing ethers and their analogues, the substitution of the halogen in halogenoacetylenic compounds, the reactions involving the elimination of mercaptans and alcohols, isomerisation with migration of multiple bonds, and the reactions of metal acetylides and alkali metal ethynoxides.[1]

Acetylenic ethers, sulphides, and selenides as well as their halogeno-derivatives have been obtained by the dehydrohalogenation of various saturated and ethylenic αβ- and ββ-dihalogenoethers and their analogues.[7–16]

Ethoxyethyne can be obtained particularly conveniently by the dehydrobromination of 1-bromo-2-ethoxyethene with potassium hydroxide in diglyme[17] or petroleum ether.[18,19]

The dehydrohalogenation of saturated βββ-trifluoro-substituted ethers and sulphides with the aid of lithium alkyls lengthens the hydrocarbon chain.[20] Alkylthio(seleno)ynamines $R_2NC{\equiv}CXR$ (X = S, Se) have been obtained by dehydrohalogenation with lithium dialkylamides.[21–23] The dehydrohalogenation of ββ-dichlorovinylorganyl sulphides with the aid of potassium mercaptides results in the formation of di(organylthio)acetylenes.[24,25] The dialkoxyacetylenes with an analogous structure are unstable; dimethoxyacetylene has been detected only by NMR spectroscopy in pentane at −40 °C:[26]

$$Z\text{-}CH_3OCCl{=}CHOCH_3 \xrightarrow[NH_3(liq.)]{NaNH_2} CH_3OC{\equiv}COCH_3.$$

Di-t-butoxyacetylene is the most stable; it can be stored at room temperature for several days.[27]

A vinylethynyl sulphide has been synthesised in 60% yield by the opening of the ring in 1,1-dichloro-2,2-dimethyl-3-phenylthiocyclopropane with subsequent dehydrochlorination of the 1,3-dienyl sulphide:[28,29]

$$C_6H_5SCH\text{—}C(CH_3)_2 \xrightarrow{(CH_2)_3COK} C_6H_5SCH{=}CClC(CH_3){=}CH_2 \xrightarrow{-HCl}$$
$$\xrightarrow{-HCl} C_6H_5SC{\equiv}CC(CH_3){=}CH_2.$$

A series of diacetylenic sulphides have been synthesised by the dechlorination of chlorine-containing 1,3-dienyl or vinylethynyl sulphides:[30]

$$RSCCl{=}CClCCl{=}CCl_2 \xrightarrow[-70\ ^\circ C]{C_4H_9Li} RSC{\equiv}CC{\equiv}CLi \xrightarrow{R^1Hal} RSC{\equiv}CC{\equiv}CR^1,$$

R = cycloalkyl, Ph; R^1 = H, $(CH_3)_3Si$, $(C_6H_5)_3Sn$, organyl.

A method of synthesis of an ethynyl vinyl sulphide has been developed:[31]

$$(CH_3)_3SiC{\equiv}CSCH_2CH_2Cl \xrightarrow[NH_3(liq.)]{LiNH_2} LiC{\equiv}CSCH{=}CH_2 \xrightarrow{H_2O} HC{\equiv}CSCH{=}CH_2.$$

Phenylethynyl ethers have been obtained in a low yield from phenylethynyl halides on treatment with alkoxides:[32,33]

$$C_6H_5C{\equiv}CX \xrightarrow{RONa} C_6H_5C{\equiv}COR,$$
$$X = Cl, Br;\quad R = alkyl.$$

A reaction mechanism, including addition, β-elimination and sulphenium ion formation stages, has been proposed as a result of a study of the nucleophilic substitution of chlorine in t-butylchloroacetylene by the thiophenoxide ion.[34,35] The rate constants for the substitution of a halogen[36] are correlated with Charton's steric constants of the alkylthio-groups σ_{SR}.[37]

Substituted acetylenic ethers,[38,39] sulphides,[38,41] and selenides[40,41] as well as ethynyl vinyl sulphides[42,43] have been obtained from the corresponding acetylenic halides by a similar procedure.

A two-stage method of synthesis of terminal ethynyl sulphides has been developed. It is based on the reaction of chloroethynyldimethylcarbinol with alkali metal thiolates and subsequent cleavage of the resulting dimethyl(organylthioethynyl)carbinol by heating with potassium hydroxide.[3,44–46] Terminal acetylenic ethers have been obtained similarly but in low yields.[47,48]

Halogen-containing acetylenic ethers and sulphides enter into the reaction involving the nucleophilic substitution of the halogen on treatment with organometallic compounds:[3,24,49–51]

$$RZC{\equiv}CX + R^1M \rightarrow RZC{\equiv}CR^1 + MX,$$
$$Z{=}O: R{=}C_2H_5;\ X{=}I;\ R^1{=}Ar;\ M{=}Cu{\cdot}MgBr_2;$$
$$Z{=}S: R = alkyl,\ C_6H_5;\ X = Cl, Br;\ R^1 = organyl;$$
$$N(C_2H_5)_2;\ M{=}Li,\ Cu{\cdot}MgX_2.$$

Chloroethynyl organyl sulphides react with mercaptoethanol in the presence of potassium hydroxide to form di(organylthio)-acetylenes.[52] The reactions with secondary amines have afforded organylthioynamines,[14,53,54] while those with tertiary amines and phosphines gave rise to ammonium and phosphonium salts:[14,15,55]

$$RSC{=}CCl \xrightarrow{HNR^1_2} RSC{\equiv}CNR^1_2,$$
$$R = alkyl;\ R^1_2N = morpholinyl, piperidinyl, piperazinyl.$$

$$[RSC{\equiv}CP(C_2H_5)_3]^+Cl^- \xleftarrow{(C_6H_5)_3P} RSC{\equiv}CCl \xrightarrow{R^1_3N} [RSC{\equiv}CNR^1_3]^+Cl^-,$$
$$R, R^1 = alkyl.$$

Trialkyl phosphites react with chloroethynyl organyl sulphides in accordance with the mechanism of the Arbuzov rearrangement to form organylthioethynylphosphonates:[15,56]

$$RSC{\equiv}CCl + P(OR^1)_3 \rightarrow RSC{\equiv}CP(O)(OR^1)_2 + R^1Cl;\ R, R^1 = alkyl.$$

The 1,4-elimination of a mercaptan from 1,4-dialkyl- or 1,4-di(phenylthio)but-2-ynes on treatment with potassium alkoxide in liquid ammonia by a standard procedure[1] led to high yields of vinylethynyl sulphides.[57] When an attempt was made to synthesise a vinylethynyl ether from 1,4-dialkoxybut-2-yne, ethynyl vinyl ether or a butatrienyl ether were obtained.[58] Vinylethynyl ethers were synthesised by treating compound (I) with ethyllithium:[59]

$$ROCH{=}C{=}CHCR^1R^2OR \xrightarrow{C_2H_5Li} ROC{\equiv}CCH{=}CR^1R^2,$$
(I)

$$R = alkyl;\ R^1, R^2 = H, alkyl, cyclopentyl.$$

A mixture of ethynyl and 1,3-dienyl sulphides was obtained by the isomerisation of 1-t-butylthiobuta-2,3-diene in the presence of sodium ethoxide in alcohol.[60] The study of the kinetics of the isomerisation of propargyl selenides to methylethynyl selenides established the carbanionic nature of the intermediate compound.[61]

The isomerisation of allenic sulphides to acetylenic sulphides can be induced by catalytic amounts of an amine or on heating.[62] During the formation of propargyl sulphides, their isomerisation to allenic and acetylenic sulphides is frequently observed.[63]

Metal acetylides have found extensive application as the starting materials for the synthesis of acetylenic sulphides and their analogues. An ethynyl sulphide has been obtained by refluxing copper phenylacetylide with 4,6,8-trimethyl-1-thiocyanato-azulene in dimethylformamide (DMF).[64] The Iotsich reagent reacts with arenesulphenyl chloride to form acetylenic sulphides.[65] Acetylenic selenides have been obtained by the reaction of silver[66] or lithium[67] acetylide with benzene selenyl bromide. Arylethynyl tellurides have been prepared by treating metal acetylides with arene-tellurenyl halides.[68,69]

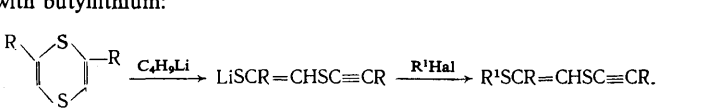
The reaction of lithium acetylide with α-bromodithioisobutyric acid ester leads to the formation of an ethynyl sulphide:[70]

$$(CH_3)_3CC{\equiv}CLi + (CH_3)_2CBrC(S)SCH_3 \rightarrow$$
$$\rightarrow (CH_3)_3CC{\equiv}CSC(SCH_3){=}C(CH_3)_2 + LiBr.$$

The first[1] and a series of subsequent attempts at the synthesis of ethynyl ethers from lithium alkylethynoxide[71] or an acetylenic potassium dithiolate,[72,73] by treating them with alkyl halides were unsuccessful. However, the reaction of lithium alkylethynoxide with trialkylsilyl chloride[74] or diethyl phosphorochloridite[75] leads to the formation of the corresponding ethynyl ethers.

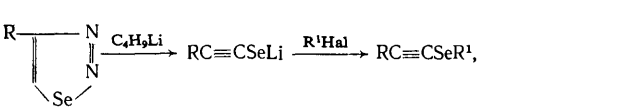
The simplest method of synthesis of ethynyl sulphides and their analogues became the reaction of a metal acetylide with the chalcogen and subsequent alkylation of the metal thiolate.[1] The methods of synthesis of acetylenic alkali metal thiolates have been published in reviews[76,77] and their use for the synthesis of ethynyl sulphides and their analogues has been described in a monograph.[78] A series of ethynyl sulphides,[3,79–84] selenides, and tellurides[41,69,85–87] have been obtained by this method. Dialkyl thiosulphonates have been used as alkylating agents for the synthesis of asymmetric di(alkylthio)acetylenes.[88] Acetylenic lithium thiolate has been used in an especially great variety of ways as the reagent for the synthesis of ethynyl sulphides.[89–98]

Ethynyl sulphides have also been obtained by treating 1,4-dithiines with butyllithium:[99]



$$R = H, alkyl;\ R^1 = alkyl.$$

Acetylenic lithium selenolates are obtained by treating substituted selenodiazoles with butyllithium:[100]



$$R = alkyl, aryl;\ R^1 = alkyl.$$

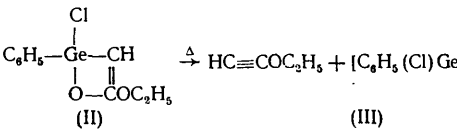
Acetylenic alkali metal thiolates (selenolates, tellurolates), which are ambient anions, enter into reactions involving the anionic 1,3-cycloaddition and nucleophilic addition to the triple bond, apart from the nucleophilic substitution of the metal.[100,101] Ethynyl selenides[100,102,103] and tellurides[100] are therefore frequently formed in a mixture with heterocyclic compounds.

Acetylenic potassium selenolates react with epichlorohydrin to substitute the chlorine atom or to cleave the epoxide ring.[104]

An ethynyl telluride has been obtained by oxidising sodium phenylethynyltellurolate with iodine:[105]

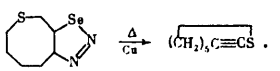
$$2C_6H_5C{\equiv}CTeNa \xrightarrow[-NaI]{I_2} [C_6H_5C{\equiv}CTeTeC{\equiv}CC_6H_5] \xrightarrow{-Te} \rightarrow C_6H_5C{\equiv}CTeC{\equiv}CC_6H_5.$$

A new aspect of the methods of synthesis of acetylenic ethers and their analogues is thermosynthesis. Thus ethoxyacetylene and a germoxane (III) have been obtained in 25–30% yield by the decomposition of the unstable compound (II):[106]



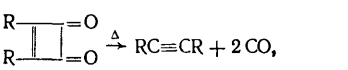
(II) (III)

1-Thiacyclooct-2-yne (V) was synthesised for the first time in 15% yield by heating compound (IV) in the presence of copper:[107]



(IV) (V)

Acetylenes have been obtained by the thermal decomposition of 3,4-di(methylthio)- or 3,4-di(methylseleno)cyclobutene-1,2-diones:[108]



R = CH_3S, CH_3Se.

Di(ethylthio)acetylene has been synthesised in 53% yield by the thermolysis of the phosphorylide (VI):[109]

$$(C_6H_5)_3\overset{+}{P}-\overset{-}{C}=C(SC_2H_5)_2 \xrightarrow{\Delta} C_2H_5SC{\equiv}CSC_2H_5.$$

(VI)

The thermolysis of the phosphorylides (VII) afforded internal ethynyl selenides:[110]

$$(C_6H_5)_3\overset{+}{P}-\overset{-}{C}(SeAr)COR \xrightarrow{\Delta} RC{\equiv}CSeAr,$$

(VII)

R = alkyl, aryl.

Terminal ethynyl ethers and sulphides can be readily converted into the corresponding internal compounds by the substitution of the terminal hydrogen atom by metals. Thus various element-containing and functional derivatives of a metal-substituted ethoxyacetylene have been obtained from the latter:

$$C_2H_5OC{\equiv}CM \xrightarrow{RHal} C_2H_5OC{\equiv}CR,$$

M = Li, MgBr; R = CH_3CO (Ref.111), Alk_2P, Ar_2P (Refs.112, 113), $(CH_3)_3Si$ (Ref.2), $(CH_3)_2C_6H_5Si$ (Ref.114), Alk_3Ge, Alk_3Sn (Ref.6).

Lithium ethoxyethynylboranate has been synthesised by treating lithium ethoxyacetylide with a trialkylborane. Treatment of the boranate with iodine led to the synthesis of internal ethynyl ethers in 30–58% yields:[115,116]

$$R_3B + LiC{\equiv}COC_2H_5 \xrightarrow[THF]{0°C} Li^+R_3\overline{B}C{\equiv}COC_2H_5 \xrightarrow{I_2} RC{\equiv}COC_2H_5,$$

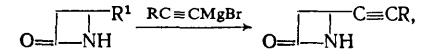
R = C_4H_9, $C_2H_5CHCH_3$.

The interaction of lithium ethoxyacetylide with epoxyethane or epoxypropane gave rise for the first time to vinylethynyl ethers.[117]

The reaction of dialkylamino(trialkyl)stannanes with ethoxyacetylene is a convenient method of synthesis of tin-containing ethynyl ethers.[6]

Phosphorus-containing ethynyl sulphides have been obtained from a methylthioacetylenic Iotsich reagent and phosphinic acid chlorides.[118]

The reaction of ethoxy- or phenylthio-ethynylmagnesium bromide with 4-benzenesulphonyl- or acetoxy-azetidine has been used to synthesise a heterocyclic ethynyl ether and sulphide:[119]



R = C_2H_5O, C_6H_5S; R^1 = $C_6H_5SO_2$, CH_3COO.

Alkynyl carboxylates and phosphates (X) have been obtained for the first time from the iodonium salts (VIII) by an ion-exchange reaction in the presence of an ion-exchange resin saturated with the anion A^-.[75] In contrast to compounds (IX, A = $OCOR^1$), compounds [IX, A = $OP(O)(OC_2H_5)_2$] are stable crystalline substances:

$$[RC{\equiv}ClPh]^+\,Ts^- \xrightarrow{A^-} [RC{\equiv}ClPh]^+\,A^- \rightarrow RC{\equiv}CA + PhI,$$

(VIII) (IX) (X)

A = $OCOR^1$, $OP(O)(OC_2H_5)_2$; R = alkyl, R^1 = aryl.

III. Physical properties

The electronic structure of ethynyl ethers and their analogues has been investigated by various physical methods. Previously published studies involving the analysis of the dipole moments (d.m.) of ethynyl sulphides and ethers did not provide unambiguous data about the direction of polarisation of the triple bond in the $-C{\equiv}C-S-$ system.[1]

As a result of the investigation of the dipole moments of phenylethynyl sulphides and their analogues p-$YC_6H_4XC{\equiv}CR$ (R = H, C_6H_5; X = S, Se, Te; Y = H, CH_3, Cl, Br, CH_3O, NO_2), new studies led to the discovery of the dependence of the direction of polarisation of the triple bond on the character of the substituents at the heteroatom and at the triple bond.[120–130] It was shown that, in the case of electron-donating substituents, the sulphur, selenium, and tellurium atoms behave as π-donors in relation to the triple bond, which increases the $X-C_{sp}$ bond order. The character of the polarisation of the triple bond is the same in this case: $-XC^{\delta+}=C^{\delta-}-$. An electron-accepting substituent (Y = NO_2) reverses the direction of polarisation of the triple bond. The occurrence of direct conjugation in the $-XC{\equiv}CC_6H_4Y$ group with the varied substituent (Y) via the benzene ring with inversion of the direction of the shift of electron density in the triple bond on passing from Y = CH_3O to Y = NO_2 was established.

The dependence of the dipole moments of ethynyl sulphides on the induction constants of the ethynyl[81] and alkyl groups at the heteroatoms[131] confirms the high sensitivity of the $-C{\equiv}CX$-system to the influence of substituents.

The influence of Group VIA heteroatoms at the triple bond on the degrees of shielding of the carbon atoms is clearly manifested in the ^{13}C NMR spectra. The inversion of the relative shielding of the α- and β-carbon atoms of the triple bond on passing from ethers to sulphides has been adopted as evidence for the manifestation of the $-M$ effect by the alkylthio-group in contrast to the alkoxy-group.[132,133] The shielding of the α-carbon atoms and the deshielding of the β-carbon atoms increase linearly with decrease in the electronic activity of the heteroatom in the series of ethynyl chalcogenides.[134,135]

Correlation analysis of the ^{13}C NMR spectra of acetylenic compounds established the additivity of the contribution of the substituents to the chemical shifts of the carbon atoms of the triple bond. The effects of the substituents constitute a linear combination of their induction, resonance, and steric constants.[136,137]

The study of the NMR spectra of ethoxyacetylene[138] and silicon-, germanium-, and tin-containing ethynyl ethers[139–141] and sulphides[142] showed that the alkoxy-group is an effective *p*-donor in relation to the triple bond, while the alkylthio-group is a weak *p*-acceptor.[143] However, the deshielding of the tellurium atom in 1-methyltellurobut-3-en-1-yne compared with dimethyl telluride, established from the ^{125}Te NMR spectra,[144] may be a consequence of a weak electron-donating effect of the methyltelluro-group in relation to the triple bond.

The $^{77}Se-^{13}C$ spin–spin coupling constants (SSCC) of ethynyl selenides have been measured and the influence of the medium on the shielding of the ^{77}Se atoms has been investigated.[145–147]

The carbon atoms of the triple bond in di(ethylthio)acetylene are deshielded compared with the terminal ethynyl sulphides.[148]

An equation which simplifies the assignment of the signals of the carbon atoms of the triple bond in ethynyl sulphides and their analogues has been proposed.[149]

The intensity of the band due to the triple bond in the Raman spectrum of t-butylthioacetylene is approximately twice as great as in the spectrum of butylacetylene, which is evidence of an effect of the conjugation of the triple bond with the alkylthio-group.[150,151] The stretching vibration frequencies of the triple bond in the Raman spectra of phenylethynyl sulphides and their analogues, $CH_3XC{\equiv}CC_6H_5$ and $p\text{-}YC_6H_4XC{\equiv}CC_6H_5$ (X = S, Se, Te; Y = H, CH_3, CH_3O, F, Cl, Br, NO_2), decrease in the sequence S > Se > Te, whilst their integral intensities increase. It has been concluded that the sulphur and selenium atoms participate in the transmission of conjugation via the triple bond. In relation to tellurides, a distinct manifestation of this effect has not been observed.[126,152]

The intensity of the absorption bands of the triple bond in the IR spectra of ethoxy- and ethylthio-acetylenes is determined by the resonance interaction with the substituent. It has been shown that the sulphur atom in the molecules of methylthiophenylacetylene and 1-ethylthio-3,3-dimethylbut-1-yne is involved in conjugation with both π-bonds of the acetylenic fragment.[153] The integral intensities of the triple bond in ethoxy- and phenoxy-acetylenes are not correlated with the induction constants of the substituents.[154]

The force constants of the bonds in the molecules of methoxyacetylene and trimethylsilylmethoxyacetylene have been calculated.[155,156] The absorption bands in the IR spectrum of methylthioacetylene have been assigned.[151]

A combined study of the IR, UV, and NMR spectra of silicon-, germanium-, and tin-containing ethynyl ethers and sulphides demonstrated the occurrence of interaction via the triple bond.[143,157] It has been established that the intensity of the absorption bands of the triple bond in the IR spectra of structurally similar germanium- and tin- containing compounds depends on the inductive effect of the substituents. In the case of silicon-containing compounds, there is in addition the influence of the specific interaction of the silicon atom with the triple bond.

The possibility of an approximate quantum-mechanical approach to the description of the behaviour of the stretching vibration frequencies of the $C_{sp}-H$ bond in methoxyacetylene has been examined.[158]

Apart from the absorption bands assigned to the $\pi \rightarrow \pi^*$ electronic transition, the UV spectra of vinyl- and phenyl-ethynyl sulphides and their analogues contain a band which has been assigned to the $n \rightarrow \pi^*$ transition, the band being most pronounced in the spectra of the tellurides.[126,159–161] Analysis of the UV spectra indicates an increase in the degree of interaction of the heteroatoms with the triple bond in the electronically excited state in the direction Te < Se < S, which is the opposite of the direction of variation in the ground state. This interaction can be attributed to the variation of the ionisation potentials, diminishing on passing to the tellurides, which promotes charge transfer to the triple bond in the excited state. The ionisation potentials of ethynyl sulphides have been obtained in the study of the mass spectra[162,163] and those of the sulphides and selenides have been determined by the method of photoelectron ionisation.[108,164] The ionisation potentials of di(methylthio)acetylene have been calculated by the MNDO method.[165]

The photoelectron spectra of 1-ethoxybut-3-en-1-yne[166] and ethynyl sulphides have been obtained.[167] Radicals have been detected in the laser photoionisation of the deuterium-containing di(methylthio)acetylene[168] and a radical-cation has been detected in the radiation-induced ionisation of methoxyacetylene.[169]

The decrease in the $C_{sp}-X$ bond length in methoxyacetylene,[170,171] ethoxyacetylene,[172] and methylthio-[173] and ethylthio-acetylenes,[174] established by microwave spectroscopy, may be a consequence of the effect of p,π conjugation. The potential energy of the internal rotation of the methylthio-group in methylthioacetylene is higher than that of the methoxy-group in methoxyacetylene,[175] which has not so far been satisfactorily explained. The microwave spectrum of ethoxyacetylene has been used in a computer program for the identification of the radiospectra of the molecular clouds in space.[176]

It has been established by gas electron diffraction that the di(methylthio)acetylene molecule exists preferentially as the conformer with a CSSC dihedral angle of 86°.[148]

The study of the X-ray fluorescence *K* spectra of sulphur in aryl and pentafluorophenylethynyl sulphides established that the *d* orbitals of sulphur are appreciably populated with retention of the p,π conjugation effects.[65]

The formation energies of methoxy- and methylthio-acetylenes,[177] the geometrical parameters of methoxyacetylene,[178] the distribution of electron density,[179] and the stabilisation energy[180,181] have been calculated by quantum-chemical methods.

Thus the triple bond in ethynyl sulphides and their analogues differs from that in the ethynyl ethers by an increased sensitivity to the influence of substituents associated with the possibility of the manifestation of the effect of d,π interaction by the heteroatoms.

The differences between the electronic structures of ethynyl ethers and their analogues are manifested by the greater acidity of the terminal ethynyl sulphides compared with the ethers and acetylenic hydrocarbons.[150,182] A linear relation between the kinetic and thermodynamic CH acidities of ethynyl ethers or sulphides has been established.[183] The state of the exchange equilibrium in the ethoxyacetylene–*p*-fluorophenylethynylcyclohexylmercury has been investigated by ^{19}F and ^{1}H NMR.[184] The stabilisation energy of methoxyacetylene in the reaction involving the exchange of the methoxy-group has been calculated by the quantum-chemical method.[185]

The formation of hydrogen bonds in aryloxyacetylenes has been investigated by IR spectroscopy.[186] It has been shown that the basicity of ethoxyacetylene in the interaction with phenol depends on the inductive effect of the ethoxy-group.[187] The energy of the hydrogen bond between phenol and vinylethynyl sulphides, selenides, and tellurides increases on passing to the tellurides[188] in parallel with

the energy of the electronic excitation of the molecules. The oxygen or sulphur atom is the centre involved in the hydrogen bond with phenol in the molecules of silicon-, germanium-, and tin-containing ethynyl ethers and sulphides.[157]

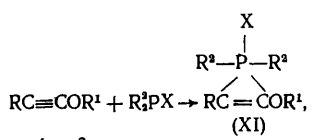
The antiparallel variation of the electronic structure of the molecules in the series of ethynyl ethers and their analogues with their susceptibility to the perturbing effect of reagents is manifested by the regioselectivity of the addition of the reagents to the triple bond in ethynyl sulphides.

IV. Chemical properties

1. The addition of electrophiles

It was established previously that the addition of electrophiles to ethynyl ethers and sulphides takes place with the attachment of the electrophilic component of the reagent to the β-carbon atom of the triple bond.[1] The addition of phosphorus pentachloride, phosphorus trihalides, dialkylhalogenophosphines, dialkyl phosphorohalidites, mercury chloride, Group IV element tetrachlorides, and trialkylstannyl chloride to ethynyl ethers proceeds in accordance with this rule.[2,6,189–195] Asymmetric di(alkylthio)- and di(arylthio)-acetylenes react with phosphorus pentachloride to form equal amounts of regioisomers.[196,197] Ethynyl sulphides react with phosphorus tribromide similarly to the ethers.[198] The reaction of 3-t-butyl-1-ethoxy-3-methylprop-1-yn-3-ol with phosphorus trichloride in the presence of pyridine leads to the formation of ethyl 2-dichlorophosphino-3,4,4-trimethylpent-2-enoic acid.[199]

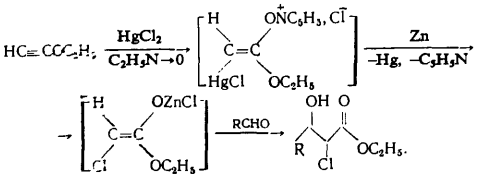
In the absence of a catalyst, new representatives of phosphirenes (XI) are formed in almost quantitative yields from dialkyl and diaryl-halogenophosphines by the reaction with internal ethynyl ethers:[200]



(XI)

R, R^1, R^2 = alkyl, aryl; X = Cl, Br.

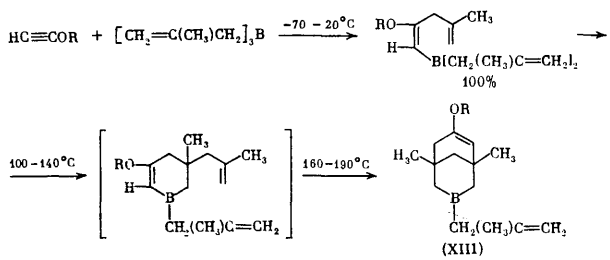
The successive treatment of ethoxyacetylene with mercury chloride, pyridine *N*-oxide, and zinc dust leads to the formation of the enolate (XII), which reacts with aldehydes to form α-chloro-β-hydroxyesters:[201]



(XII)

Triethylsilane reacts with phenoxyacetylene in the presence of a modified Speier catalyst predominantly with attachment of the triethylsilyl group to the β-carbon atom of the triple bond.[202] Triethylgermane reacts at the triple bond under similar conditions with 90% regioselectivity, forming a 1 : 1 mixture of the (*Z*)- and (*E*)-isomers.[203]

Boron-containing reagents, which we have formally classified as electrophilic, add to terminal ethynyl ethers with attachment of the boron atom to the β-carbon atom of the triple bond and the formation of ethylenic boranes. Thus the hydroboration of ethoxyacetylene[204,205] leads to the formation of tri(*trans*-2-ethoxyvinyl)-borane. The mode of addition of dialkyl- and triorganyl-boranes to ethoxyacetylene is similar.[204–209] The stereoselectivity of the addition of dialkylboranes to ethynyl selenides with subsequent acidolysis of the intermediate has been used to synthesise (*Z*)-vinyl selenide.[110,210,211] (*Z*)-β-Trimethylsilylvinyl ether has been obtained by the same method.[212] The allylboration of alkoxyacetylene proceeds stereoselectively as *cis*-addition.[213–215] Heating of the adduct leads to the allyl rearrangement with formation of the bicyclic borane (XIII):

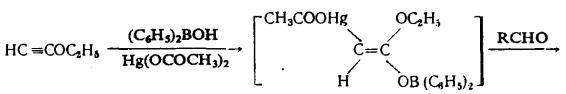


(XIII)

R = alkyl.

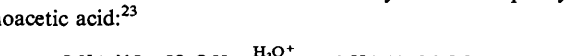
The use of the products of the addition of allylboranes to ethynyl ethers as synthons has been the basis of a method of synthesis of other unsaturated compounds. Thus 2-alkoxypenta-1,4-dienes have been synthesised[217] by the alcoholysis of the products of the addition of dialkylallylboranes to ethynyl ethers.[216] The addition of triallylborane to ethoxyacetylene and subsequent treatment of the products with triethylaluminium led to the synthesis of pent-1-en-4-yne.[218] The regioselectivity of the addition of the dialkylborylmethylcyclobut-1-ene–dialkylboryl-2-methylene-cyclobutane system is similar to the regioselectivity of the addition of allylboranes.[207]

Ethoxyacetylene reacts with aldehydes in the presence of diphenylboronic acid and mercury acetate with formation of approximately equal amounts of β-hydroxy- and β-acetoxy-esters.[219] The coupled addition of diphenylboronic acid and mercury acetate to ethoxyacetylene apparently takes place initially:



R = alkyl, aryl.

The study of the mechanism[3] and regioselectivity of the hydration reactions of internal ethynyl ethers and their analogues has been continued. Thus the hydration of diethylaminophenylselenoacetylene leads to the formation of the diethylamide of 2-phenylselenoacetic acid:[23]



The mode of hydration of 4,4-dichloro-1-methoxybut-1-yn-3-one[220] and 1-alkylselenobut-3-en-1-ynones[85] is similar to the familiar hydration reaction of ethynyl ethers.[1]

The product of the addition of two alcohol molecules to ethoxyacetylene can be used as a plasticiser of solid polymers.[221] Phenols react with ethoxyacetylene regiospecifically with formation of α-aryloxyvinyl ethers.[222]

The bromination of ethoxyacetylene[223] and phenoxyacetylene[224] leads to the formation of di- and tetra-bromides. The halogenation of vinylethynyl sulphides and selenides involves predominantly the triple bond.[225,226] The tetrabromide has been obtained by the

bromination of 1-methyltellurobut-3-en-1-yne as a result of the addition of bromine to the double bond and to the tellurium atom.[227]

The joint chlorination of ethoxyacetylene and epoxyethane afforded a chlorine-containing orthoester:[228]

$$HC{\equiv}COC_2H_5 + 2\,Cl_2 + 2\,CH_2{-}CH_2 \rightarrow CHCl_2C(OCH_2CH_2Cl)_2(OC_2H_5).$$

The interaction of ethynyl ethers with sulphur monochloride pentafluoride proceeds with substitution of the alkoxy-group and the formation of 2,2-difluoro-1-pentafluorothioethylene.[229]

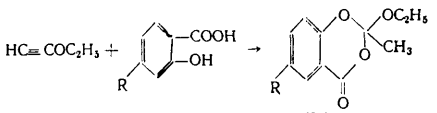
The hydrohalogenation of substituted ethynyl ethers[230] and sulphides[118] is regioselective[1] and proceeds in accordance with the *trans*-addition rule. The hydrochlorination of di(alkylthio)- and di(alkylseleno)-acetylenes proceeds predominantly as *trans*-addition with 80% regioselectivity for asymmetric di(alkylthio)acetylenes.[231] Vinylethynyl selenides combine with hydrogen chloride selectively via the triple bond:[232]

$$CH_2{=}CHC{\equiv}CSeR \xrightarrow{HCl} CH_2{=}CHCH{=}C(Cl)SeR,$$
$$R = \text{alkyl}.$$

The bond between the acetylenic carbon atom and tellurium in vinylethynyl tellurides is cleaved on treatment with hydrogen chloride.[232] The hydrochlorination of a diethynyl sulphide[233] and selenide[234] afforded only the 1,3-diene products of the addition of two molecules of hydrogen chloride: $C_2H_5CH{=}CClCH{=}CClXCH_3$ (X = S, Se). Calculation by the CINDO/2 method of the perturbation energy of the hydrochlorination reaction of vinylethynyl sulphides and selenides in an ionising solvent has led to the conclusion that the reaction is subject to orbital control.[234]

The mode of addition of carboxylic acids to ethynyl ethers[224,235–239] is of the usual type.[1] Acid anhydrides are formed from trimethylsilylethoxyacetylene by reaction with carboxylic acids.[240]

Ethoxyacetylene and 5-(4-fluorophenyl)salicylic acid react to form the benzodioxane (XIV), which has analgesic properties:[241]



(XIV)

$R = p\text{-}FC_6H_4.$

Certain products of the addition of carboxylic acids exhibit chemiluminescence[239,242] or can be recommended as UV-stabilisers of polymers.[238]

Alkanesulphonic acids in the form of pyridinium salts add to ethoxyacetylene with the usual mode of addition of the acid residue.[243]

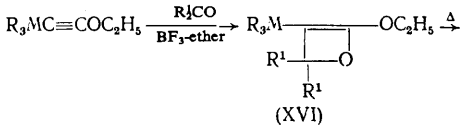
Fluorosulphonic acid adds to the ethoxyacetylene regiospecifically with formation of compound (XV):[244]

$$HC{\equiv}COC_2H_5 \xrightarrow[SO_2ClF,\ -60\ ^\circ C]{FSO_3H} CH_2{=}C(OC_2H_5)OSO_2F.$$
(XV)

Like the analogous ethynyl ethers, ethynyl sulphides[3] and vinylethynyl sulphides,[245] selenides,[246] and tellurides[188] combine with carboxylic acids chemoselectively via the triple bond with the usual mode of addition of the acid residue. On being refluxed in acetic acid, 1-methyltellurobut-3-en-1-yne is protodemetallated with formation of vinylacetylene. Di(alkylthio)acetylenes react with carboxylic acids to form predominantly the (*E*)-isomers of vinyl sulphides.[247]

Methanesulphenyl chloride adds to vinylethynyl sulphides at the triple bond with formation of 1-chloro-2-methylthiobutadienyl sulphides.[248]

One of the methods of synthesis of αβ-unsaturated acid esters is the reaction of ethynyl ethers with carbonyl compounds in the presence of boron trifluoride etherate.[249–252] Substituted oxetenes (XVI) are sometimes formed, isomerising on heating:



(XVI)

$$\rightarrow (CX)_2C{=}C(MR_3)COOC_2H_5,$$
$$M = Si, Ge;\ R^1 = CF_3,\ CF_2Cl,\ \text{alkyl};\ R = \text{alkyl},$$
$$R_3M = H,\ R^1 = CF_3,\ CF_2NO_2.$$

In the absence of the catalyst, trimethylstannylethoxyacetylene adds to ketones, the adduct isomerising to an α-stannylated acrylate after the addition of a catalyst:[250]

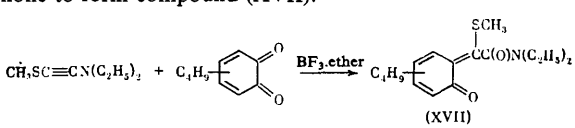
$$(CH_3)_3SnC{\equiv}COC_2H_5 \xrightarrow{(CF_2Cl)_2CO} (CF_2Cl)_2C[OSn(CH_3)_3]C{\equiv}$$
$$\equiv COC_2H_5 \xrightarrow{BF_3\text{.ether}} (CF_2Cl)_2C{=}CSn(CH_3)_3COOC_2H_5.$$

The reaction of diisopropylaminophenylselenoacetylene with perfluoroacetone leads to the formation of the amide of an αβ-unsaturated acid.[23]

$$(\text{iso-}C_3H_7)_2NC{\equiv}CSeC_6H_5 \xrightarrow[BF_3\text{.ether}]{(CF_3)_2CO} (CF_3)_2C_2{=}C(SeC_6H_5)CON(\text{iso-}C_3H_7)_2.$$

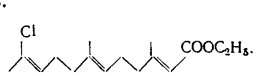
Phosgene[253] and acetyl chloride[254] add to internal ethynyl ethers with formation of α-chlorovinyl ethers.

Diethylamino(methylthio)acetylene reacts with a substituted *o*-quinone to form compound (XVII):[51]



(XVII)

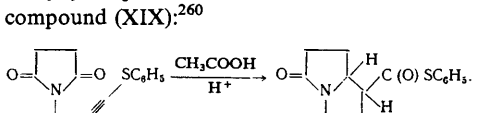
Ethoxyacetylene has been used in the synthesis of αβ-unsaturated esters,[255–257] among which compounds of type (XVIII) are juvenile-hormonal insecticides:[258]



(XVIII)

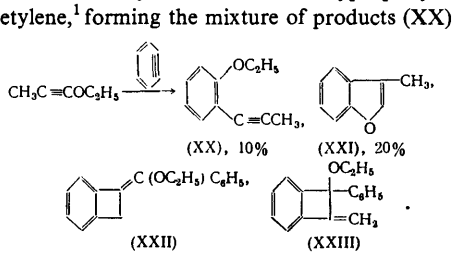
The reaction of terminal ethynyl sulphides with thiophenaldehydes afford esters of αβ-unsaturated thio-acids.[259]

The intramolecular addition of the carbonyl group to the triple bond of an ethynyl sulphide in an acid medium leads to the formation of compound (XIX):[260]



(XIX)

Dehydrobenzene readily reacts with 1-ethoxyprop-1-yne[261] as well as ethoxyacetylene,[1] forming the mixture of products (XX)–(XXIII):



(XX), 10% (XXI), 20%

(XXII) (XXIII)

The main product of the reaction of dehydrobenzene with ethylthioacetylene is benzothiophen.[261]

2. The addition of nucleophiles

The previously established different modes of addition of nucleophiles to ethynyl ethers and sulphides are usually interpreted from the standpoint of the concept of the mesomeric stabilisation of cryptoanions by the sulphur atom.[1] A new aspect of the study of the electrophilic activity of the triple bond in ethynyl ethers and sulphides involves the investigation of the addition of organometallic and organophosphorus reagents. The high regio- and stereoselectivities of the addition of organometallic reagents to ethynyl ethers and sulphides make it possible to obtain vinyl ethers and sulphides with a specified structure. Thus mixed organic copper-magnesium (lithium) compounds and Grignard reagents add to ethynyl ethers and sulphides with the mode of addition of the organic group characteristic of nucleophiles.[3,262–264] The hydrolysis of the intermediate and treatment with carbon dioxide or iodine lead to the formation of the *cis*-isomers of substituted vinyl ethers and sulphides:

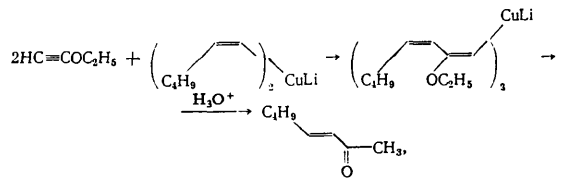
$$HC{\equiv}COC_2H_5 \xrightarrow{RCu.MgBr} [CH(Cu,\ MgBr){=}C(R)OC_2H_5] \xrightarrow[(CO_2,\ I_2)]{H_2O} \rightarrow XCH{=}C(R)OC_2H_5,$$

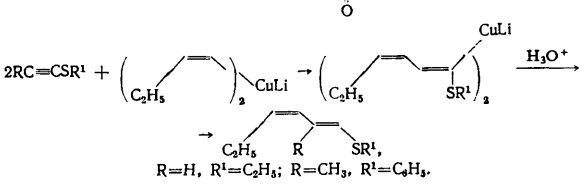
$$HC{\equiv}CSC_2H_5 \xrightarrow{RCU.MgBr} [RCH{=}C(Cu,\ MgBr)SC_2H_5] \xrightarrow[(CO_2,\ I_2)]{H_2O} \rightarrow RCH{=}C(X)SC_2H_5,$$

R = alkyl; X = H, COOH, I.

Phenylmagnesium bromide adds chemoselectively to 1-methylthiohexa-1,3-diyne in the presence of Ni^{2+} ions at the triple bond adjoining the sulphur atom with attachment of the phenyl group to the α-carbon atom and the predominant formation of (*E*)-ethynylvinyl sulphide.[265]

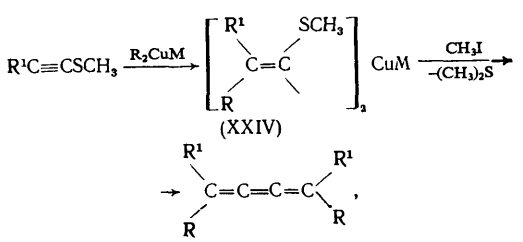
A vinylketone has been obtained by the reaction of an ethylenic lithium cuprate with ethoxyacetylene.[266] 1,3-Dienyl sulphides have been obtained from ethynyl sulphides under similar conditions:





R=H, $R^1=C_2H_5$; $R=CH_3$, $R^1=C_6H_5$.

The methylation of the intermediate (XXIV) by methyl iodide leads to the elimination of the methylthio-group and the formation of a vinylidene, which is converted into a cumulene hydrocarbon:[3,267]



R, R^1 = alkyl, M = MgHal, Li.

The copper-aluminium hydride complex adds to ethynyl sulphides regio- and stereo-selectively; (*Z*)-vinyl sulphides are formed after hydrolysis:[268]

$$RC{\equiv}CSR^1 \xrightarrow{\text{"CuH"}} [RCH{=}C(Cu)SR^1]^-Li^+ \xrightarrow{H_2O} RCH{=}CHSR^1,$$

R = alkyl, R^1 = alkyl, Ph; "CuH" = $LiCuHBr.Al(OCH_3)_3$.

In the absence of copper ions, the reaction with lithium trimethoxyhydroaluminate affords a mixture of regioisomers of (*E*)-vinyl sulphides.[269]

The 1,4-addition of alkylsilver to vinylethynyl sulphides leads to allenyl sulphides after hydrolysis:[270]

$$CH_2{=}CR^1C{\equiv}CSCH_3 \xrightarrow{RAg} RCH_2C(R^1){=}C{=}CHSCH_3,$$

R^1 = H, CH_3; R = alkyl.

Lithium alkyls add to ethynyl ethers with formation of allenyl and ethynyl ethers, whose ratio depends on the structure of the lithium alkyl, the ethynyl ether, and the solvent:[271]

$$R^2R^3C(OR^1)-C{\equiv}C-OR \xrightarrow{R^4Li} R^2R^3C{=}C{=}CR^4(OR) + R^2R^3C(OR^1)-C{\equiv}C-R^4,$$

R, R^1 = alkyl; R^2, R^3 = H, alkyl; R^4 = alkyl, Ph.

The chemoselective addition of lithium alkyls to the double bond in vinyl ethynyl sulphides is a convenient method of synthesis of allenyl sulphides.[272–274] The ambient nature of the intermediate in this reaction makes it possible to obtain alkylthioethynylcarbinols on oxidation of the intermediate by oxygen[275] or silicon-containing ethynyl sulphides on treatment with chlorotrimethylsilane.[276]

The acetylenic carbon atom–selenium bond in ethynyl selenides is readily cleaved on treatment with a lithium alkyl.[110] The reaction of phenyltelluroacetylene with butyllithium involves the simultaneous cleavage of the acetylenic carbon atom–tellurium bond and substitution at the acetylenic carbon atom.[68]

The synthetic possibilities of the reactions of organometallic compounds with vinylethynyl sulphides have been considered in a review.[277] On treatment with lithium alkyls of alkyl diacetylenic sulphides, the alkylthio-groups are substituted and diacetylenic hydrocarbons are formed.[233]

The reactions of vinylethynyl sulphides, selenides, and tellurides with lithium in liquid ammonia lead to the substitution of the alkyl group in the sulphides and of the alkylheteroatom group in the selenides and tellurides.[278] The alkyl group in the sulphides can be substituted by employing acetoxydiazomethane in the presence of copper salts.[3,279]

A method has been developed for the synthesis of tin- and lead-containing vinyl ethers and sulphides by the coupled hydrostannylation or hydroplumbylation of ethynyl ethers and sulphides.[280–284] The regioselectivities are different for ethers and sulphides:

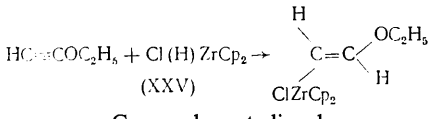
$$HC{\equiv}COR \xrightarrow{(C_2H_5)_3MNa} CH_2{=}C[M(C_2H_5)_3]OR,$$

$$HC{\equiv}CSR \xrightarrow{(C_2H_5)_3MNa} (C_2H_5)_3MCH{=}CHSR,$$

M = Sn, Pb; R = CH_3, C_2H_5.

In the stannylation reaction, tin-containing ethynyl ethers and sulphides are formed as side products. The metallation process predominates in the reaction of phenoxyacetylene with triethylgermyl-lithium.[203] The Schwartz reagent (XXV) adds regio- and

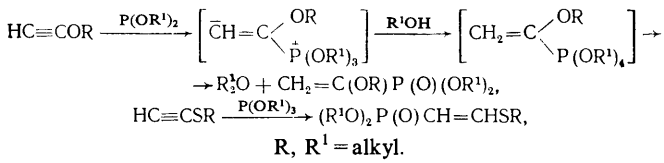
stereo-specifically to ethoxyacetylene with formation of an (*E*)-vinyl ether in which zirconium is readily substituted by electrophiles.[285,286]



(XXV)

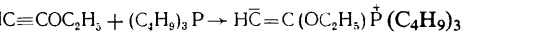
Cp = cyclopentadienyl.

Di- and tri-alkyl phosphites undergo the opposite type of addition to ethynyl ethers and sulphides:[287–294]

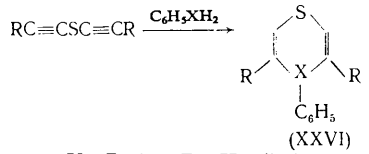


R, R^1 = alkyl.

According to the authors, the product of the addition of tributylphosphine to ethoxyacetylene has the structure of a dipolar ion:[295–298]



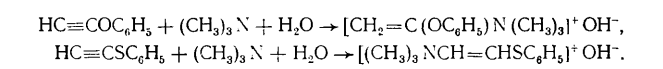
Phenylphosphine and phenylarsine react with di(alkylethynyl) sulphide in liquid ammonia in the presence of lithium amide to form the heterocyclic compounds (XXVI):[299]



(XXVI)

X = P, As; R = H, alkyl.

Tertiary amines readily add to terminal ethynyl ethers and sulphides in aqueous solution with the opposite mode of addition:[300]

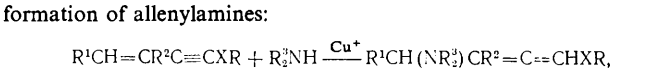


Internal phenoxy- and phenylthio-acetylenes do not react with triethylamine.

The addition of secondary amines to ethynyl sulphides leads to thioamides.[79,80,84] In the presence of an electron-accepting group at the triple bond in the ethynyl sulphide molecule, the usual mode of addition of amines changes and the amino-group is attached to the α-carbon atom of the triple bond.[118] Di(alkylthio)acetylenes and their selenium and tellurium analogues combine with diethylamine non-stereoselectively with formation of vinylamines.[301]

2-Methyloxazoline has been obtained as a result of the double addition of monoethanolamine to phenoxyacetylene.[224]

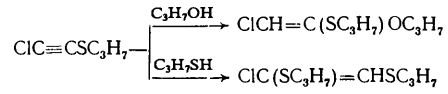
Secondary amines add to vinylethynyl sulphides,[302] selenides, and tellurides[303] in the presence of copper ions as the catalyst with formation of allenylamines:



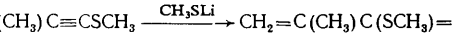
X = S, Se, Te; R^1, R^2 = H, alkyl; R = alkyl; R^3 = alkyl, organyl.

Ethynyl ethers[39] and sulphides[118] with an electron-accepting group at the triple bond combine with phenol and methanol with a similar mode of addition. The mode of addition of allyl alcohols to phenoxyacetylene[304] is the same as that in the addition of ethanol to ethoxyacetylene.[1] Intramolecular cyclisation occurs in the reactions of acylthioacetylenes with alcohols.[305,306]

The different modes of addition of alcohols and mercaptans to 1-chloro-2-propylthioacetylene[307] are a consequence of the charge and orbital control of the reactions:

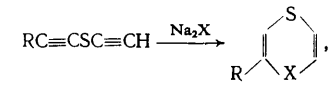


The addition of mercaptans to phenoxyacetylene[308] and ethynyl sulphides[9,88,309] takes place in conformity with the familiar rules.[1] Lithium methane-thiolate reacts with vinylethynyl sulphides chemoselectively via the triple bond with the attachment of the methylthio-group to the β-carbon atom and the formation of a (*Z*)-1,3-diene bis-sulphide:[310]



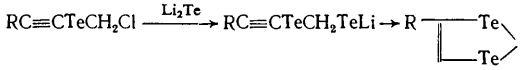
The attachment of the phenylthio-group to the α-carbon atom takes place in the addition of benzenethiol to ethynyl sulphides with electron-accepting substituents at the triple bond.[259]

The addition of sodium sulphide (selenide, telluride) to diethynyl sulphides leads to the formation of substituted 1,4-dithianes and their analogues:[5,311]



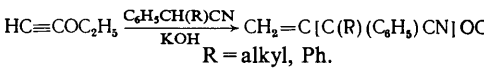
X = S, Se, Te; R = alkyl, isopropenyl.

Ethynyl tellurides react with lithium telluride, affording a substituted 1,3-ditellurole:[87]



R = H, alkyl, Ph.

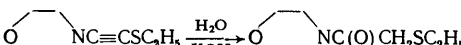
The rule governing the addition of nucleophiles holds in the reaction of a carbanion to ethoxyacetylene:[312]



R = alkyl, Ph.

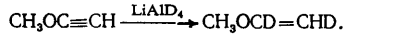
Ethynyl sulphides react non-regioselectively under similar conditions.

The mode of hydration of ethylthioethynylmorpholine in an alkaline medium is determined by the polarisation of the triple bond by the morpholino-group:[54]



Alkaline hydrolysis of 1-thiacyclooct-2-yne leads to the cleavage of the acetylenic carbon atom–sulphur bond.[107]

The reduction of methoxyacetylene with lithium tetradeuterio-aluminate constitutes a method of synthesis of deuteriated vinyl ethers:[313,314]



Ethynyl selenides can be hydrogenated by lithium tetrahydro-aluminate with formation of (*Z*)-ethynyl selenides.[110] The hydrogenation of vinylethynyl sulphides by lithium tetrahydro-aluminate in the presence of copper bromide leads to (*Z*)-1,3-dienyl sulphides, while in the absence of copper ions their (*E*)-isomers are formed.[315]

3. The radical addition reactions

Radical reagents add to ethynyl ethers and sulphides as a rule with the attachment of the radical to the β-carbon atom of the triple bond.[1] However, exceptions are known. Thus the reactions involving the photochemical addition of phosphorus tribromide to terminal ethynyl ethers[316] and sulphides[198] take place in different ways:

$$ROC{\equiv}CH + PBr_3 \xrightarrow{h\nu} ROC(PBr_2){=}CHBr,$$
$$RSC{\equiv}CH + PBr_3 \xrightarrow{h\nu} RSC(Br){=}CHPBr_2,$$
$$R = \text{alkyl}.$$

The free-radical addition of mercaptans to ethoxy- or phenoxyacetylene[308,317,318] and to substituted ethynyl sulphides[9,39,118] takes place in accordance with the familiar rule.

In the case of vinyl ethynyl sulphides, mercaptans undergo radical addition to the double bond:[319]

$$CH_2{=}CHC{\equiv}CSCH_3 + C_2H_5SH \rightarrow C_2H_5SCH_2CH_2C{\equiv}CSCH_3.$$

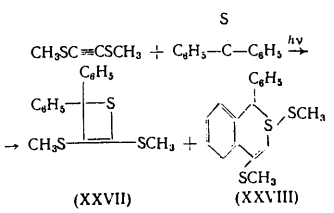
Under similar conditions, vinylethynyl selenide combines with ethanethiol via both multiple bonds with formation of a mixture of isomers.

Grignard reagents add chemoselectively and regioselectively to vinylethynyl sulphides at the double bond with formation, after hydrolysis, of a mixture of acetylenic (75%) and allenic isomers:[320,321]

$$CH_2{=}CHC{\equiv}CSR \xrightarrow{R^1MgHal} R^1CH_2CH_2C{\equiv}CSR + R^1CH_2CH{=}C{=}CHSR,$$
$$R,\ R^1 = \text{alkyl}.$$

Under similar conditions, 1-methylselenobut-3-en-1-yne forms an allenyl selenide in 38% yield. Vinylethynyl tellurides react with cleavage of the acetylenic carbon atom–tellurium bond.[322]

The mode of photochemical addition of ethynyl ethers[323,324] to ketones is of the usual type.[1] Thioketones add to di(methylthio)acetylene predominantly in accordance with the [2 + 2]cycloaddition mechanism with formation of compounds (XXVII). The [4 + 2]-cycloaddition product (XXVIII) is formed in 5–10% yield:[325–329]



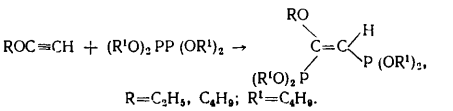
(XXVII) (XXVIII)

The reaction of 1,2-diones with ethynyl sulphides leads to the formation of a mixture of (*Z*)- and (*E*)-alkylthiobut-2-ene-1,4-diones.[3] Products having a similar structure have been obtained as a result of the [2 + 2]cycloaddition of phenanthrenequinone to internal ethynyl sulphides.[330]

The free-radical addition of trialkylgermanes and trialkyl- or triphenylstannanes to terminal ethynyl ethers[331] is similar to the already known reaction of trialkylstannanes.[1] The mode of addition of trialkylstannanes is retained in relation to silicon-, germanium-, and tin-containing ethynyl ethers.[6,212]

A substituted triazole adds to methoxyacetylene at the triple bond with the attachment of the triazole ring at the α-position relative to the methoxy-group.[332]

Tetraalkoxydiphosphines add stereospecifically to terminal ethynyl ethers:[333]



$R = C_2H_5,\ C_4H_9;\ R^1 = C_4H_9.$

The hydrogenation of ethoxyacetylene in the presence of a palladium catalyst has been investigated.[334] Vinylethynyl sulphides are slowly reduced at the palladium catalyst to the (*Z*)-1,3-dienyl sulphides.[335] The attempts to reduce ethynyl tellurides by various reductants led to the cleavage of the acetylenic carbon atom–tellurium bond.[69]

The energy of the interaction of singlet oxygen with dimethoxyacetylene has been calculated by the INDO method; a mechanism has been proposed for the oxidation reaction.[336]

The photochemical interaction of 1,4-dithiine and its homologues with di(ethylthio)acetylene leads to the formation of unstable coloured complexes as a result of [2 + 2]cycloaddition.[337]

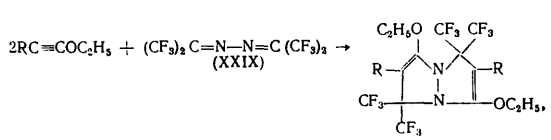
For the electrochemical reduction and oxidation of ethynyl sulphides, selenides, and tellurides, see Tomilov et al.[338]

4. Cycloaddition

The cycloaddition reactions of ethynyl ethers and sulphides with diazomethane, organyl azides, 1,3-dipolar reagents, ketens, cyclic ketones, and 1,3-dienes have been developed further.[1] Diazomethane adds to methoxyacetylene,[339] 4-bromo-1-methoxy-4-methyl-3-oxopent-1-yne,[220] and silicon-, germanium-, and tin-substituted ethynyl ethers[340] with formation of the corresponding 4-alkoxypyrazoles, similarly to the familiar reaction of ethoxyacetylene.[1] The reaction of dimethyldiazomethane with terminal ethynyl sulphides[341] leads to the predominant formation of the product of the opposite mode of addition, similarly to the familiar reaction of ethylthioacetylene.[1]

The reaction of organyl azides with ethoxyacetylene[1] has been used to obtain a series of substituted 1,2,3-triazoles,[342–344] one of which is a potential antibiotic.[345]

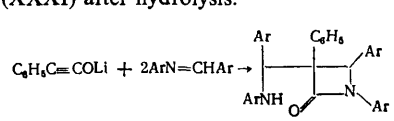
Hexafluoroacetone azene (XXIX) reacts with two molecules of ethynyl ether to form a mixture of compound (XXX) and its regioisomers:[346–348]



(XXIX) (XXX)

R=H, CH_3.

Aromatic imines add to lithium phenylethynoxide with formation of compound (XXXI) after hydrolysis:[349]

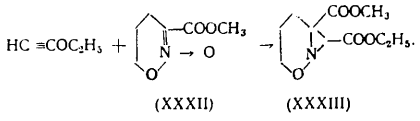


(XXXI)

The 1,3-dipolar cycloaddition of nitrile oxides to ethoxyacetylene has been used in the synthesis of isoxazole-containing *C*-nucleosides[350] and other isoxazole derivatives.[351]

The perturbation energy of the methoxyacetylene MO in the reaction with 1,3-dipoles has been calculated by quantum-chemical methods.[352,353]

Oxazine *N*-oxide (XXXII) reacts with ethoxyacetylene to form the aziridine derivative (XXXIII):[354]

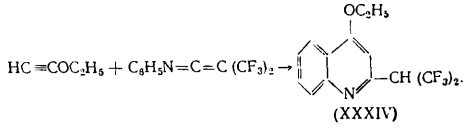


(XXXII) (XXXIII)

The nitro-derivative of the *N*-oxide reacts with elimination of the nitro-group and the formation of a substituted oxazine.[355,356]

The [2 + 2]cycloaddition of dimethylketen,[357,358] dichloroketen,[359] ring-containing ketens,[360,361] and vinylketen[362] to ethoxyacetylene and of dichloroketen to silicon- and germanium-containing ethynyl ethers[363] leads to the formation of the corresponding cyclobutenones, similarly to the familiar reactions.[1] The reaction of bis(trifluoromethyl)keten with silicon- and germanium-containing ethynyl ethers affords products having a linear structure in addition to the substituted cyclobutenone.[363] Aromatic ketens react as a rule with ethoxyacetylene via the [2 + 2]- and [2 + 2 + 2]cycloaddition mechanisms.[362,364] The mode of reaction of diphenylketen with ethoxyacetylene has been calculated by the CNDO/2 method.[365] Diphenyl keten reacts with organylthioalkynes via the [2 + 2]cycloaddition mechanism.[92]

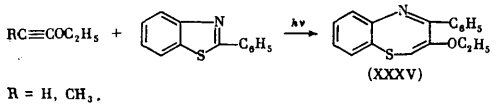
The [2 + 4]cycloaddition of *N*-phenylbis(trifluoromethyl)keten imine to ethoxyacetylene leads to the formation of the ethoxyquinoline (XXXIV):[366]



(XXXIV)

Isocyanates react with organylthioalkynylamines[92] and thioisocyanates react with 1-ethoxyprop-1-yne[367] in accordance with the [2 + 4]cycloaddition mechanism.

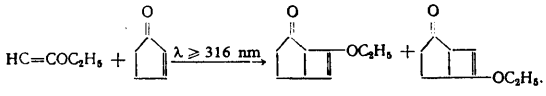
The photocyclisation reaction of 2-phenylbenzothiazole with ethynyl ethers, accompanied by linear expansion, leads to the formation of substituted 1,5-benzothiazepines (XXXV):[368,369]



(XXXV)

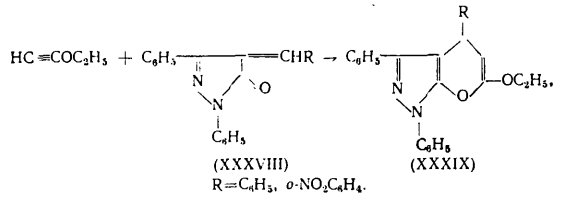
R = H, CH_3.

The photochemical [2 + 2]cycloaddition of 2-cyclopent-1-enone to ethoxyacetylene proceeds with a low regioselectivity—compounds (XXXVI) and (XXXVII) are formed:[370,371]



The photocycloaddition of 5,8,9,10-tetrahydro-*p*-naphthoquinone to ethoxyacetylene leads to the formation of 4-ethoxy-2,7-dioxotricyclo-[6.4.0.0^{3,6}]dodeca-4,10-diene.[372]

Cyclopentadiene enters into the Diels–Alder reaction with 1,3-dimethoxy-3-oxoprop-1-yne and 3-methoxy-1-phenylthio-3-oxoprop-1-yne.[373] Compounds (XXXIX) have been obtained by the [2 + 4]cycloaddition of arylidenepyrazolones (XXXVIII) to ethoxyethylene:[374]

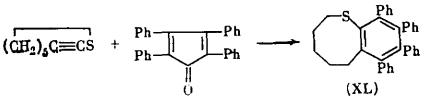


(XXXVIII) (XXXIX)

R = C_6H_5, *o*-$NO_2C_6H_4$.

Substituted 3-methyleneoxindole reacts with ethoxyacetylene similarly.[375]

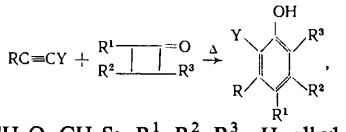
A tetrasubstituted cyclopentadienone reacts quantitatively with 1-thiacyclooct-2-yne, forming compound (XL):[107]



(XL)

The perturbation energy of the MO of 2-pyridone and ethoxyacetylene in the [2 + 4]cycloaddition reaction has been calculated by the CNDO/2 method.[376]

Substituted phenols have been obtained by heating ethynyl ethers and sulphides with cyclobutenone:[377]



R = alkyl, Y = CH_3O, CH_3S; R^1, R^2, R^3 = H, alkyl, C_2H_5O, Cl.

5. Substitution reactions

It was established previously that alkylheteroatom groups are substituted in the reactions of internal ethynyl ethers and sulphides with organolithium compounds.[1] The effect of organyl halides on element-containing ethynyl sulphides with heteroatoms at the sulphur atom has been studied. Thus treatment of ethoxy(trimethylsilyl)-acetylene with an excess of bromotrimethylsilane afforded bis-(trimethylsilyl)keten.[2]

The reaction of lithium dialkylamides with alkoxy(silyl)- and alkoxy(germyl)-acetylenes leads to the formation of silyl- and germyl-alkynylamines:[378]

$$R^1_3MC{\equiv}COR \xrightarrow{R_2NLi} R^1_3MC{\equiv}CNR_2,$$

M = Si, Ge; R, R^1 = alkyl.

Ethoxy(trimethylstannyl)acetylene reacts with lithium diethylamide with cleavage of the tin–carbon atom bond. Transmetallation of ethoxy(trimethylstannyl)acetylene yielded a germanium-containing ethynyl ether.[6]

Alkoxyethynyl ketones have been synthesised by treating tin-containing ethynyl ethers with carboxylic acid chlorides:[220,379]

$$(CH_3)_3SnC{\equiv}COR \xrightarrow{R^1COCl} R^1COC{\equiv}COR,$$

R = alkyl, R^1 = organyl.

Tin-containing alkynylamines have been obtained in 40% yield by the reaction of ethoxy(trimethylsilyl)acetylene with diethyl-(trimethylstannyl)amine:

$$(CH_3)_3SiC{\equiv}COC_2H_5 \xrightarrow{(CH_3)_3SnN(C_2H_5)_2} (CH_3)_3SnC{\equiv}CN(C_2H_5)_2.$$

Diethylamino(trimethylsilyl)acetylene is formed as an intermediate.

The methylseleno-group is readily substituted by the triethylstannyl group in reactions of di(methylseleno)acetylene with triethylstannylsodium in liquid ammonia.[380]

Trialkylstannylthioacetylenes have been obtained by substituting the acetyl group in acetylthioacetylenes by the trialkylstannyl group:[381,382]

$$RC{\equiv}CSCOCH_3 \xrightarrow{R_3SnOR} RC{\equiv}CSSnR_3,$$
$$R = \text{alkyl}.$$

The "transmetallation" reactions of compounds (XLI) have been described:[94,381,382]

$$RC{\equiv}CSMR_3 \xrightarrow{R^1_3M^1X} RC{\equiv}CSM^1R^1_3,$$
(XLI)
$$M{=}Sn,\ M^1{=}Si,\ Ge;\ M{=}Si,\ M^1{=}Ge,\ Sn,\ Pb.$$

The trialkylsilyl group at the sulphur atom is readily split off on treatment of compound (XLII) with methanol with formation of compound (XLIII):[94]

$$(CH_3)_3SiC{\equiv}CSSi(CH_3)_3 \xrightarrow{CH_3OH} [(CH_3)_3SiC{\equiv}CSH] \rightarrow$$
(XLII)
$$\rightarrow [(CH_3)_3SiCH{=}C{=}S] \xrightarrow{CH_3OH} (CH_3)_3SiCH_2C(S)OCH_3.$$
(XLIII)

The cyano-group in ethynyl thiocyanates is substituted on treatment with lithium acetylide[5,311] or lithium dialkylamide:[90]

$$RC{\equiv}CSCN \xrightarrow{LiC{\equiv}CR^1} RC{\equiv}CSC{\equiv}CR^1$$
$$RC{\equiv}CSCN \xrightarrow{R_2NLi} RC{\equiv}CSNR_2$$
$$R = \text{alkyl},\ R^1 = R_3Si.$$

Ethynyl disulphides react with secondary amines at 0 °C with cleavage of the sulphur–sulphur bond and the addition of an amine molecule to the thioketen formed.[89]

Ethynyl sulphides are oxidised by an equimolar amount of H_2O_2 in acetic anhydride with formation of ethynyl sulphoxides:[383,384]

$$HC{\equiv}CSR \xrightarrow{[O]} HC{\equiv}CS(O)R,$$
$$R = \text{alkyl}.$$

Terminal ethynyl sulphones have been obtained by oxidising ethynyl sulphides with acetyl hydroperoxide[385] or with hydrogen peroxide.[386]

Phenylethynyl selenides are oxidised by *m*-chloroperbenzoic acid with cleavage of the acetylenic carbon atom–selenium bond:[387]

$$RC{\equiv}CSeR^1 \xrightarrow{m\text{-}ClC_6H_4COOOH} RC{\equiv}CC{\equiv}CR,$$
$$\text{R-aryl, cyclohexenyl};\ R^1 = \text{alkyl, aryl}.$$

In the presence of water, only terminal acetylenic hydrocarbons are formed.[388]

In contrast to ethynyl sulphides and selenides, ethynyl tellurides give rise to telluronium compounds in the reaction with ethyl iodide.[231,389,390] The ammonium salt is formed in the reaction of ethylthiomorpholinoacetylene with methyl iodide.[54]

6. Complex formation

It was shown previously that methoxyacetylene readily forms a complex with iron carbonyl.[1]

The carbene complex of tungsten pentacarbonyl (XLIV) adds to the triple bond of ethoxyacetylene with formation of the unstable complex (XLV), which isomerises to the complex (XLVI):[391]

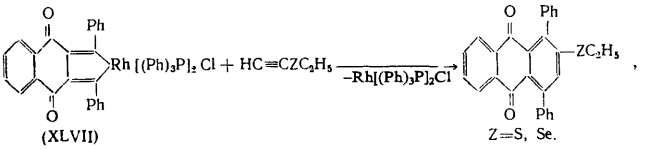
$$HC{\equiv}COC_2H_5 + (CO)_5W{=}CHC_6H_5 \rightarrow \left[\begin{array}{l} C_6H_5 \\ | \\ (CO)_5W{-}CH \\ | \\ C_2H_5O{-}C{=}CH \end{array}\right] \rightarrow$$
(XLIV) (XLV)
$$\rightarrow (CO)_5W{=}C(OC_2H_5)CH{=}CHC_6H_5.$$
(XLVI)

Ruthenium carbonyl hydrides react with ethoxyacetylene to form the allyltriruthenium cluster.[392] Aromatic compounds have been obtained by the reaction of cyclobutadiene-tricarbonyliron with ethoxyacetylene.[393] The reaction of internal ethynyl ethers with carbene pentacarbonylchromium also leads to the formation of aromatic compounds.[394,395]

Dimethoxyacetylene forms complexes with iron nonacarbonyl and cobalt octacarbonyl at –60 °C:[26]

$$CH_3OC{\equiv}COCH_3 \xrightarrow{Fe_2(CO)_9} (CH_3OC{\equiv}COCH_3)_2Fe(CO)_6.$$

Substituted anthraquinones have been obtained by the reaction of the rhodium complex (XLVII) with ethylthio- and ethylseleno-acetylenes:[396]



(XLVII)

Di(methylthio)acetylene forms complexes with cyclopentadienylmolybdenum and cyclopentadienyltungsten carbonyls and iron, cobalt, and ruthenium carbonyls.[397,398] In the complex with tungsten carbonyl, the di(methylthio)acetylene ligand is substituted in the reaction with bis(dimethylphosphino)ethane.[399]

In the reaction with 1-t-butylthioprop-1-yne, the dimeric tungsten t-butoxide gives rise to an unstable tungsten complex:[400]

$$CH_3C{\equiv}CSR \xrightarrow{W_2(OR)_6} (RO)_3W{\equiv}CSR,$$
$$R = t\text{-}C_4H_9.$$

Aryl ethynyl sulphides and their analogues $p\text{-}XC_6H_4EC{\equiv}CC_6H_4Y\text{-}p$ (E = S, Se, Te; X = H, CH_3OCH_3, F, Cl, Br; Y = H, Cl) form charge-transfer complexes with tetracyanoethylene, the tellurides being the strongest electron donors in this series.[401] The pentafluorophenyl derivatives of the sulphides do not form charge-transfer complexes with tetracyanoethylene as a consequence of the reduced electron-donating capacity of the $-C{\equiv}C-S-$ fragment.[65]

7. Rearrangements and isomerisation

It was established previously that allenyl ethynyl sulphides undergo the thio-Claisen rearrangement in the presence of secondary amines.[1] The study of this rearrangement was continued in the presence of secondary amines[83,93,402,403] and lithium amides[404] and on heating.[97] Allenyl ethynyl selenides undergo the same rearrangement.[98]

Methoxyethynylphosphine undergoes an unusual rearrangement in the course of its synthesis with formation of compound (XLVIII):[113]

$$R_2PC{\equiv}COCH_3 \rightarrow R_2(CH_3)P{=}C{=}C{=}O,$$
(XLVIII)
$$R = \text{alkyl, aryl}.$$

The sigmatropic rearrangement of ethynyl sulphides takes place in the presence of sodium amide and bromobenzene in liquid ammonia:[405]

$$RCH_2C{\equiv}CSCH_2R^1 \xrightarrow[NaNH_2]{C_6H_5Br} C_6H_5SCHR^1CHRC{\equiv}CH,$$
$$R,\ R^1{=}H,\ CH_3.$$

Internal ethynyl ethers and sulphides are known to isomerise readily to allenyl ethers and sulphides in the presence of bases.[1] 3-Methoxy-1-methylthioprop-1-yne isomerises to the methylthioallenyl ether in the presence of lithium diisopropylamide.[3] Allenyl sulphides have been obtained by the isomerisation of other ethynyl sulphides under similar conditions.[406,407]

8. Thermolysis and polymerisation

The thermal decomposition of ethynyl ethers and sulphides, leading to the formation of ketens and thioketens, has been examined in other reviews.[1,6] Pyrolysis of methoxyacetylene at 600 °C for 10 min leads to the formation of formaldehyde, acetylene, ethylene, and ethane.[408] The gas-phase pyrolysis of di(phenylthio)-acetylene at 560 °C afforded mainly diphenyl sulphide, thiophenol, and acetylene.[409]

The polymerisation of ethynyl ethers has been examined in a review.[1] The study of the polymerisation process was later extended to ethynyl sulphides.[410,411]

In the presence of boron trifluoride, diethylamino(phenylthio)-acetylene dimerises:[412]

$$2\,C_6H_5SC{\equiv}CN(C_2H_5)_2 \xrightarrow[THF]{BF_3} (C_2H_5)_2N{-}C{=}C{-}SC_6H_5$$
$$\qquad\qquad\qquad

23. S Piettre, Z Janousek, H G Viehe *Synthesis*, 1982, 1083
24. J F Normant, A Commercon, J Villieras *Tetrahedron Lett.*, 1975, 1465
25. A S Atavin, A N Mirskova, E F Zorina, USSR P. 420 621; *Byull. Izobret.*, 1974(11), 86
26. A Messeguer, F Serratosa, J Rivera *Tetrahedron Lett.*, 1973, 2895
27. M A Pericas, F Serratosa *Tetrahedron Lett.*, 1977, 4433
28. W E Parham, S Kajigaeshi, S H Groen *Bull. Chem. Soc. Jpn.*, 1972, **45** 509
29. W E Parham, W D McKown, V Nelson, et al. *J. Org. Chem.*, 1973, **38** 1361
30. M Barz, G Z Himbert *Z. Naturforsch., B*, 1985, **40** 645
31. W Verboom, J Meijer, L Brandsma *Synthesis*, 1978, 577
32. R Tanaka, S I Miller *Tetrahedron Lett.*, 1971, **21** 1753
33. R Tanaka, M Rodgers, R Simonaitis, S I Miller *Tetrahedron*, 1971, **27** 2651
34. H G Viehe, S Y Delavarenne *Chem. Ber.*, 1970, **103** 1216
35. S Y Delavarenne, H G Viehe *Chem. Ber.*, 1970, **103** 1209
36. M C Verploegh, L Donk, H J T Bos, W Drenth *Recl. Trav. Chim. Pays-Bas*, 1970, **90** 765
37. M Charton, B I Charton *J. Org. Chem.*, 1978, **43** 1161
38. V A Garibina, A V Dogadina, B I Ionin, A A Petrov *Zh. Obshch. Khim.*, 1979, **49** 2152
39. V A Garibina, A A Leonov, A V Dogadina, et al. *Zh. Obshch. Khim.*, 1985, **55** 1994
40. E G Kataev, T G Mannafov, USSR P. 345 152; *Byull. Izobret.*, 1972(22), 94
41. L M Kataeva, Yu V Rydvanskii, R I Vinokurova *VI Vsesoyuznaya Konferentsiya po Khimii Atsetilena. Tezisy Dokladov* (The VI All-Union Conference on the Chemistry of Acetylene. Abstracts of Reports), Izd. Azineftekhim, Baku, 1979, Part II, p. 127
42. A Roedig, G Zaby, W Scharf *Chem. Ber.*, 1977, **110** 1484
43. A Roedig, G Zaby *Liebigs Ann. Chem.*, 1979, 1606, 1614, 1626
44. A V Shchelkunov, L A Krichevskii, USSR P 387 983; *Byull. Izobret.*, 1973(28), 72
45. L A Krichevskii, A V Shchelkunov, A K Amirkhanova *Eksperimental'nye Metody Issledovaniya v Khimii i Biologii* (Experimental Research Methods in Chemistry and Biology), Izd. Karagand. Univ., Karaganda, 1975, Vol. 2, p. 168
46. A V Shchelkunov, L A Krichevskii, M F Shostakovskii *Dokl. Akad. Nauk SSR*, 1983, **268** 1419
47. L A Krichevskii, A V Shchelkunov *Trudy Khim.-Met. Inst.Akad. Nauk Kazakh. SSR*, 1972, 14
48. L A Krichevskii, A V Shchelkunov *Khimiya Atsetilena i Tekhnologiya Karbida Kal'tsiya* (The Chemistry of Acetylene and the Technology of Calcium Carbide), Alma-Ata, Kazakhstan, 1972, p. 86
49. W Verboom, H Westmijze, H J T Bos, P Vermeer *Tetrahedron Lett.*, 1978, 1441
50. A S Kende, P Fludzinski, J H Hill, et al. *J. Am. Chem. Soc.*, 1984, **106** 3551
51. W Verboom, H J T Bos *Recl. Trav. Chim. Pays-Bas*, 1979, **98** 559
52. A N Mirskova, S G Seredkina, I D Kalikhman, M G Voronkov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2330
53. A N Mirskova, S G Seredkina, M G Voronkov, USSR P. 1 097 616; *Byull. Izobret.*, 1984(22), 75
54. A N Mirskova, S G Seredkina, M G Voronkov *Zh. Org. Khim.*, 1985, **21** 2506
55. A N Mirskova, S G Seredkina, I D Kalikhman, et al. *Zh. Org. Khim.*, 1984, **20** 657
56. A N Mirskova, N V Lutskaya, M G Voronkov *Zh. Obshch. Khim.*, 1979, **49** 2668
57. R H Everhardus, L Brandsma *Synthesis*, 1978, 359
58. R Mantione, A Alves *Tetrahedron Lett.*, 1969, 2483
59. P E Van Rijn, R H Everhardus, L Brandsma *Rec.: J. R. Royal Neth. Chem. Soc.*, 1982, **101** 180
60. E N Prilezhaeva, V N Petrov, G S Vasil'ev, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, 2473
61. G Pourcelot, J-M Cense *Bull. Soc. Chim. Fr.*, 1976, 1578
62. L Brandsma, D Schuijl-Laros *Recl. Trav Chim. Pays-Bas*, 1970, **89** 110
63. S Saito, S Hamano, M Ihaba, T Moriwake *Synth. Commun.*, 1984, **14** 1105
64. Yu N Porshnev, T N Dvorikova, V B Mochalin *Zh. Org. Khim.*, 1976, **12** 2019
65. O I Andreevskaya, S A Krupoder, G N Dolenko, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 129
66. T Hagama, S Tomoda, Y Takeuchi, Y Nomura *Chem. Lett.*, 1982, 1249
67. J V Comasseto, J T B Ferreira, N Petragnani *J. Organomet. Chem.*, 1981, **216** 287
68. T Kaufmann, H Ahlers *Chem. Ber.*, 1983, **118** 1001
69. M J Dabdoub *J. Organomet. Chem.*, 1986, **308** 211
70. J C Wesdorp, J Meijer, P Vermeer, et al. *Recl. Trav. Chim. Pays-Bas*, 1974, **93** 184
71. U Schöllkopf, I Hoppe *Angew. Chem., Int. Ed. Engl.*, 1975, **14** 765
72. F A Uribe, P R Sharp, A J Bard *J. Electroanal. Chem. Interfacial Electrochem.*, 1983, **152** 173
73. C K Taylor *Diss. Abstr. Int. B*, 1983, **44** 177
74. P J Stang, K A Roberts *J. Am. Chem. Soc.*, 1986, **108** 7125
75. P J Stang, M L J Boehshar *J. Am. Chem. Soc.*, 1986, **108** 7832
76. J F Arens, L Brandsma, P J W Schuijl, H E Wijers *Quart. Rep. Sulfur Chem.*, 1970, **5** 1
77. B A Trofimov *Zh. Org. Khim.*, 1986, **22** 1991
78. L Brandsma *Preparative Acetylenic Chemistry*, Elsevier, Amsterdam, 1971, p. 121
79. M L Petrov, B S Kupin, A A Petrov *Zh. Org. Khim.*, 1971, **7** 1120
80. M L Petrov, B S Kupin, A A Petrov *Zh. Org. Khim.*, 1971, **7** 1113
81. M L Petrov, K S Mingaleva, B S Kupin *Zh. Org. Khim.*, 1972, **8** 32
82. R K Zaripov, I N Azerbaev, K Sh Shamgunov, U A Aimakov *Doklady IV Vsesoyuznoi Konferentsii po Khimii Atsetilena* (Reports at the IV All-Union Conference on the Chemistry of Acetylene), Alma-Ata, 1972, p. 22
83. J Meijer, P Vermeer, H J T Bos, L Brandsma *Recl. Trav. Chim. Pays-Bas*, 1974, **93** 26
84. M L Petrov, B S Kupin, A A Petrov *Zh. Org. Khim.*, 1969, **5** 1759
85. Yu A Boiko, B S Kupin, A A Petrov *Zh. Org. Khim.*, 1969, **5** 1553
86. S I Radchenko *Zh. Org. Khim.*, 1977, **13** 2229
87. S L Bender, M R Detty, N F Haley *Tetrahedron Lett.*, 1982, **23** 1531
88. H E Wijers, H Boelns, A Van der Gen *Recl. Trav. Chim. Pays-Bas*, 1969, **88** 519

89. J Meijer, H E Wijers, L Brandsma *Recl. Trav. Chim. Pays-Bas*, 1972, **91** 1423
90. J Meijer, L Brandsma *Recl. Trav. Chim. Pays-Bas*, 1971, **91** 1098
91. R S Sukhai, J Meijer, L Brandsma *Rec. Trav. chim.*, 1977, **96** 179
92. E Schaumann, J Lindstaedt, W R Foerster *Chem. Ber.*, 1983, **116** 509
93. E Schaumann, J Lindstaedt *Chem. Ber.*, 1983, **116** 1728
94. S J Harris, D R M Walton *J. Organomet. Chem.*, 1977, **127** C1
95. S J Harris, D R M Walton *J. Chem. Soc., Chem. Commun.*, 1976, 1008
96. R S Sukhai, L Brandsma *Recl. Trav. Chim. Pays-Bas*, 1979, **98** 55
97. E Schaumann, F F Grabley *Tetrahedron Lett.*, 1977, 4307
98. E Schaumann, F F Grabley *Tetrahedron Lett.*, 1980, **21** 4251
99. M Schoufs, J Meyer, P Vermeer, L Brandsma *Recl. Trav. Chim. Pays-Bas*, 1977, **96** 259
100. M L Petrov, A A Petrov *Usp. Khim.*, 1987, **56**(2) 267 [English translation in *Russ. Chem. Rev.*, 1987(2)]
101. M L Petrov, Abstract of Doctoral Thesis in Chemical Sciences, Lensovet Leningrad Technological Institute, Leningrad, 1982
102. A Shafiee, I Lalezari, F Savabi *Synthesis*, 1977, 764
103. M L Petrov, V Z Laishev, A A Petrov *Zh. Org. Khim.*, 1981, **17** 667
104. I Ganjian, I Lalezari *J. Heterocycl. Chem.*, 1985, **22** 857
105. M L Petrov, V Z Laishev, A A Petrov *Zh. Org. Khim.*, 1980, **16** 2236
106. P Riviere, A Castel, J Satge *J. Am. Chem. Soc.*, 1980, **102** 5413
107. H Meier, E Stavridou, C Storek *Angew. Chem.*, 1986, **98** 838
108. H Bock, U Stein, W Reid *Chem. Ber.*, 1981, **114** 673
109. H J Bestmann, K Roth *Tetrahedron Lett.*, 1981, **22** 681
110. A L Brage, J V Comasseto, N Petragani *Synthesis*, 1984, 240
111. J A Hyatt, P L Feldman, R J Clemens *J. Org. Chem.*, 1984, **49** 5105
112. N V Lukashev, O I Artyushin, V A Roznyatovskii, et al. *Zh. Obshch. Khim.*, 1984, **54** 2390
113. O I Artyushin, N V Lukashev, M A Kazankova, et al. *Tezisy Dokladov VIII Vsesoyuznoi Konferentsii po Khimii i Primeneniyu Fosfororganicheskikh Soedinenii, Posvyashchennoi 80-Letiyu Reaktsii A E Arbuzova* (Abstracts of Reports at the VII All-Union Conference on the Chemistry and Applications of Organophosphorus Compounds, Commemorating the 80th Anniversity of the Arbuzov Reaction), Izd. Kazan. Univ., Kazan, 1985, Part I, p. 138
114. G Himbert, L Henn *Liebigs Ann. Chem.*, 1984, 1358
115. B M Mikhailov, M E Gurskii, M G Gverdtsiteli *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 1456
116. B M Mikhailov, M E Gurskii, M G Gverdtsiteli, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 855
117. J Link, P Vermeer, J G A Kooiman, et al. *Recl. Trav. Chim. Pays-Bas*, 1974, **93** 92
118. W Hagens, H J T Bos, J F Arens *Recl. Trav. Chim. Pays-Bas*, 1973, **92** 762
119. T Kobayashi, N Ishida, T Hiroka *J. Chem. Soc., Chem. Commun.*, 1980, 736
120. L M Kataeva, E G Kataev, T G Mannafov *Teor. Eksper. Khim.*, 1968, **4** 689
121. N S Podkovyrina, L M Kataeva *Sbornik Aspirantskikh Rabot Kazanskogo Universiteta. Khimiya. Geografiya. Geologiya* (Collected Postgraduate Studies at the Kazan University. Chemistry. Geography. Geology), Izd. Kazan. Univ., Kazan, 1971, p. 43
122. L M Kataeva, N S Podkovyrina, T G Mannafov, et al. *Dipol'nye Momenty i Struktura Selenoorganicheskikh Soedinenii* (The Dipole Moments and Structure of Organoselenium Compounds), Kazan, 1973. Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 28.06.73, No.6382-73.
123. N S Podkovyrina, L M Kataeva *Dipol'nye Momenty Etinilovykh Tio- i Selenoefirov po Rezul'tatam Kvantovokhimicheskikh Raschetov* (The Dipole Moments of Ethynyl Thio- and Seleno-Ethers Based on the Results of Quantum-Chemical Calculations), Kazan, 1973. Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 28.06.73, No. 6387-73
124. N S Podkovyrina, L M Kataeva *Zh. Fiz. Khim.*, 1973, **47**(11) 2945 [English translation in *Russ. J. Phys. Chem.*, 1973(11)]
125. L M Kataeva, N S Podkovyrina, Yu V Rydvanskii *V Vsesoyuznaya Konferentsiya po Khimii Atsetilena. Tezisy Dokladov* (The V All-Union Conference on the Chemistry of Acetylene. Abstracts of Reports), Izd. Metsniereba, Tbilisi, 1975, p. 105
126. L M Kataeva, T N Pylaeva, E G Kataev *Dipol'nye Momenty, UF- i IR-Spektry Alkiltellurofenylatsetilenov* (The Dipole Moments and the UV and IR Spectra of Alkyltellurophenylacetylenes), Kazan, 1975. Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 09.10.75, No. 2886-75
127. L M Kataeva, N S Podkovyrina, I A Krivosheeva *Raspredelenie Elektronnoi Plotnosti v Molekulakh Etinilovykh Telluroefirov po Rezul'tatam Kvantovo-khimicheskogo Rascheta Ikh Dipol'nykh Momentov* (Distribution of Electron Density in the Molecules of Ethynyl Telluroethers on the Basis of the Results of a Quantum-chemical Calculation of Their Dipole Moments), Kazan, 1975. Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 24.06.75, No. 1868-75
128. R I Vinokurova, L M Kataeva, S G Vul'fson, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 1665
129. L M Kataeva, N S Podkovyrina, Yu V Rydvanskii *Raspredelenie Elektronnoi Plotnosti v Molekulakh Atsetilenovykh Tio- i Selenoefirov po Rezul'tatam Kvantovokhimicheskogo Rascheta Ikh Dipol'nykh Momentov* (Distribution of Electron Density in the Molecules of Acetylenic Thio- and Seleno-ethers on the Basis of the Results of a Quantum-chemical Calculation of Their Dipole Moments), Kazan, 1979. Deposited at the ONIITEKhIM, 20.06.79. No. 2740/79
130. L M Kataeva, Yu V Rydvanskii, V Z Latypova, E G Kataev *Zh. Obshch. Khim.*, 1981, **51** 2685
131. S I Radchenko, K S Mingaleva *Zh. Org. Khim.*, 1977, **13** 2476
132. D Rosenberg, J W De Haan, W Drenth *Recl. Trav. Chim. Pays-Bas*, 1968, **87** 1387
133. D Rosenberg, W Drenth *Tetrahedron*, 1971, **27** 3893
134. S I Radchenko, A S Khachaturov, B I Ionin *Zh. Org. Khim.*, 1978, **14** 680
135. G A Kalabin, V M Bzhezovskii, D F Kushnarev, A G Proidakov *Zh. Org. Khim.*, 1981, **17** 1143
136. G A Kalabin, V I Donskikh, B I Istomin, A G Proidakov *Zh. Org. Khim.*, 1980, **16** 2441
137. A G Proidakov, *Abstract of Candidate's Thesis in Chemical Sciences*, Izd. Irkutsk. Univ., Irkutsk, 1981, 19 pp.
138. G A Kalabin, D F Kushnarev, S M Shostakovskii, T K Voropaev *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975, 2459

139. Yu K Grishin, S V Ponomarev, S A Lebedev *Zh. Org. Khim.*, 1974, **10** 404
140. B Wrackmeyer *J. Organomet. Chem.*, 1979, **166** 353
141. A Sebald, B Wrackmeyer *Spectrochim. Acta, Part A*, 1981, **37**, 365
142. E O Tsetlina, V A Pestunovich, M G Voronkov, et al. *Dokl. Akad. Nauk SSSR*, 1979, **245** 400
143. N N Shergina, L V Sherstyannikova, R G Mirskov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1280
144. G A Kalabin, R B Valeev, D F Kushnarev *Zh. Org. Khim.*, 1981, **17** 947
145. G A Kalabin, D F Kushnarev *Magn. Reson. Relat. Phenom. Proc. XX Congr. AMPERE*, 1978, 492
146. D F Kushnarev, *Abstract of Candidate's Thesis in Chemical Sciences*, Izd. Irkutsk Univ., Irkutsk, 1979, 21 pp.
147. R B Valeev, G A Kalabin, D F Kushnarev *Zh. Org. Khim.*, 1980, **16** 2482
148. B Beagly, V Ulbrecht, S Katsumata, et al. *J. Chem. Soc., Faraday Trans. 2*, 1977, **73** 1278
149. G A Kalabin, A G Proidakov, S I Radchenko *Zh. Org. Khim.*, 1980, **16** 512
150. E D Lubuzh, V I Loba, K N Prilezhaeva *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 223
151. D H Christensen *Spectrochim. Acta, Part A*, 1970, **26**, 1747
152. L M Kataeva, R R Shagidullin, Yu V Rydvanskii, et al. *Zh. Prikl. Spektrosk.*, 1979, **39** 742
153. T B Grindley, K F Johnson, A R Katritzky, et al. *J. Chem. Soc., Perkin Trans*, 1974, 276
154. N I Shergina, L V Sherstyannikova, V B Pukhnarevich, et al. *Dokl. Akad. Nauk SSSR*, 1975, **225** 1128
155. T F Tenisheva, A N Lazarev, L A Shchukovskaya *Zh. Prikl. Spektrosk.*, 1970, **13** 118
156. A N Lazarev, T F Tenisheva, L L Shchukovskaya, R I Pal'chik *Dokl. Akad. Nauk SSSR*, 1970, **190** 1106
157. M G Voronkov, N I Shergina, L V Sherstyannikova, T V Kashik *Stroenie i Reaktsionnaya Sposobnost' Kremniiorganichskikh Soedinenii. II. Vsesoyuznyi Simposium. Tezisy Dokladov* (The Structure and Reactivity of Organosilicon Compounds. II. All-Union Symposium. Abstracts of Reports), Irkutsk, 1981, p. 30
158. I F Tupitsin, A A Kane *Zh. Strukt. Khim.*, 1979, **20** 987
159. S I Radchenko *Zh. Prikl. Spektrosk.*, 1973, **19** 940
160. Yu V Rydvanskii, T N Pylaeva, L M Kataeva, E G Kataev *Sbornik Aspirantskikh Rabot Kazanskogo Universiteta. Estestvoznanie. Khimiya. Biologiya* (Collected Postgraduate Studies at the Kazan University. Natural Science. Chemistry. Biology), Izd. Kazan. Univ., Kazan, 1976, p. 24
161. L M Kataeva, Yu V Rydvanskii, Z D Valishina, E G Kataev, *UF-Spektry Ryada Atsetilenovykh Tioefirov* (The UV Spectra of a Series of Acetylenic Thioethers), Kazan, 1981. Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 20.03.81, No. 193 khp-D81.
162. V F Plotnikov, M L Petrov, G M Bogolyubov, A A Petrov *Zh. Org. Khim.*, 1972, **8** 967
163. G M Bogolyubov, V F Plotnikov, Yu A Boiko, A A Petrov *Zh. Obshch. Khim.*, 1969, **39** 2467
164. B A Trofimov, U Kh Mel'der, R I Pikver, E P Vyalykh *Teor. Eksp. Khim.*, 1975, **11** 165
165. H Bock, B Solouki *Angew. Chem., Int. Ed. Engl.*, 1981, **20** 427
166. J K Terlouw, P C Burgers, J L Holmes *J. Am. Chem. Soc.*, 1979, **101** 225
167. N V Villem, Ya Ya Villem, O V Saks *XVI Konferentsiya po Khimii i Tekhnologii Organicheskikh Soedinenii Sery i Sernistykh Neftei. Tezisy Dokladov* (The XVI Conference on the Chemistry and Technology of Organosulphur Compounds and Sulphur Petroleums. Abstracts of Reports), Izd. Zinatne, Riga, 1984, p. 55
168. S Ruhman, Y Hass, J Laukemper, et al. *J. Phys. Chem.*, 1984, **88** 5162
169. M C R Symons, B W Wren *Tetrahedron Lett.*, 1983, **24** 2315
170. D Engelsen *J. Mol. Spectrosc.*, 1969, **30** 466
171. B P Van Eijck, A Dubrulle, J Demaison, J L Ripole *J. Mol. Spectrosc.*, 1985, **112** 95
172. A Bjorseth *J. Mol. Struct.*, 1974, **20** 61
173. D Engelsen *J. Mol. Spectrosc.*, 1969, **30** 474
174. A Bjorseth *J. Mol. Struct.*, 1974, **20** 1
175. G Ruitenberg *J. Mol. Spectrosc.*, 1972, **42** 161
176. B E Turner *Symp. Int. Astron. Union.*, 1980, **87** 45
177. H Bock, S Mohmand, T Hirabayashi, A Semkow *Chem. Ber.*, 1982, **115** 339
178. M F Powell, M R Peterson *Theochem.*, 1983, **9** 323
179. S Marriot, R D Topsom *Theochem.*, 1984, **15** 277
180. M Charton, A Greenberg, T A Stevenson *J. Org. Chem.*, 1985, **50** 2643
181. A Greenberg, T A Stevenson *J. Am. Chem. Soc.*, 1985, **107** 3488
182. E S Petrov, M I Terekhova, A I Shatenshtein, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975, 2351
183. N N Zatsepina, A A Kane, I F Tupitsin *Zh. Org. Khim.*, 1977, **13** 1793
184. D N Kravtsov, A S Peregudov, V F Ivanov, E I Fedin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 1626
185. P Furet, G Hallak, R L Matcha, R Fuchs *Can. J. Chem.*, 1985, **63** 2990
186. M F Shostakovskii, Yu L Frolov, O A Zasyadko, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, 2229
187. I A Koppel', A I Payu, V O Pikhl *Reaktsionnaya Sposobnost' Organicheskikh Soedinenii*, 1973, **10** 921
188. S I Radchenko, I G Savich, A A Petrov *Zh. Org. Khim.*, 1974, **10** 2269
189. M A Kazankova, I F Lutsenko *II Vsesoyuznaya Konferentsiya po Metalloorganicheskoi Khimii. Tezisy Dokladov* (The II All-Union Conference on Organometallic Chemistry. Abstracts of Reports), Gorky, 1982, p. 88
190. I L Rodionov, O I Artyushin, M A Kazankova, I F Lutsenko , USSR P. 1 030 366; *Byull. Izobret.*, 1983(27), 107
191. I L Rodionov, M A Kazankova, E N Tsvetkov, I F Lutsenko, USSR P. 1 004 400; *Byull. Izobret.*, 1983(10), 108
192. I L Rodionov, M A Kazankova, I F Lutsenko *Zh. Obshch. Khim.*, 1984, **54** 468
193. I L Rodionov, E V Luzikova, M A Kazankova, I F Lutsenko, USSR P. 1 074 880; *Byull. Izobret.*, 1984(7) 89
194. B E Kalganov, I V Efremova, M A Kazankova, I F Lutsenko *Zh. Obshch. Khim.*, 1985, **55** 708
195. I L Rodionov, Yu N Luzikov, M A Kazankova, I F Lutsenko, USSR P. 1 097 632; *Byull. Izobret.*, 1984(22), 77
196. V E Kolbina, V G Rozinov, A N Mirskova, et al. *Zh. Obshch. Khim.*, 1981, **51** 2147
197. S G Seredkina, V E Kolbina, V G Rozinov, et al. *Zh. Obshch. Khim.*, 1982, **52** 2694
198. S A Shilov, M V Sendyurev *Zh. Obshch. Khim.*, 1985, **55** 223
199. V K Brel', O G Prudnikova, A N Pushin, et al. *Zh. Obshch. Khim.*, 1986, **56** 2160

200. R L Rodionov, E I Lazhko, I V Efimova, et al. *Tezisy Dokladov VIII Vsesoyuznoi Konferentsii po Khimii i Primeneniyu Fosfororganicheskikh Soedinenii, Posvyashchennoi 80-Letiyu Reaktsii A E Arbuzova* (Abstracts of Reports at the VIII All-Union Conference on the Chemistry and Applications of Organophosphorus Compounds Commemorating the 80th Anniversary of the Arbuzov Reaction), Izd. Kazan. Univ., Kazan, 1985, Part 2, p. 30
201. T Mukaiyama, M Murakami *Chem. Lett.*, 1981, 1129
202. M F Shostakovskii, S P Sushchinskaya, V B Pukhnarevich, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, 2599
203. O A Kruglaya, G S Lyashenko, A Kh Filippova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 682
204. Yu N Bubnov, V S Bogdanov, B M Mikhailov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1970, 2416
205. N Miyaura, K Maeda, H Suginome *J. Org. Chem.*, 1982, **47** 2217
206. Yu N Bubnov, B M Mikhailov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1970, 2156
207. Yu N Bubnov, M E Gurskii, L I Lavrinovich *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1918
208. B M Mikhailov, T A Shchegoleva, E M Shashkova *Zh. Obshch. Khim.*, 1974, **44** 2193
209. B M Mikhailov, T A Shchegoleva, E M Shashkova *Doklady IV Vsesoyuznoi Konferentsii po Khimii Atsetilena* (Reports at the IV All-Union Conference on the Chemistry of Acetylene), Alma-Ata, 1972, Vol. 2, p. 69
210. S Raucher, M R Hansen, M A Gloter *J. Org. Chem.*, 1978, **43** 4885
211. J V Comasseto *J. Organomet. Chem.*, 1983, **253** 131
212. S V Ponomarev, N Yu Belavin, G P Simirskaya *Tezisy Dokladov VI Vsesoyuanoi Konferentsii po Khimii Atsetilena i Ego Proizvodnykh* (Abstracts of Reports at the VI All-Union Conference on the Chemistry of Acetylene and its Derivatives), Izd. Azineftekhim, Baku, 1979, p. 48
213. V M Mikhailov, Yu N Bubnov, M Sh Grigoryan *Doklady IV Vsesoyuznoi Konferentsii po Khimii Atsetilena* (Reports at the IV All-Union Conference on the Chemistry of Acetylene), Alma-Ata, 1972, Vol. 2, p. 64
214. V M Mikhailov, Yu N Bubnov, M Sh Grigoryan *Zh. Obshch. Khim.*, 1974, **44** 2466
215. B M Mikhailov, Yu N Bubnov, M Sh Grigoryan, V S Bogdanov *Zh. Obshch. Khim.*, 1974, **44** 2715
216. B M Mikhailov, Yu N Bubnov, A V Tsyban' *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975, 483
217. Yu N Bubnov, M Sh Grigoryan, A V Tsyban, B M Mikhailov *Synthesis*, 1980, 902
218. Yu N Bubnov, A V Tsyban, B M Mikhailov *Synthesis*, 1980, 904
219. M Murakami, T Mukaiyama *Chem. Lett.*, 1982, 241
220. G Himbert, L Henn *Org. Prep. Proced. Int.*, 1982, **14** 169
221. R R McGuire, R E Cochoy, S A Shackelford US P. 4 424 398; *Chem. Abs.*, 1984, **100** 88196
222. R J Broekema *Recl. Trav. Chim. Pays-Bas*, 1975, **94** 209
223. L A Shchukovskaya, R I Pal'chik *Zh. Obshch. Khim.*, 1969, **5** 583
224. A Kh Filippova, A I Borisova, G S Lyashenko *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1971, 162
225. S I Radchenko, V A Naumov *Zh. Org. Khim.*, 1973, **9** 1798
226. B Cemil *Chem. Acta Turc.*, 1983, **11** 253
227. S I Radchenko, A A Petrov *Zh. Org. Khim.*, 1974, **10** 1986
228. M M Shovsumzade, L A Shabanov, V S Mamedzade, et al. *Azerb. Khim. Zh.*, 1976, 45
229. B Poetter, G Kleemann, K Seppelt *Chem. Ber.*, 1984, **117** 3255
230. M A Kazankova, V A Ilyushin, I F Lutsenko *Zh. Obshch. Khim.*, 1980, **50** 690
231. S I Radchenko, A A Petrov *Zh. Org. Khim.*, 1977, **13** 40
232. S I Radchenko *Zh. Org. Khim.*, 1977, **13** 254
233. S I Radchenko, *Zh. Org. Khim.*, 1976, **12** 229
234. S I Radchenko, V Ya Komarov, B I Ionin *Zh. Org. Khim.*, 1985, **21** 244
235. M S Newman, W M Stalick *J. Org. Chem.*, 1973, **38** 3386
236. M S Newman, V K Khanna *J. Org. Chem.*, 1975, **40** 3283
237. S Fukuoka, K Yasui, Japanese P. 7 914 569; *Chem. Abs.*, 1980, **92** 198269
238. J Plostnieks, US P. 3 723 428; *Chem. Abs.*, 1973, **79** 31863
239. E H White, M G Steinmetz, J D Miano, et al. *J. Am. Chem. Soc.*, 1980, **102** 3199
240. Y Kita, S Akai, M Yoshigi, et al. *Tetrahedron Lett.*, 1984, **25**, 6027
241. J H Fried, US P. 3 741 985; *Chem. Abs.*, 1974, **79** 92239
242. E H White, N Suzuki, J D Miano *J. Org. Chem.*, 1978, **43** 2366
243. N K Kochetkov, A I Usov, V V Deryabin *Zh. Obshch. Khim.*, 1972, **42** 2763; 1974, **44** 904
244. G A Olah, R J Spear *J. Am. Chem. Soc.*, 1975, **97** 1845
245. S I Radchenko, I B Lopatina *Zh. Org. Khim.*, 1972, **8** 1153
246. S I Radchenko *Zh. Org. Khim.*, 1972, **8** 1329
247. S I Radchenko, K S Mingaleva *Zh. Org. Khim.*, 1980, **16** 720
248. S I Radchenko, A A Petrov *Zh. Org. Khim.*, 1972, **8** 1572
249. I A Savost'yanova, M S Burmistrova, Yu I Baukov *Zh. Obshch. Khim.*, 1975, **45** 2348
250. Yu I Baukov, G S Zaitseva, L I Livantsova, et al. *Zh. Obshch. Khim.*, 1981, **51** 1304
251. G S Zaitseva, L I Livantsova, N A Orlova, et al. *Zh. Obshch. Khim.*, 1982, **52** 2076
252. E A Avetisyan, L A Simonyan, N P Gambaryan *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, 2742
253. G Van den Bosch, H J T Bos, J F Arens *Recl. Trav. Chim. Pays-Bas*, 1970, **89** 133
254. Yu I Baukov, G S Zaitseva, L I Livantsova, et al. *Zh. Obshch. Khim.*, 1979, **49** 2156
255. A I Dyadchenko, A V Semenovskii, V A Smit, M Kurbanov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 1345
256. M Z Krimer, L L Simonova, A I Spektor, USSR P. 727 624; *Byull. Izobret.*, 1980(14), 113
257. W Biernacki *Pol. J. Chem.*, 1980, **54** 777
258. M Z Krimer, L L Simonova, V I Spektor, et al., USSR P. 731 712; *Byull. Izobret.*, 1981(28), 304
259. A S Nakhmanovich, E N Deryagina, M G Voronkov *Doklady IV Vsesoyuznoi Konferentsii po Khimii Atsetilena* (Reports at the IV All-Union Conference on the Chemistry of Acetylene), Alma-Ata, 1972, Vol. 2, p. 449
260. P M M Nossiu, W N Speckamp *Tetrahedron Lett.*, 1979, 4411
261. H H Wasserman, J M Fernandez *J. Am. Chem. Soc.*, 1968, **90** 5322
262. P Vermeer, C De Graaf, J Meijer *Recl. Trav. Chim. Pays-Bas*, 1974, **93** 24
263. M Bourgain-Commercon, J P Foulon, J F Normant *Tetrahedron Lett.*, 1983, **24** 5077
264. P Vermeer, J Meijer, C Eylander *Recl. Trav. Chim. Pays-Bas*, 1974, **93** 240

265. S I Radchenko, L N Cherkasov, A A Petrov *Zh. Org. Khim.*, 1976, **12** 909
266. A Alexakis, G Cahiez, J F Normant *Tetrahedron*, 1980, **36** 1961
267. P J Stang *Chem. Rev.*, 1978, **78** 383
268. P Vermeer, J Meijer, C Eylander, L Brandsma *Recl. Trav. Chim. Pays-Bas*, 1976, **95** 25
269. J J Eisch, H Gopal, Rhee-Sue-Goo *J. Org. Chem.*, 1975, **40** 2064
270. H Westmijze, H Kleijn, P Vermeer *J. Organomet. Chem.*, 1982, **234** 117
271. J F H Braams, P P Moatijn, H J T Bos *Recl. Trav. Chim. Pays-Bas*, 1972, **91** 700
272. S I Radchenko, L N Cherkasov, B S Kupin, A N Krivosheya *Zh. Org. Khim.*, 1970, **6** 1961
273. S I Radchenko, L N Cherkasov, B S Kupin, A N Krivosheya *Zh. Org. Khim.*, 1971, **7** 104
274. L N Cherkasov, S I Radchenko, B S Kupin *Khim. Geterotsikl. Soed.*, 1971, 354
275. S I Radchenko, L N Cherkasov, A N Krivosheya *Zh. Org. Khim.*, 1972, **8** 28
276. L N Cherkasov, S I Radchenko *Izv. Vys. Ucheb. Zaved. Khim. Khim. Tekhnol.*, 1982, **25** 1441
277. L Miginiac *J. Organomet. Chem.*, 1982, **238** 235
278. S I Radchenko *Zh. Org. Khim.*, 1971, **7** 1306
279. W Ando, H Higuchi, T Migita *J. Org. Chem.*, 1977, **42** 3365
280. T P Zubova, V S Zavgorodnii, V N Strelets, A A Petrov *Zh. Obshch. Khim.*, 1971, **41** 1646
281. V S Zavgorodnii, T P Zubova, A A Petrov *Zh. Obshch. Khim.*, 1973, **43** 115
282. T P Zubova, V S Zavgorodnii, A A Petrov *Zh. Obshch. Khim.*, 1973, **43** 120
283. V S Zavgorodnii, A A Petrov, T P Zubova, et al. *Khimiya i Prakticheskoe Primenenie Kremnii- i Fosfororganicheskikh Soedinenii* (The Chemistry and Practical Applications of Organosilicon and Organophosphorus Compounds), Izd. LTI im. Lensoveta, Leningrad, 1977, p. 74
284. V S Zavgorodnii, N D Grigor'eva, A A Petrov *Zh. Obshch. Khim.*, 1981, **51** 2155
285. Ei-ichi Negishi, D E Van Horn *J. Am. Chem. Soc.*, 1977, **99** 3168
286. P Vincent, J-P Beaucourt, L Pichat *Tetrahedron Lett.*, 1982, **23** 63
287. M L Petrov, A A Petrov *Zh. Obshch. Khim.*, 1972, **42** 1863
288. M L Petrov, A A Petrov *Zh. Obshch. Khim.*, 1972, **42** 2345
289. M L Petrov, A A Petrov *Zh. Obshch. Khim.*, 1973, **43** 691
290. M L Petrov, V G Salishchev, A A Petrov *Zh. Obshch. Khim.*, 1974, **44** 2107
291. M L Petrov, V G Salishchev, A A Petrov *V Vsesoyuznaya Konferentsiya po Khimii Atsetilena. Tezisy Dokladov* (The V All-Union Conference on the Chemistry of Acetylene. Abstracts of Reports), Izd. Metsniereba, Thilisi, 1975, p. 225
292. V G Salishchev, M L Petrov, A A Petrov *Khimiya Elementoorganicheskikh Soedinenii* (the Chemistry of Organoelemental Compounds), Izd. Nauka, Leningrad, 1976, p. 91
293. M L Petrov, V G Salishchev, A A Petrov *Zh. Obshch. Khim.*, 1976, **46** 2390
294. V G Salishchev, M L Petrov, A A Petrov *Zh. Obshch. Khim.*, 1977, **47** 756
295. A M Torgomyan, M Sh Ovakimyan, M G Indzhikyan *Arm. Khim. Zh.*, 1979, **32** 288
296. A M Torgomyan, A S Pogosyan, M Shch Ovakimyan, M G Indzhikyan *Arm. Khim. Zh.*, 1980, **33** 408
297. G G Minasyan, G Ts Gasparyan, A M Torgomyan, et al. *Arm. Khim. Zh.*, 1982, **35** 583
298. R S Asatryan, N Sh Mailyan, M G Indzhikyan *Tezisy Dokladov VIII Vsesoyuznoi Konferentsii po Khimii i Primeneniyu Fosfororganicheskikh Soedinenii, Posvyashchennoi 80-Letiyu Reaktsii A E Arbuzova* (Abstracts of Reports at the VIII All-Union Conference on the Chemistry and Applications of Organophosphorus Compounds Commemorating the 80th Anniversary of the Arbuzov Reaction), Izd. Kazan. Univ., Kazan, 1985, Part 1, p. 143
299. M Schoufs, J Meijer, P Vermeer, L Brandsma *Recl. Trav. Chim. Pays-Bas*, 1974, **93** 241
300. A Kh Filippova, T V Kashik, G S Lyashenko, et al. *Zh. Obshch. Khim.*, 1983, **53** 1141
301. S I Radchenko *Zh. Org. Khim.*, 1977, **13** 504
302. M L Petrov, S I Radchenko, B S Kupin, A A Petrov *Zh. Org. Khim.*, 1971, **7** 1123
303. M L Petrov, S I Radchenko, B S Kupin, A A Petrov *Zh. Org. Khim.*, 1973, **9** 663
304. R C Cookson, R Gopalan *J. Chem. Soc., Chem. Commun.*, 1978, 924
305. W Drenth, H J Gruijter *Recl. Trav. Chim. Pays-Bas*, 1970, **89** 379
306. H Wevers, W Drenth *Rec. Trav. Chim. Pays-Bas*, 1974, **93** 99
307. A N Mirskova, N V Lutskaya, I D Kalikhman, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 572
308. A I Borisova, A Kh Filippova, V K Voronov, M F Shostakovskii *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, 498
309. N A Pogorzhel'skaya, I A Maretina, A A Petrov *Zh. Org. Khim.*, 1968, **4** 1148
310. M Reglier, O Ruel, R Lorne, S A Julia *Synthesis*, 1983, 624
311. A Zilverschonn, J Meijer, P Vermeer, L Brandsma *Recl. Trav. Chim. Pays-Bas*, 1975, **94** 163
312. M Makosza, M Jawdosiuk *Bull. Pol. Acad. Sci., Chem.*, 1968, **16** 589
313. J R Dombroski, C Schuerch *Macromolecules*, 1970, **3** 257
314. H Morii, S Fujishige, K Matsuzaki, U Toshiyaki *Makromol. Chem.*, 1982, **183** 1445
315. R Gräfing, A V E George, L Brandsma *Recl.: J. Royal Neth. Chem. Soc.*, 1982, **101** 346
316. S A Shilov, M V Sandyurëv, A V Dogadina, et al. *Zh. Obshch. Khim.*, 1984, **54** 457
317. D K Wedegaerther, R M Kopchik, J A Kampmeier *J. Am. Chem. Soc.*, 1971, **93** 6890
318. R I Shekhtman, I A Rybakova, E N Prilezhaeva, USSR P. 721422; *Byull. Izobret.*, 1980(10), 96
319. S I Radchenko, I G Sulimov, A A Petrov *Zh. Org. Khim.*, 1974, **10** 2456
320. S I Radchenko, L N Cherkasov, G I Pis'mennaya, Kh V Bal'yan *Zh. Org. Khim.*, 1970, **6** 2146
321. S I Radchenko, L N Cherkasov *Zh. Org. Khim.*, 1973, **9** 1352
322. S I Radchenko, L N Cherkasov *Zh. Org. Khim.*, 1972, **8** 1988
323. H J T Bos, H T Van der Bend, J S M Boleij, et al. *Recl. Trav. Chim. Pays-Bas*, 1972, **91** 65
324. H Polman, J S M Boleij, H J T Bos *Recl. Trav. Chim. Pays-Bas*, 1972, **91** 1088
325. A C Brouwer, H J T Bos *Tetrahedron Lett.*, 1976, 209
326. A C Brouwer, A V E George, D Seykens, H J T Bos *Tetrahedron Lett.*, 1978, 4839

327. A C Brouwer, H J T Bos *Recl. Trav. Chim. Pays-Bas*, 1983, **102** 484
328. A C Brouwer, H J T Bos *Recl. J. Royal Neth. Chem. Soc.*, 1983, **102** 103
329. A C Brouwer, H J T Bos *Recl. J. Royal Neth. Chem. Soc.*, 1983, **102** 91
330. A Mosterd, R E L J Lecluijze, H J T Bos *Recl. Trav. Chim. Pays-Bas*, 1975, **94** 72
331. M A Kazankova, T I Zverkova, I F Lutsenko *Doklady IV Vsesoyuznoi Konferentsii po Khimii Atsetilena* (Reports at the IV All-Union Conference on the Chemistry of Acetylene), Alma-Ata, 1972, Vol. 2, p. 173
332. H Schubert, M Regitz *Angew. Chem.*, 1983, **95** 564
333. M V Proskurina, N B Karlstedt, M V Livantsov *Zh. Obshch. Khim.*, 1979, **49** 1910
334. A M Sokol'skaya *Trudy Inst. Khim. Nauk Akad. Nauk Kazakh. SSR*, 1968, **22** 32
335. S I Radchenko, USSR P. 523088; *Byull. Izobret.*, 1976(28), 62
336. K Ohkubo, H Sato *Bull. Chem. Soc. Jpn.*, 1980, **53** 533
337. K Gollnick, H Hartmann *Tetrahedron Lett.*, 1982, **23** 2651
338. A P Tomilov, Yu M Kargin, I N Chernykh *Elektrokhimiya Elementoorganicheskikh Soedinenii. Elementy IV, V, VI Grupp Periodicheskoi Sistemy* (Electrochemistry of Organoelemental Compounds. Group IV, V, and VI Elements), Izd. Nauka, Moscow, 1986, p. 215
339. J Bastide, N El Chandour, O Henri-Rousseau *Tetrahedron Lett.*, 1972, 4225
340. A S Kostyuk, K A Knyaz'kov, S V Ponomarev, I F Lutsenko *Zh. Obshch. Khim.*, 1985, **55** 2088
341. M Franck-Neumann, J I Lohmann *Tetrahedron Lett.*, 1978, 3729
342. R E Harmon, R A Earl, S K Gupta *J. Chem. Soc. D*, 1971, 296
343. G Himbert, M Regitz *Chem. Ber.*, 1972, **105** 2975
344. P Ykman, G L'Abbe, G Smets *Chem. Ind.*, 1972(22), 886
345. C E Newall, A P Tinge, B. P. 2006769; *Chem. Abs.*, 1980, **92** 22497
346. F Hein, K Burger, J Firl *J. Chem. Soc. Chem. Commun.*, 1979, 792
347. K Burger, F Hein, C Zettl, H Schickaneder *Chem. Ber.*, 1979, **112** 3609
348. K Burger, F Hein *Chem.-Ztg.*, 1978, **102** 152
349. R M Adlington, A G M Barrett, P Quayle, et al. *J. Chem. Soc., Chem. Commun.*, 1981, 404
350. A P Kozikowski, S Goldstein *J. Org. Chem.*, 1983, **48** 1139
351. A P Kozikowski, Li Chun-Sing *J. Org. Chem.*, 1985, **50** 778
352. J Bastide, O Henri-Rousseau *Bull. Soc. Chim., Fr.*, 1973, 2294
353. J Bastide, O Henri-Rousseau *Bull. Soc. Chim., Fr.*, 1974, 1037
354. I E Chlenov, I L Sokolova, S S Novikov, V A Tartakovskii *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 473
355. I E Chlenov, I L Sokolova, S S Novikov, V A Tartakovskii *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 960
356. I E Chlenov, I L Sokolova, V N Khasanov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 382
357. N S Isaacs, P Stanbury *J. Chem. Soc., Perkin Trans. 2*, 1973, 166
358. C C McCarney, R S Ward, D W Roberts *Tetrahedron*, 1976, **32** 1189
359. N Morita, T Asao, Y Kitahara *Chem. Lett.*, 1972, 927
360. H H Wasserman, J U Piper, E V Dehmolow *J. Org. Chem.*, 1973, **38** 1451
361. M F Semmelhack, S Tomoda, H Nagaoka, et al. *J. Am. Chem. Soc.*, 1982, **104** 747
362. J D Wuest *Tetrahedron*, 1980, **36** 2291
363. G S Zaitseva, L I Livantsova, Yu I Baukov, I F Lutsenko *Zh. Obshch. Khim.*, 1984, **64** 1323
364. H Teufel, E F Jenny *Tetrahedron Lett.*, 1971, 1769
365. M Kuzuya, F Miyake, K Kamiya, T Okuda *Tetrahedron Lett.*, 1982, **23** 2593
366. D P Del'tsova, N P Gambaryan, G V Zeifman, I L Knunyants *Zh. Org. Khim.*, 1972, **8** 856
367. J Goerdeler, M L Tiedt, K Nandi *Chem. Ber.*, 1981, **114** 2713
368. M Sindler-Kulyk, D C Neckers *J. Org. Chem.*, 1982, **47** 4914
369. M Sindler-Kulyk, D C Neckers *J. Org. Chem.*, 1983, **48** 1275
370. E P Serebryakov, S L Kulomzina, V F Kucherov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 862
371. E P Serebryakov, S P Kulomzina-Pletneva, A Kh Margaryan *Tetrahedron*, 1979, **35** 77
372. E P Serebryakov, L M Kostochka, V F Kucherov *Zh. Org. Khim.*, 1973, **9** 2375
373. I Gupta, P Yates *J. Chem. Soc., Chem. Commun.*, 1982, 1227
374. G Desimoni, G Tacconi *Gazz. Chim. Ital.*, 1988, **98** 1329
375. P Righetti, G Tacconi, A Piccolini, et al. *J. Chem. Soc., Perkin Trans. 1*, 1979, 863
376. S El-Basil, M Said *Indian J. Chem., Sect. B*, 1980, **19**, 1071
377. R L Danheiser, S K Gee *J. Org. Chem* , 1984, **49** 1672
378. S V Ponomarev, O A Zakharova, S A Lebedev, I F Lutsenko *Zh. Obshch. Khim.*, 1975, **45** 2680
379. G Himbert, L Henn *Tetrahedron Lett.*, 1981, 2637
380. V S Zavgorodnii, E S Sivenkov, V N Shchipkova, A A Petrov *Zh. Obshch. Khim.*, 1970, **40** 2257
381. R G Mirskov, S P Sitnikova, M G Voronkov *Zh. Obshch. Khim.*, 1978, **48** 2137
382. R G Mirskov, O S Stankevich, S P Sitnikova, M G Voronkov *V Vsesoyuznaya Konferentsiya po Khimii Atsetilena. Tezisy Dokladov* (The All-Union Conference on the Chemistry of Acetylene. Abstracts of Reports), Izd. Metsniereba, Tbilisi, 1975, p. 201
383. V I Laba, A V Sviridova, E N Prilezhaeva *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, 212
384. V I Laba, A V Sviridova, E N Prilezhaeva *Doklady IV Vsesoyuznoi Konferentsii po Khimii Atsetilena* (Reports at the IV All-Union Conference on the Chemistry of Acetylene), Alma-Ata, 1972, Vol. 1, p. 537
385. V I Laba, M K Polievktos, E N Prilezhaeva, S G Mairanovskii *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, 2149
386. W Verboom, R S Sukhai, J Meuer *Synthesis*, 1979, 47
387. J V Comasseto, V Catani, J T B Ferreira, A L Braga *J. Chem. Soc., Chem. Commun.*, 1986, 1067
388. J V Comasseto, C C Silveira, J T B Ferreira *Synth. Commun.*, 1986, **16** 283
389. S I Radchenko, E A Ivanova *Zh. Org. Khim.*, 1973, **9** 1601
390. S I Radchenko, A A Petrov *Zh. Org. Khim.*, 1975, **11** 1988
391. C P Casey, S W Polichuowski, A J Shusterman, C R Jones *J. Am. Chem. Soc.*, 1979, **101** 7282
392. L R Beanan, J B Keiser *Organometallics*, 1985, **4** 1713
393. A V Gist, P C Reeves *J. Organomet. Chem.*, 1981, **215** 221
394. A Yamashita, T A Scahill, C G Chidester *Tetrahedron Lett.*, 1985, **26** 1159
395. A Yamashita, A Toy *Tetrahedron Lett.*, 1986, **27** 3471
396. E Müller, G Odenigbo *Chem. Ztg.*, 1973, **97** 387
397. J A Connor, G A Hudson *J. Organomet. Chem.*, 1975, **97** C43

398. J A Connor, G A Hudson *J. Organomet. Chem.*, 1978, **160** 159
399. J A Connor, G A Hudson *J. Organomet. Chem.*, 1980, **185** 385
400. M L Listemann, R R Schrock *Organometallics*, 1985, **4** 74
401. Yu V Rydvanskii, L M Kataeva, E G Kataev *Zh. Fiz. Khim.*, 1977, **51**(5) 1280 [English translation in *Russ. J. Phys. Chem.*, 1977(5)]
402. J Meijer, L Brandsma *Recl. Trav. Chim. Pays-Bas*, 1972, **91** 578
403. E Schaumann, F-F Grabley *Liebigs Ann. Chem.*, 1979, 1746
404. L Brandsma, P J W Schuijl, D Schuijl-Laros, et al. *Intern. J. Sulfur Chem., Pt. B*, 1971, **6** 85
405. L Brandsma, S Hoff, H D Verkruijsse *Recl. Trav. Chim. Pays-Bas*, 1973, **92** 272
406. S Hoff, L Brandsma, J F Arens *Recl. Trav. Chim. Pays-Bas*, 1969, **88** 609
407. R M Carlson, J L Isidor *Tetrahedron Lett.*, 1973, 4819
408. G J Baxter, R F C Brown, F W Eastwood, K J Harrington *Aust. J. Chem.*, 1977, **30** 459
409. M G Voronkov, E I Deryagina, V N Sukhomazova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 1188
410. G G Naumova, E I Brodskaya, A Kh Filippova, M G Voronkov *Vysokomol. Soedin., Ser. A*, 1974, **16** 1505
411. G G Naumova, A Kh Filippova, V N Salaurov, M G Voronkov *Vysokomol. Soedin., Ser. A*, 1975, **17** 2168
412. R Gompper, S Mensch, G Seybold *Angew. Chem. Int., Ed. Engl.*, 1975, **14** 704
413. A A Berlin, M I Cherkashin, I P Chernysheva *Khimiya Atsetilena* (The Chemistry of Acetylene), Izd. Nauka, Moscow, 1968, p. 331
414. G G Naumova, E I Brodskaya, A Kh Filippova, M G Voronkov *Doklady IV Vsesoyuznoi Konferentsii po Khimii Atsetilena* (Reports at the IV All-Union Conference on the Chemistry of Acetylene), Alma-Ata, 1972, Vol. 3, p. 155
415. T L Jacobs, N Juster *J. Chem. Eng. Data*, 1969, **14** 125
416. M G Chauser, G A Vakul'skaya, G A Vinogradov, et al. *Izv. Akad. Nauk SSR, Ser. Khim.*, 1971, 1591
417. N V Komarov, O G Yarosh, Z G Ivanova, USSR P. 326199; *Byull. Izobret.*, 1972(4), 79
418. H L Cohen *J. Polym. Sci., Polym. Chem. Ed.*, 1981, **19** 1337
419. E Fanghaenel, A M Richter, J M Richter, DDR P. 21118; *Chem. Abs.*, 1985, **102** 25247
420. S M Makin, I E Mikerin, O A Shavrygin, et al. *Zh. Org. Khim.*, 1984, **20** 2317
421. S M Makin, I E Mikerin, O A Shavrygin *Zh. Org. Khim.*, 1985, **21** 48
422. P M Smid, J Kalter, BRD P. 2228974; *Chem. Abs.*, 1973, **78** 84401
423. P M Smid, J Kalter, BRD P. 2264602; *Chem. Abs.*, 1974, **81** 49675
424. G Kruger, US P. 4134891; *Chem. Abs.*, 1979, **91** 39728
425. J Goto, T Nambara *Chem. Ind.*, 1972, 977
426. S C Welch, C P Hagan, D H White, et al. *J. Am. Chem. Soc.*, 1977, **99** 549
427. U Stache, W Fritsch, W Haede, K Radscheit *Liebigs Ann. Chem.*, 1977, 1461
428. E Flaskamp, H Budzikiewicz *Z. Naturforsch, B*, 1977, **32** 187
429. A Astier, A Pancrari, Khuong Hun Qui *Tetrahedron*, 1978, **34** 1487
430. J R Schauder, A Krief *Tetrahedron Lett.*, 1982, **23** 4389
431. M Anastasia, P Allevi, P Ciuffreda, et al. *J. Chem. Soc., Perkin Trans. 1*, 1985, 595
432. M Adinolfi, L Mangoni, G Barone, G Laonigro *Gazz. Chim. Ital.*, 1973, **103**
433. J L Martin, J S Tou, W Reusch *J. Org. Chem.*, 1979, **44** 3666
434. D M Hollinshead, S C Howell, S V Ley, et al. *J. Chem. Soc., Perkin Trans. 1*, 1983, 1579
435. J A Findlay, D N Desai, G C Lonergan, P S White *Can. J. Chem.*, 1980, **58** 2827
436. M Duraisamy, H M Walborsky *J. Am. Chem. Soc.*, 1983, **105** 3252, 3270
437. M H Tankard, J S Whitehurst *J. Chem. Soc., Perkin Trans. 1*, 1973, 615
438. M H Tankard, J S Whitehurst *Tetrahedron*, 1974, **30** 451
439. R K Hill, F W Lander *Tetrahedron Lett.*, 1975, 989
440. C Schmidt *Can. J. Chem.*, 1976, **54** 2310
441. A J G M Peterse, A DeGroot *Recl. Trav. Chim. Pays-Bas*, 1977, **96** 219
442. B A Sydney, G L Martin, J R H Ewart *J. Chem. Soc., Perkin Trans. 1*, 1977
443. F Sondheimer *J Org. Chem.*, 1978, **43** 2158
444. T Sano, Y Horoguchi, Y Tsuda *Heterocycles*, 1979, **12** 1427
445. R A Kuroyan, L A Akopyan, S A Vartanyan, E S Marashyan *Arm. Khim. Zhur.*, 1981, **34** 56
446. E E Van Tamelen, R G Nadeau *Bioorg. Chem.*, 1982, **11** 197
447. V K Sharma, H Shahriari-Zavareh, P J Garratt, F Sondheimer *J. Org. Chem.*, 1983, **48** 2379
448. T Tokoroyama, Y Fukuyama, T Kubota, K Yokotani *J. Chem. Soc., Perkin Trans. 1*, 1981, 1557
449. E Gelencher, T Dloukhby, N V Zotchik, I A Rubtsov *Biologicheski Aktivnye Soedineniya Atsetilenovogo Ryada* (Biologically Active Compounds of the Acetylene Series), Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 01.1978, No. 380-78 Dep.
450. G Kruger, BRD P. 2455279; *Chem. Abs.*, 1975, **83** 131844
451. V F Della, A Romeo, Belgian P. 894022; *Chem. Abs.*, 1983, **99** 58893
452. F Dorn, A Pfiffner, B Zehnder, Europ. P. 137456; *Chem. Abs.*, 1985, **103** 160396
453. T Murae, T Honda, S Ota, et al. *Tennen Yuki Kagobutsu Toroknkai Koen Yoshishu*, 24th, 1981, p. 348
454. T Takaya, Z Tozuka, N Yasuda, K Kawabata, French P. 2554115; *Chem. Abs.*, 1985, **103** 178109
455. H S Be, Y Kimura, A Suzuki *Agric. Biol. Chem.*, 1982, **46**

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Prospects for the chemistry of pyrrole

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ABSTRACT. The principal advances and trends in the development of the chemistry of monopyrrole compounds in the last 15 years are analysed and new approaches to the construction of the pyrrole ring and the introduction of functional groups into the latter as well as the possibilities of pyrroles as building blocks in organic synthesis are discussed.

The bibliography includes 116 references.

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I. Introduction

The modern chemistry of pyrrole is so extensive, is developing so rapidly, and covers so many different aspects that an adequate description of all its prospects and trends is hardly feasible in a single review.

Nature has assigned to pyrrole structures a fundamental role in the molecular logic of the entire living world. The two most important and interrelated biological processes — the photosynthesis of plants and the respiration of animals — are controlled by pyrrole systems — chlorophyll and haemoglobin. The non-fortuitously linked pyrrole rings (tetrapyrroles) have been chosen by evolution to create a microreactor in a molecular cavity with a very high degree of perfection and operating on a principle which we are only now beginning to understand and assimilate in relation to macrocyclic polyethers and their analogues. Special Conferences have been devoted to the properties and structures of tetrapyrroles.[1] In the present review, one can only conclude in the introduction that the chemistry of tetrapyrroles — porphyrins, chlorophylls, and haems — is now at an accelerating stage in its development: methods for their synthesis are being improved,[2–4] their biosynthesis is being investigated,[5–7] preparations for oxygen transport in living organisms are being synthesised from them,[8,9] metal complex catalysis using tetrapyrrole ligands is developing rapidly,[10–12] etc. (The literature on all these problems is extensive and here only some of the latest studies are quoted as an illustration.)

To make the picture complete, it is necessary to note just as briefly that during the last several years the polymerisation of pyrroles, especially electrochemical polymerisation, has received a powerful stimulus.[13–15] It has opened up a pathway to electrically conducting materials[16–22] with extensive prospects for their employment in electrical engineering (light, flexible conductors, powerful accumulators,[16,20] antistatic materials, ribbon heaters, HF screens), in electronics[16–18] (semiconductor devices, solar batteries and photoconductors,[18] photoelectrochromic memory and display devices,[17,19] electrophotographic systems[16]), in lithography,[21] for the photoelectrolysis of water,[22] etc.

The subject of the present review is the principal advances and trends in the development of the modern chemistry of monopyrrole compounds.

II. New methods for the construction of the pyrrole ring

Together with the improvement and modification of the traditional pyrrole syntheses (the Knorr, Paal–Knorr, Hantzsch, Piloti, Chichibabin and Yur'ev synthesis), new effective methods have been discovered for the construction of the pyrrole ring (see the review of Trofimov et al.[23] and the references therein) frequently from more readily available starting materials and perhaps preparatively more attractive. These include the following:

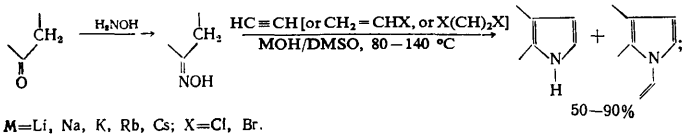
1. The reaction of ketoximes with acetylenes or their cryptoforms — vinyl halides and dihalogenoalkanes (see Refs. 23–25 and the references therein).
2. The condensation of βγ-dihalogenoketones with ammonia and primary amines.[26–34]
3. The decomposition of 1,3-oxazolidines in the presence of bases.[35–39]
4. The condensation of ketimines with 1-cyano-1-(*N*-methylanilino)alk-1-enes.[40,41]
5. The condensation of acetylenes with trimethylsilyl cyanide.[42,43]

1. The reaction of ketoximes with acetylenes (vinyl halides, dihalogenoalkanes)

The method based on the reaction of ketoximes with acetylenes, vinyl halides, or dihalogenoalkanes has developed to the greatest extent. More than 120 papers, more than 30 patents (see Refs. 23–25 and the references therein), a number of monographs[23,25,44] and reviews,[24,45] and a series of dissertations[46–50] have been devoted to this method. This reaction, its modifications, and its products are now being investigated by a series of research groups both in the USSR and abroad. An important place has been assigned to it in the new technical encyclopedia published in the USA (in the article "Acetylenes"[51]).

Here we shall consider mainly new results which have not been included in the existing monographs and reviews.

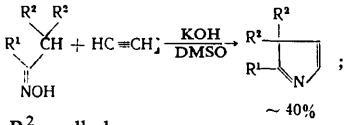
In a general form, the reaction can be represented schematically as follows:



M=Li, Na, K, Rb, Cs; X=Cl, Br.

Pyrroles and *N*-vinylpyrroles (when acetylene is used in excess) are formed from ketoximes with α-methylene or α-methyl groups without substituents sensitive to strong bases. The reaction is catalysed specifically by a superbasic alkali metal hydroxide–dimethyl sulphoxide (DMSO) system, whose activity increases in the sequence LiOH < NaOH < KOH < CsOH, and also in the presence of additives—open-chain additive or macrocyclic polyethers, which weaken ionic association and increase basicity. The KOH–DMSO system, which is readily available, convenient to use, and ensures satisfactory yields of pyrrole, is usually employed in practice. In fact, the chemistry of heterocyclic compounds now has at its disposal a reliable two-stage process involving the conversion of ketones into pyrroles with a wide variety of structures and their *N*-vinyl derivatives.

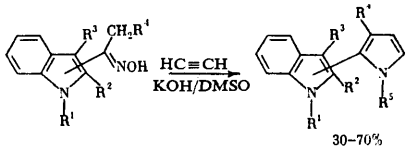
3*H*-Pyrroles, stabilised by two substituents in the 3-position, are formed from the reaction of ketoximes with an aliphatic α-CH group:[25,50,52]



R^1=Ar, R^2= alkyl.

Thus the reaction of ketoximes with acetylene leads to highly reactive but nevertheless difficult to obtain and therefore little investigated pyrrole isomers with an impaired aromatic conjugation. This is one of the promising aspects of the study of the given reaction.

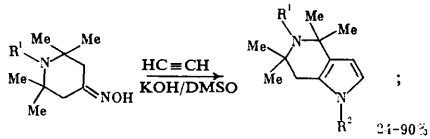
Studies[53,54] where this reaction was successfully extended to the oximes of 2- and 3-acylindoles and where a general approach to the synthesis of pyrrolylindoles—a whole class of previously unknown pyrrole compounds—was developed have made a definite contribution to the development of the process leading to the heterocyclisation of ketoximes by reaction with acetylene:



R^1, R^2, R^3=H, Me; R^4=H, Me, Pr^i, Ph; R^5=H, CH=CH$_2$.

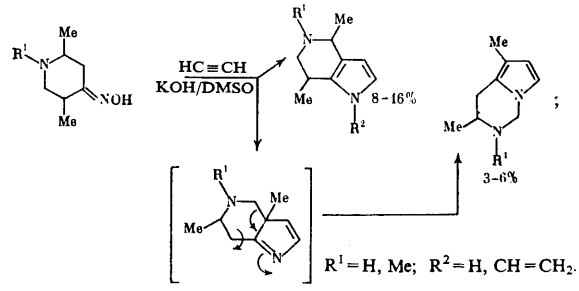
At the same time unambiguous evidence has been obtained for the *O*-vinyloxime heterocyclisation pathway.

Two research teams have recently independently extended this reaction to yet another class of ketoximes—piperidinone oximes, including those with a nitroxy-radical centre.[50,55–59] The latter fact is particularly important, since it indicates the absence of a one-electron stage in the process involving the conversion of ketoximes into pyrroles on treatment with acetylene. Otherwise, the nitroxy-radical, being an effective radical trapping agent, would have prevented the reaction. The outcome of these studies was the development of a general method of synthesis of rare azaindoles—pyrrolo[3,2-*c*]piperidines:



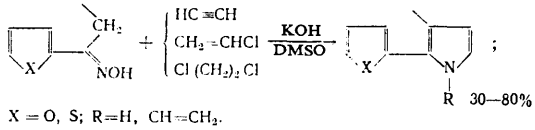
R^1 = H, OH, O$^-$; R^2 = H, CH=CH$_2$.

It is of interest that 1,2,3,4-tetrahydropyrrolo[1,2-*c*]pyrimidines have also been obtained from the oximes of 1,2,5-trimethyl- and 2,5-dimethyl-4-piperidinones apparently as a consequence of the rearrangement and aromatisation of the intermediate 3*H*-pyrroles formed via an alternative reaction involving the CH and not the CH_2 group:



R^1=H, Me; R^2=H, CH=CH$_2$.

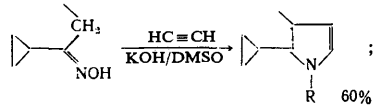
Furyl- and thienyl-pyrroles, which are now readily obtained from the oximes of acylfurans and acylthiophens,[23,25,60–64] have lost their exotic nature:



X = O, S; R=H, CH=CH$_2$.

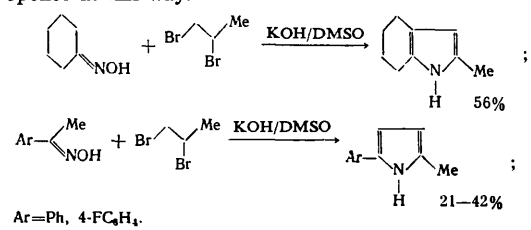
Thus the problem of the synthesis of compounds in which the pyrrole ring is linked to other five-membered aromatic heterocycles has now been obviated. Until recently this problem was solved in more complex ways.[65]

The first representatives of the class of cyclopropylpyrroles have been synthesised from the oximes of cyclopropyl ketones:[66]



R=H, CH=CH$_2$.

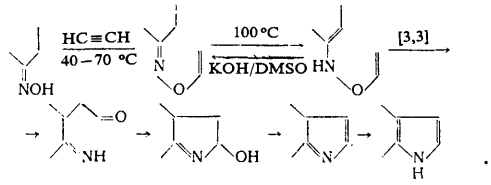
It has been shown recently that, together with dihalogenoethanes, 1,2-dihalogenopropanes can be used successfully in the synthesis of pyrroles from ketoximes.[67] The pathway to 2-R-5-methylpyrroles has been opened in this way:



Ar=Ph, 4-FC$_6$H$_4$.

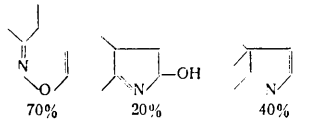
Since 1,2-dihalogenopropanes split off hydrogen chloride under the reaction conditions and are converted into methylacetylene and allene, these results suggest the possibility of pyrrole syntheses based on the industrially available methylacetylene–allene mixture and also on other alkylacetylenes and allenes.

Additional evidence for the intermediate formation of *O*-vinyloximes and for their [3,3]sigmatropic rearrangment has been obtained in a study of the interaction of the oximes of acylindoles and acetylene[49,54] and also of acetophenone oxime and acetylene.[68] It was shown that, even if this is not the only reaction path, it is at any rate the main one:



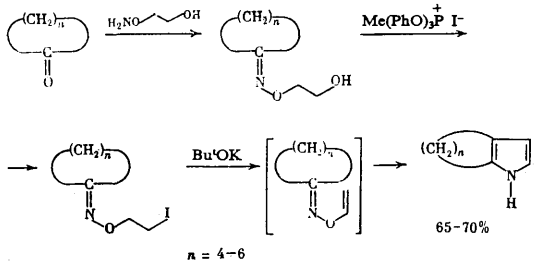
A convenient two-step method has been proposed on the basis of this mechanism[49,54,68] for the selective synthesis of pyrroles free from admixtures of *N*-vinyl derivatives: the *O*-vinyloxime is obtained initially at 40–70 °C from a ketoxime and acetylene and then it is rearranged, without being isolated, into a pyrrole at a temperature of the order of 100 °C.

In a number of instances, the reaction can be arrested at stages involving the formation of 2-hydroxy-2,3-dihydropyrroles and 3*H*-pyrroles:[25,69]



The chemistry of these relatively unstable but undoubtedly very interesting classes of pyrrole compounds developed fairly sluggishly until recently because of the lack of reliable methods of their synthesis. Nowadays, when this limitation has apparently been removed, one may expect an acceleration of the research in this field.

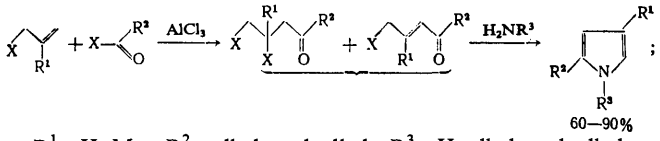
The method of synthesis of pyrroles from ketones via *O*-vinylketoximes has been used recently by English investigators[70] to obtain tetrahydroindole and pyrroles annelated to seven- and eight-membered saturated rings. For this purpose, *O*-(2-hydroxyethyl)ketoximes, prepared from the ketones and *O*-(2-hydroxyethyl)hydroxylamine, were treated with an excess of methyltriphenoxyphosphonium iodide and then the resulting iodide was converted by treatment with potassium t-butoxide into an *O*-vinyloxime, which was rearranged to the pyrrole:



Despite the high yield of pyrroles in the last stage, the advantages of this modification of the ketoxime method[24,25] do not appear unduly convincing in view of the large number of stages and the exotic nature of the reagents.

2. Condensation of βγ-dihalogenoketones with ammonia and primary amines

βγ-Dihalogenoketones or the αβ-ethylene-γ-halogeno-ketones, linked preparatively to them and readily obtainable by acylating allyl and methylallyl halides via the Kondakov reaction, afford 2,4-di- or 1,2,4-tri-substitute pyrroles in 60–90% yield on treatment with ammonia or primary amines:[26–34]

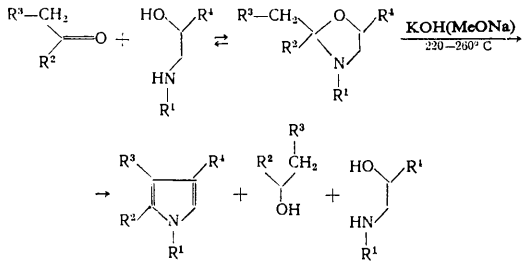


R^1 = H, Me; R^2 = alkyl, cycloalkyl; R^3 = H, alkyl, cycloalkyl, $CH_2=CHCH_2$ Ph.

The attempts to extend this method to other allyl halides were unsuccessful.[29] Nevertheless the synthetic potential of the method is very considerable: by varying the groups in the initial acid chlorides and amines, it is apparently possible to obtain fairly representative series of substituted pyrroles. The most complete publication on this reaction dates back to 1976.[29] Unfortunately this promising method has not been developed further.

3. Alkaline pyrrolysis of *N*-substituted 1,3-oxazolidines

When *N*-substituted 1,3-oxazolidines are fused with potassium hydroxide or alkali metal alkoxides, *N*-substituted pyrroles, secondary alcohols corresponding to the carbonyl component of the molecule, and the corresponding hydroxyalkylamines are formed. It is believed[35–39] that the "disproportionation" of the 1,3-oxazilidines takes place:



R^1 = alkyl, cycloalkyl, Ph, CH_2Ph, $(CH_2)_2OH$, $CH_2CH_2CH(CH_3)OH$;
R^2 = Et, Pr^n;
R^3 = Me, Et, Pr^i;
R^4-H, Me;
$R^2-R^3 = (CH_2)_4$, $(CH_2)_3CH(CH_3)$, $(CH_2)_5$.

The yield of pyrroles is 15–40% relative to the oxazolidine or 30–80% on the basis of the disproportionation mechanism, as stated in the original communications.[35–39] A limitation of the method is the impossibility of obtaining *N*-unsubstituted pyrroles. The conversion of *N*-β-hydroxyethyl derivatives into *NH*-pyrroles[71] (*N*-β-hydroxyethyl → *N*-vinyl → NH) requires at least a further

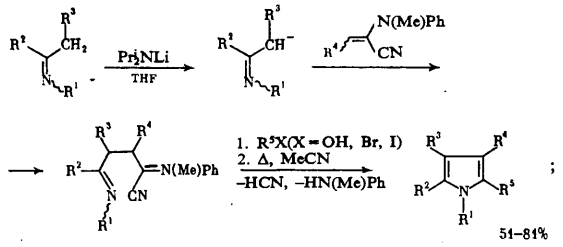
two–three preparative stages. *N*-Benzylpyrroles, which can be reduced to *NH*-pyrroles in one stage,[72] can be obtained by this method in a low yield (20% relative to oxazolidine).

The reaction mechanism has not been discussed.[35–39] It is however clear that this is a complex oxidation-reduction process occurring under the conditions of ultrahigh basicity (ultra-concentrated solutions of strong bases, chelation of alkali metal cations by 2-aminoalkanol molecules), where the dehydrogenating agent is the carbonyl component of the 1,3-oxazolidine. Although it had been established[38] that the addition of a ketone or an aldehyde to the reaction mixture promotes the reaction, subsequently this fact was ignored.[39]

Despite the low yield of products, severe reaction conditions, and the disadvantages and limitations associated with it, this method apparently merits attention and further improvement as a single-reactor synthesis of pyrrole from ketones and amiono-alkanols.

4. Condensation of ketimines with 1-cyano-1-(*N*-methylanilino) alk-1-enes

Yet another reaction permitting the conversion of ketones into pyrroles and based on the condensation of ketimines with 1-cyano-1-(*N*-methylanilino) alk-1-enes in the presence of the Pr^i_2NLi–tetrahydrofuran (THF) superbasic system, has been discovered recently:[40,41]

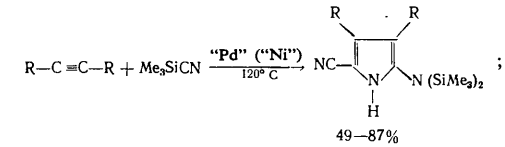


R^1 = Me, Pr^i, cyclo-C_6H_{11}, CH_2Ph;
R^2 = Me, Et, Bu^n;
R^3 = H, Me, Bu^n;
$R^2–R^3 = (CH_2)_3$;
R^4 = H, Et;
R^5 = H, Me, Et, Bu^n.

The key stage of this synthesis is the addition of the ketimine carbanion to the double bond. The carbanion adduct is subsequently protonated or alkylated and is then converted by heating in acetonitrile into the pyrrole with elimination of hydrogen cyanide and *N*-methylaniline, apparently via the [2,3]sigmatropic shift; the yield of the pyrrole is 50–80%. This is a one-pot method and in terms of its possibilities it is in essence similar to the syntheses of pyrroles from ketoximes and acetylene (1-anilino-1-cyanoalk-1-enes behave here as acetylenic synthons). However, in contrast to the ketoxime method, it does not permit the synthesis of *NH*- and *N*-vinyl pyrroles, is applied under dry conditions and in an inert atmosphere (argon), and requires reagents which are more expensive, more difficult to obtain, and less convenient to handle. It is also not clear whether other 1-amino-1-cyanoalk-1-enes can be used just as effectively in this synthesis.

5. Condensation of acetylenes with trimethylsilyl cyanide

Two groups of Japanese investigators[42,43] have recently discovered independently that the reaction of substituted acetylenes, catalysed by palladium or nickel compounds, with an excess of trimethylsilyl cyanide quite unexpectedly leads to 2-cyano-5-[*NN*-bis(trimethylsilyl)amino] pyrroles;



R = H, alkyl, aryl, 2-C_4H_3S, C≡CSiMe$_3$;
"Pd" = Pd(0), Pd/C, $PdCl_2$, $PdBr_2$, $Pd(OAc)_2$, $Pd(CN)_2$, $Pd(PhCN)_2$, $PdCl_2/C_5H_5N$, $PdCl_2(PPh_3)_2$, $Pd(PPh_3)_4$;
"Ni" = Ni(0), $NiCl_2/Bu^i_2AlH$, $NiCl_2/Et_3Al$.

There is such a profound redistribution of the atoms of trimethylsilyl cyanide during the reaction that so far it is difficult to put forward any reasonable mechanism for this process, particularly since in the case of disubstituted acetylenes it is necessary to assume the transfer of hydrogen from the methyl group to the nitrogen atom, since there are no other hydrogen donors in the system.

The single-stage nature and regioselectivity of the reaction, the availability of the initial compounds, and the high yields of pyrroles with reactive functional groups, which are difficult to introduce into the pyrrole ring by the usual methods, are all factors leading to good prospects for the new method.

6. General comments

In conclusion of this Section of the review, we may note that the majority of new methods for the construction of the pyrrole ring are based on ketones and acetylenes or their synthons and ultrastrong bases are used in many methods. These are the trends in modern pyrrole synthesis.

Unfortunately none of the methods examined permits the synthesis of pyrroles having both α-positions free (including, paradoxically, pyrrole itself), although such pyrroles are necessary, for example, for the construction of porphyrin structures. The search for reactions which might fill this gap remains urgently necessary.

III. Trends in the study of the reactivity of pyrrole compounds

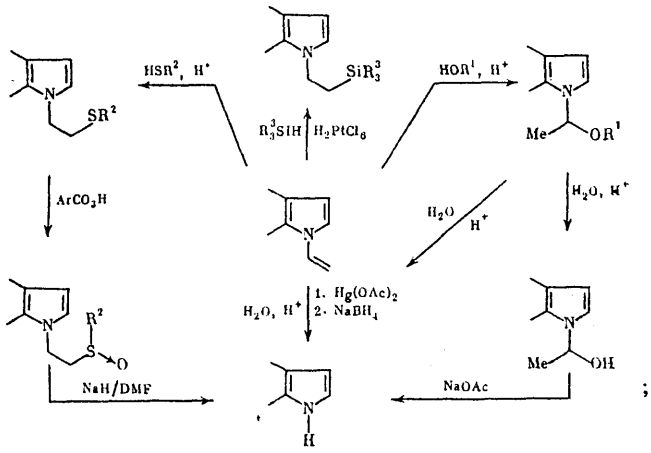
The following new trends have come to the fore in the field of the reactivity of pyrrole compounds: (a) systematic study of *N*-vinylpyrroles which have become available; (b) development of new methods for the introduction of functional groups into the pyrrole ring; (c) the growth of interest in 2*H*- and 3*H*-pyrroles as azadienes.

1. The reactions of *N*-vinylpyrroles

After it became possible to obtain *N*-vinylpyrroles in high yields in a single stage from ketoximes and acetylene (see Section I), they became the most readily available class of pyrrole compounds and, being completely uninvestigated, naturally attracted the attention of not only specialists in synthetic and polymer chemistry and biologists[25] but also of spectroscopists[25,44,46,73] and theoreticians.[75] The question arose how the reactivity and spectroscopic parameters of the pyrrole ring and of the double bonds are affected by the competition between the π-systems for conjugation with the unshared electron pair of the nitrogen atom. New prospects arose

for the synthesis of *N*-substituted pyrroles which are difficult to obtain, namely by the addition of various reagents to the double bond in *N*-vinylpyrroles (Scheme 1):[25] alcohols and water add to the double bonds under the conditions of electrophilic catalysis, thiols add under the conditions of radical catalysis, and hydrosilanes add under the conditions of metal complex catalysis.

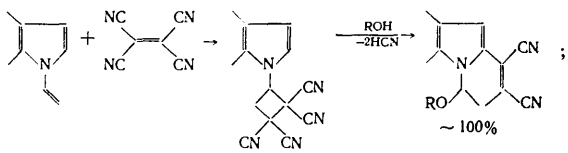
Scheme 1



R^1 = H, alkyl, aryl, $CH_2C{\equiv}CH$; R^2 = alkyl, aryl; R^3 = alkyl.

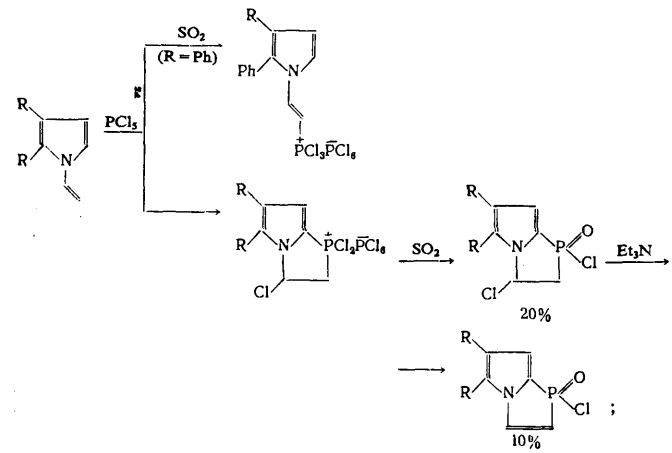
Since the *N*-vinyl and *N*-α-alkoxyethyl groups can be removed without difficulty by means of hydrolysis (for example, in the presence of mercury acetate followed by treatment with sodium tetrahydroborate[71]), *N*-vinylpyrroles are now regarded as protected *NH*-pyrroles and are used increasingly as such.[71] The *N*-β-alkylthioethyl group, into which the *N*-vinyl group can be readily converted and which can be subsequently removed if necessary after oxidation to the sulphoxide group (by treatment with peracids and then with sodium hydride in dimethylformamide[71]) can also serve successfully as a protecting group.

As expected,[25] *N*-vinylpyrroles have begun to be used for the synthesis of 1,2-fused condensed pyrrole systems. Thus they enter into [2 + 2] cycloaddition with tetracyanoethylene, forming *N*-(2,2,3,3-tetracyano-1-cyclobutyl) pyrroles, which are converted on heating with alcohols into 7,8-dicyano-5-organyloxy-5,6-dihydroindolizines in a virtually quantitative yield:[76,77]



R-alkyl, $CH_2CH{=}CH_2$, $CH_2C{\equiv}CH$, etc.

The phosphorylation of *N*-vinylpyrroles with phosphorus pentachloride opens up a pathway to new condensed pyrrole systems — pyrrolo[1,2-*a*]-1,3-dichloro-1-oxo-4,1-azaphospholans and pyrrolo[1,2-*a*]-1-chloro-1-oxo-4,1-azaphosphol-2-enes:[78]

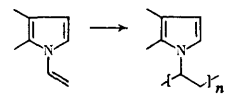


R = H, alkyl, Ph; R − R = $(CH_2)_4$.

A very pronounced competition for the electrophile between the α-position of the pyrrole ring and the double bond is observed in phosphorylation. In the case of electron-donating (alkyl) substituents, which increase the electron density in the ring, the heterocycle is phosphorylated initially and this is followed by annelation via the double bond, while phenyl substituents, which deactivate the ring, promote the attack by the electrophile on the vinyl group and the formation of a phosphorylated olefinic fragment with the (*E*)-configuration, which is incapable of further cyclisation.

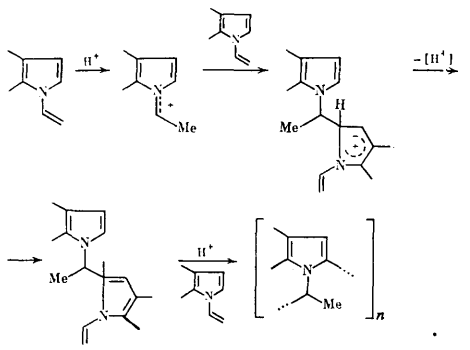
N-Vinylpyrroles are promising although little investigated systems for polymerisation. The interest in them as monomers has been growing rapidly. The principal results already achieved in this field have been surveyed in a review.[45]

N-Vinylpyrrole polymers and copolymers synthesised by the traditional radical polymerisation in the presence of azoisobutyrodinitrile have the properties of photoconductors:[79]



There are extensive possibilities for improving the properties of such polymers by altering the structural framework of the pyrrole ring and by its chemical modification. By means of the copolymerisation of *N*-vinypyrroles with other monomers, pyrrole fragments can be introduced into various polymers, imparting new properties to the latter.

The cationic oligomerisation of *N*-vinylpyrroles takes place in a non-traditional way — not as the usual vinyl polymerisation but as an alternative process — the carbonium ion, formed as a result of the addition of a proton to the *N*-vinyl group, attacks subsequently not the double bond but the heterocycle, converting it into the pyrrolium ion, which is stabilised by ejecting a proton:[80,81]



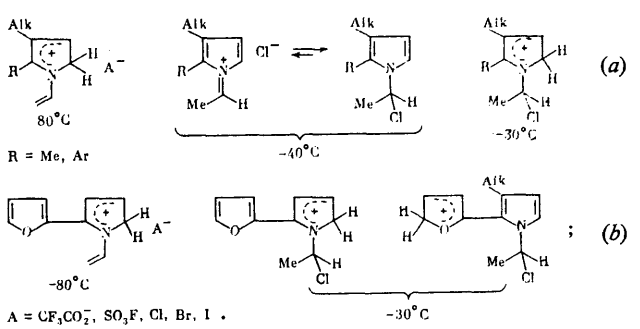
This process yet again illustrates clearly the competition between the double bond and the pyrrole ring in electrophilic reactions. The outcome of the reaction depends on the nature of the electron-deficient species: hard electrophiles (the proton) attack predominantly the double bond, while soft electrophiles (a delocalised carbonium ion) attack mainly the α-position in the pyrrole ring.

The protonated forms of *N*-vinylpyrroles — new types of stable carbonium ions and key intermediate species in the various electrophilic processes proceeding with participation of *N*-vinylpyrroles (polymerisation, addition, and substitution) — are being vigorously investigated.

The cations generated from *N*-vinylpyrroles in the presence of acids can find extensive applications in organic synthesis, in particular in the construction of new heterocyclic systems. Several examples of this kind were examined above.

The products of the protonation of *N*-vinylpyrroles both at the heterocycle and at the double bond and also both these nucleophilic centres simultaneously (Scheme 2, *a*) have been detected and characterised by NMR spectroscopy:[82]

Scheme 2



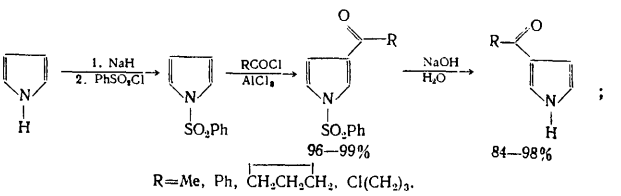
The mode of protonation and the ratio of the cations formed are determined by the strength and nature of the acid, the temperature, and the structure of the substituents in the pyrrole ring. Only the α-position of the pyrrole ring, regardless of the acid strength, is protonated at −80 °C. On raising the temperature to −30 °C in the presence of HCl taken in excess, the protonation of not only the ring but also of the double bond is observed. At −40 °C and in the presence of an equimolar amount of HCl, only *N*-α-chloroethyl derivatives are formed. It is of interest that 2-(2-furyl)-1-vinylpyrroles (Scheme 2, *b*) form selectively at −80 °C only the pyrrolium cations, whilst at a higher temperature (−30 °C) they form both pyrrolium and furanium cations at comparable concentrations. The products of the simultaneous protonation of the pyrrole and furan rings were not detected.[83]

Thus, in thermodynamically controlled electrophilic processes, the furan ring is not always significantly less reactive than the pyrrole ring, contrary to the established ideas.

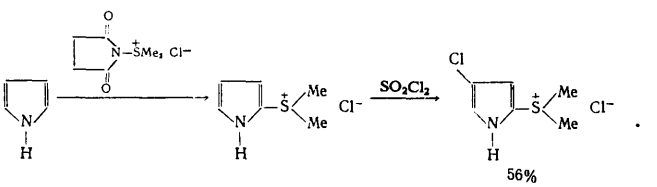
2. New methods for the introduction of functional groups into the pyrrole ring

Methods based on the alteration of the direction of attack by the reagent as a result of the introduction into the ring of polarising substituents (sulphonyl, sulphonium, etc.) have been developing to an increasing extent for the introduction of functional groups into pyrroles.[84]

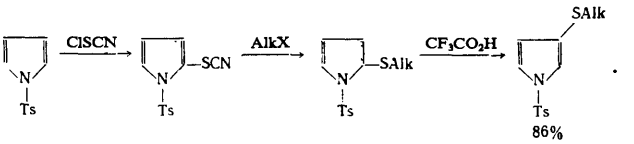
Reactions leading to electrophilic substitution in pyrroles take place predominantly in the α-position in the ring. However, in the case of *N*-sulphonylpyrroles, unprecedented regiospecific β-acylation takes place. The sulphonyl protecting and polarising group is removed just as readily as it is introduced. These preparatively simple operations constitute the basis of an effective method for the synthesis of β-acylpyrroles (in 84–98% yield):[85]



The α-dimethylsulphonium group, which can be readily introduced into the pyrrole ring with the aid of the adduct of dimethyl sulphide and *N*-chlorosuccinimide, similarly deactivates the heterocycle inductively and directs the electrophilic or radical substitution reaction (for example, chlorination[86]) to the 4-position:

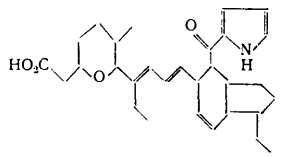


However, the redirecting effect of strong electron-accepting substituents is not always sufficient and is not sufficient for all electrophiles. For example, the direction of attack on the pyrrole ring by various sulphur chlorides cannot be altered in this way. In this case, the β-substitution products are obtained as a result of the acid-catalysed (CF_3COOH) migration of the alkylthio-group from the α- to the β-position:[87]



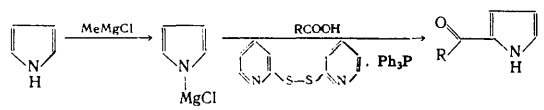
The HBr-catalysed migration of bromine from the α- to the β-position has been observed in the bromination of *N*-substituted pyrroles.[88]

In view of the important biological role of the 2-ketopyrrole structure and its role in the realisation of the programme designed for the complete synthesis of the antibiotic X-1457A, i.e.



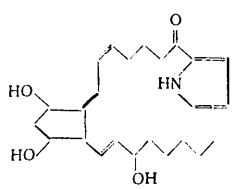
antibiotic X-1457A

a highly effective and highly selective method has been developed for the mild (−78 °C) acylation of pyrrolylmagnesium chloride by a 2-pyridyl thiolo-ester formed *in situ* from di(2-pyridyl) disulphide, triphenylphosphine, and a carboxylic acid:[89]



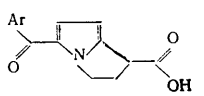
80—95%

The method is suitable even for complex polyfunctional and highly reactive compounds such as thromboxanes, prostaglandins, and monensin. For example, a ketopyrrole derivative has been obtained from prostaglandin $F_{2\alpha}$ in 95% yield:



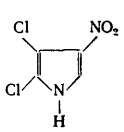
ketopyrrole derivative of prostaglandin $F_{2\alpha}$ ($PGF_{2\alpha}$).

Non-steroid anti-inflammatory and analgesic agents with the structure of 1,2-dihydro-3*H*-pyrrolo-1,2-*a*]pyrrole-1-carboxylic acid are being actively developed:

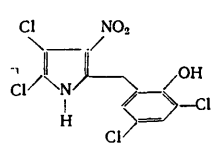


A series of novel methods for the cyclisation of pyrrole compounds have been developed for this purpose.[86,90]

The mode of halogenation and nitration of the pyrrole ring has now acquired special importance in connection with the isolation from natural substrates (*Streptomyces* SF-2080) of new chlorinated nitropyrrole antibiotics (pyrrolomycins A, B, etc.):[91,92]

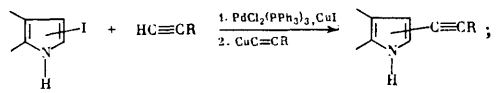


pyrrolomycin A (SF-2080 A)



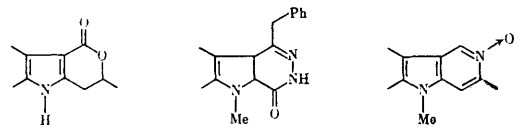
pyrrolomycin B (SF-2080 B)

The problem of the introduction of acetylenic substituents into the pyrrole ring has been solved.[93—101] Two mutually complementing versions of the condensation of iodopyrroles with acetylenes have been used for this purpose: catalytic [in the presence of $PdCl_2(PPh_3)_2$ or CuI] and acetylide. The yields of ethynylpyrroles are 50—96%:



R = H, alkyl, Ph, $C(OH)Me_2$.

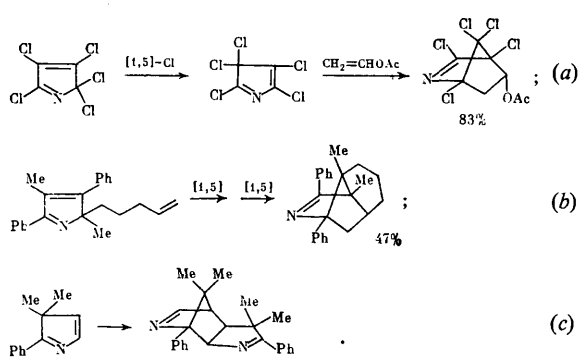
This reaction has important preparative consequences: the ethynyl substituent in the pyrrole ring provides new and unusually wide possibilities for the introduction of functional groups and the construction of complex heterocyclic systems, which has been demonstrated convincingly[102—105] in relation to the intramolecular cyclisation of functional pyrroles and indoles with ethynyl substituents, as a result of which pyran, pyridazine, and pyridine rings have been built onto the pyrrole ring:



3. 2*H*- and 3*H*-pyrroles as azadienes

The picture of the modern pyrrole chemistry would be incomplete if no mention were made of the enhanced interest in 2*H*- and 3*H*-pyrroles,[106] especially in the prospects for their employment in the Diels—Alder reaction as azadienes.[107] The first steps in this direction appear very promising. Examples of both intermolecular (Scheme 3, *a*) and intramolecular (Scheme 3, *b*) diene syntheses with participation of 3*H*-pyrroles, formed as a result of the rearrangement of 2*H*-pyrroles via a 1,5-shift, are known:[106—108]

Scheme 3



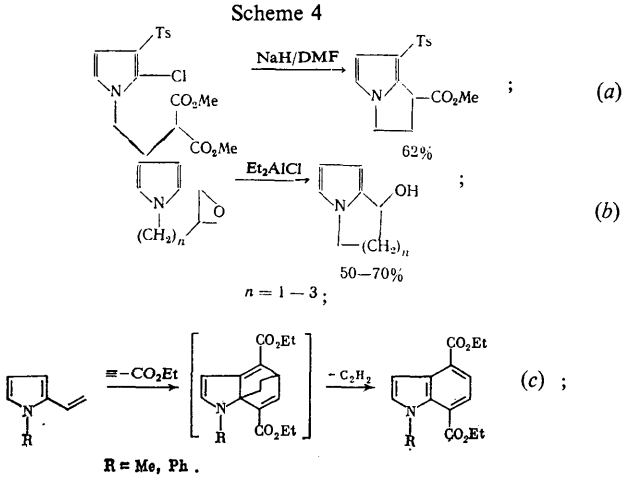
An interesting approach to new skeletal and condensed tetrahydropyridine systems may be provided by the diene autocondensation of the available 3,3-dimethyl-2-phenyl-3*H*-pyrroles (Scheme 3, *c*).[52]

IV. Pyrroles as intermediates in organic synthesis

Pyrroles have been recently investigated with increasing frequency not as objects of synthesis but as a means for the construction of particular complex molecules with a specified structure.[109] The most evident employment of pyrroles on these lines involves the synthesis of condensed heterocyclic systems by various annelation reactions.

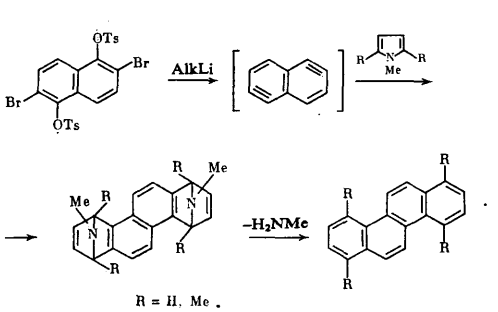
Intramolecular nucleophilic substitution of a halogen in the pyrrole ring, facilitated by the tosylate group (Scheme 4, *a*),[110] the electrophilic cyclisation of *N*-epoxyalkylpyrroles (Scheme 4, *b*),[111] and the diene condensation of 2-vinylpyrroles with electron-deficient acetylenes (Scheme 4, *c*)[109,112] are developing. *N*-Vinylpyrroles, which are now available, have led to new interesting prospects in this respect (see Section III, subsection 1).

Scheme 4



The use of the pyrrole ring itself as the 1,3-diene component in the Diels—Alder reaction for the construction of bicyclic structures with a bridging nitrogen atom is more traditional (Scheme 5).[109] Here pyrroles frequently play the role of butadiene synthons, because the adducts are capable of being deaminated. A typical example is provided by the synthesis of carcinogenic polycondensed aromatic hydrocarbons: pyrroles undergo the Diels—Alder condensation with 1,5-naphthodiyne generated *in situ* and subsequently give rise to chrysenes (in 33—49% yield) as a result of the splitting off of methylamine from the diadducts (Scheme 5):[113]

Scheme 5

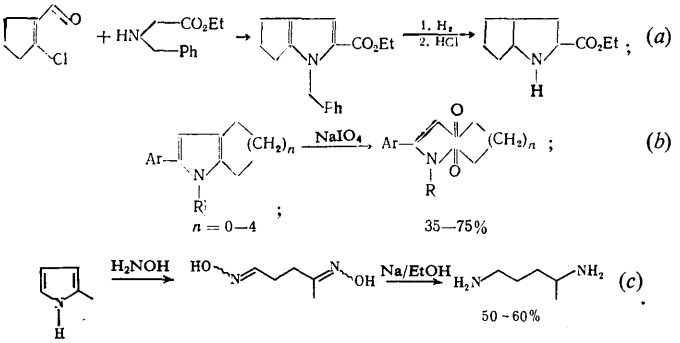


In many multistage specific syntheses, pyrroles are converted into pyrrolidine structures, for example, in the synthesis of 2-azabicyclo[3.3.0]octane-3-carboxylic acid—a key precursor of a highly active enzyme inhibitor (Scheme 6, *a*).[109,114]

The opening of the pyrrole ring is used successfully in the solution of certain synthetic problems. Thus macrocyclic ketolactams are obtained by the regiospecific oxidation of pyrroles annelated to alicyclic systems (Scheme 6, *b*).[115]

Dioximes formed from pyrroles on treatment with hydroxylamine have been used recently to synthesise 1,4-diaminobutanes, which participate, together with putrescine, spermidine, and spermine, in protein synthesis and cell proliferation (Scheme 6, *c*).[116]

Scheme 6



V. Conclusion

The chemistry of pyrroles continues to develop vigorously at the present time. In particular, this development has been stimulated by advances in the chemistry of porphyrins and organic metals. New approaches to the construction of the pyrrole ring and the introduction of functional groups into the latter are being vigorously developed. Pyrroles are being used increasingly as building blocks in organic synthesis. A close interaction and interpenetration of studies designed to seek and develop general synthetic reactions and methods, whose aim is the specific synthesis of complex structures, are characteristic of modern pyrrole chemistry.

References

1. G Blaer, H Sund (Editors) *Optical Properties and Structure of Tetrapyrroles*, Walter de Gruyter, Berlin, 1985, 536 pp
2. M Ono, R Lauftmann, K Inomata, et al. *Croat. Chem. Acta*, 1985, **58** 627
3. V A Makarov, E I Filippovich, R P Evstigneeva, et al. *Izv. Vys. Ucheb. Zaved. Khim. i Khim. Tekhnol.*, 1986, **29** 3
4. A S Semeikin, O I Koifman, B D Berezin *Khim. Geterotsikl. Soedin.*, 1986, 486
5. F J Leeper *Nat. Prod. Rep.*, 1985, **2** 561
6. S Kaur, M I Chicarelli, J R Maxwell *J. Am. Chem. Soc.*, 1986, **108** 1347
7. M W Stark, J G Hert, A R Battersby *J. Chem. Soc., Chem. Commun.*, 1986, 465
8. Japanese Appl. 60-58984; *Ref. Zh. Khim.*, 1986, 20088P
9. Japanese Appl. 60-58983; *Ref. Zh. Khim.*, 1986, 20089P

10. M-E De Carvalho, B Meunier *Nouv. J. Chim.*, 1986, **10** 223
11. J T Groves, Y Watanabe *J. Am. Chem. Soc.*, 1986, **108** 507
12. F Kojima, T Aida, S Inone *J. Am. Chem. Soc.*, 1986, **108** 391
13. R N Noufi *Appl. Phys. Commun.*, 1983, **3** 33
14. M Okano, K Itoh, A Fujishima, et al. *Chem. Lett.*, 1986, 469
15. S Ramesh, V S Muralidharan *Trans. SAEST.*, 1985, **20** 143
16. *Mater. Plast. Elast.*, 1983, (7) 390
17. O Inganas, I Lundstrom *J. Electrochem. Soc.*, 1984, **131** 1129
18. O Niwa, M Hikita, T Tamura *Appl. Phys. Lett.*, 1985, **46** 444
19. S Kuwabata, H Joneyama, H Tamura *Bull. Chem. Soc. Jpn.*, 1984, **57** 2247
20. *Chem. Eng. News*, 1986, **64** 33
21. M Hikita, O Niwa, A Sugita, et al. *Jap. J. Appl. Phys.*, 1985, **24**(2) Pt. 2, 79
22. *Chem. Eng. News*, 1982, **60** 19
23. B A Trofimov, L N Sobenina, A I Mikhaleva *Organicheskaya Khimiya. Uspekhi Sinteza Pirrolov* (Organic Chemistry. Advances in the Synthesis of Pyrroles), Izd. VINITI, Moscow, 1987, Vol. 7, 79 pp [*Itogi Nauki i Tekhniki* (Advances in Science and Engineering)].
24. B A Trofimov, A I Mikhaleva *Khim. Geterotsikl. Soedin.*, 1980, 1299
25. B A Trofimov, A I Mikhaleva *N-Vinilpirroly* (N-Vinylpyrroles), Izd. Nauka, Novosibirsk, 1984, 263 pp
26. E I Mamedov, Abstract of Candidate's Thesis in Chemical Sciences, Azerbaijan University, Baku, 1974
27. E I Mamedov, A G Ismailov *Uchenye Zapiski Min. Vysshego i Srednego Obrazovaniya Az. SSR.*, 1975, (2) 54
28. I I Ibragimov *Materialy XI Nauchnoi Sessii Posvyashchennoi Itogam Nauchno-Issledovatel'skikh Rabot, Koordiniruemykh Akademiyu Nauk Az. SSR po Problemam Estestvennykh Nauk za 1973 g.* (Proceedings of the XI Scientific Session Devoted to the Results of Research Coordinated by the Academy of Sciences of the Azerbaijan SSR on Problems in Natural Sciences during 1973), Baku, 1974, p. 44
29. I I Ibragimov, A N Kost, M M Guseinov, et al. *Khim. Geterotsikl. Soedin.*, 1976, 790
30. I I Ibragimov *Issledovaniya v Oblasti Sinteza Polimernykh i Monomernykh Produktov* (Studies in the Synthesis of Polymeric and Monomeric Products), Izd. Elm, Bakui, 1977, p. 76
31. I I Ibragimov, R A Gadzhily *III Vsesoyznaya Konferentsiya po Stereokhimii i Konformatsionnomu Analizu v Organicheskom i Neftekhimicheskom Sinteze: Tezisy Dokladov* (The III All-Union Conference on the Stereochemistry and Conformational Analysis in Organic and Petrochemical Synthesis: Abstracts of Reports), Baku–Sumgait, 1976, p. 43
32. I I Ibragimov, A N Kost *Nukleofil'nye Reaktsii Karbonil'nykh Soedinenii* (Nucleophilic Reactions of Carbonyl Compounds), Izd. Saratov. Univ., Saratov, 1977, p. 26
33. I I Ibragimov *VI International Congress of Heterocyclic Chemistry: Abstracts, Teheran*, 1977, p. 195
34. I I Ibragimov *III Vsesoyuznaya Konferentsiya po Khimii Geterotsiklicheskikh Soedinenii: Tezisy Dokladov* (The III All-Union Conference on the Chemistry of Heterocyclic Compounds: Abstracts of Reports), Rostov-on-Don, 1983, p. 15
35. B F Kukharev, A S Atavin *Khim. Geterotsikl. Soedin.*, 1973, 1580
36. B F Kukharev, A S Atavin *Zh. Org. Khim.*, 1974, **10** 670
37. USSR P. 1 047 901; *Byull. Izobret.*, 1983, (38)
38. B F Kukharev, V K Stankevich, V A Kukhareva *Khim. Geterotsikl. Soedin.*, 1984, 700
39. B F Kukharev, V K Stankevich, V A Kukhareva *Khim. Geterotsikl. Soedin.*, 1986, 533
40. H Ahlbrecht, K Pfaft *Synthesis*, 1980, 413
41. H Ahlbrecht, A Daacke *Synthesis*, 1984, 609
42. N Chatani, T Hanajusa *Tetrahedron Lett.*, 1986, 4201
43. T Kusumoto, T Hiyama, K Ogata *Tetrahedron Lett.*, 1986, 4197
44. A F Pozharskii, V A Anisimova, E B Tsupak *Prakticheskie Raboty po Khimii Geterotsiklov* (Practical Studies on the Chemistry of Heterocycles), Izd. Rostov. Univ., Rostov-on-Don, 1988, 158 pp
45. B A Trofimov, A I Mikhaleva, A I Morozova *Usp. Khim.*, 1985, **44** 1034 [English translation in *Russ. Chem. Rev.*, 1985(6)]
46. M V Sigalov, Abstract of Candidate's Thesis in Chemical Sciences, Irkutsk Institute of Organic Chemistry, Siberian Division of the USSR Academy of Sciences, Irkutsk, 1979
47. L N Sobenina, Abstract of Candidate's Thesis in Chemical Sciences, Irkutsk Institute of Organic Chemistry, Siberian Division of the USSR Academy of Sciences, Irkutsk, 1983
48. T A Tandura, Abstract of Candidate's Thesis in Chemical Sciences, Irkutsk Institute of Organic Chemistry, Siberian Division of the USSR Academy of Sciences, Irkutsk, 1980
49. V V Druzhinina, Abstract of Candidate's Thesis in Chemical Sciences, Moscow State University, Moscow, 1983
50. T N Borisova, Abstract of Candidate's Thesis in Chemical Sciences, The Friendship among Peoples University, Moscow, 1987
51. R J Tedeschi *Encyclopedia of Physical Science and Technology*, Acad. Press, New York etc., 1987, Vol. 1, p. 25
52. B A Trofimov, S G Shevchenko, S E Korostova et al. *Khim. Geterotsikl. Soedin.*, 1985, 1573
53. M A Yurovskaya, V V Druzhinina, Yu G Bundel' *III Vsesoyuznaya Konferentsiya po Khimii Geterotsiklicheskikh Soedinenii: Tezisy Dokladov* (The III All-Union Conference on the Chemistry of Heterocyclic Compounds: Abstracts of reports), Rostov-on-Don, 1983, p. 53
54. M A Yurovskaya, V V Druzhnina, M A Tyurekhodzhaeva, et al. *Khim. Geterotsikl. Soedin.*, 1984, 69
55. B A Trofimov, A I Mikhaleva, R N Nesterenko, et al. *VII Vsesoyuznaya Konferentsiya po Khimii Atsetilena: Tezisy Dokladov* (The VII All-Union Conference on the Chemistry of Acetylene: Abstracts of Reports), Erevan, 1984, p. 110
56. B A Trofimov *Z. Chem.*, 1986, **26** 41
57. T N Borisova, A V Varlamov, N S Prostakov *I Vsesoyuznaya Konferentsiya po Khimii, Biokhimii i Farmakologii Proizvodnykh Indola: Tezisy Dokladov* (The I All-Union Conference on the Chemistry, Biochemistry, and Pharmacology of Indole Derivatives: Abstracts of Reports), Tbilisi, 1986, p. 39
58. T N Borisova *VIII Molodezhnaya Konferentsiya po Sinteticheskim i Prirodnym Fiziologicheski Aktivnym Soedinenyam: Tezisy Dokladov* (The VIII Youth Conference on Synthetic and Natural Physiologically Active Compounds: Abstracts of Reports), Erevan, 1986, p. 33
59. B A Trofimov, A B Shapiro, R N Nesterenko, et al. *Khim. Geterotsikl. Soedin.*, 1988, 350
60. B A Trofimov, A I Mikhaleva, R N Nesterenko, et al. *Khim. Geterotsikl. Soedin.*, 1977, 1136
61. B A Trofimov, A I Mikhaleva, R I Polovnikova, et al. *Zh. Org. Khim.*, 1978, **14** 2461

62. B A Trofimov, A I Mikhaleva, R I Polovnikova, et al. *Khim. Geterotsikl. Soedin.*, 1981, 1058
63. B A Trofimov, S E Korostova, A I Mikhaleva, et al. *Khim. Geterotsikl. Soedin.*, 1983, 273
64. S E Korostova, A I Mikhaleva, R N Nesterenko, et al. *Zh. Org. Khim.*, 1985, **21** 406
65. W Hinz, R A Jones, S U Patel, et al. *Tetrahedron*, 1986, **42** 3753
66. I N Domnin, A I Mikhaleva, R N Nesterenko, et al. *Zh. Org. Khim.*, 1988, **24** 1788
67. I A Aliev, B R Gasanov, A I Mikhaleva, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2175
68. M A Yurovskaya, A Z Afanas'ev, Yu G Bundel' *Khim. Geterotsikl. Soedin.*, 1984, 1077
69. B A Trofimov, S E Korostova, A I Mikhaleva, et al. *Khim. Geterotsikl. Soedin.*, 1983, 276
70. D Dhanak, C B Reese, S Romana, et al. *J. Chem. Soc., Chem. Commun.*, 1986, 903
71. C Gonzales, R Greenhouse, R Tallabs, et al. *Can. J. Chem.*, 1983, **61** 1697
72. S Baroni, R Stradi, M J Saccarello *J. Heterocycl. Chem.*, 1980, **17** 1221
73. M V Sigalov, B A Trofimov, A I Mikhaleva, et al. *Tetrahedron*, 1981, **37** 3051
74. A F Ermikov, V K Turchaninov, K B Petrushenko, et al. *Zh. Obshch. Khim.*, 1988, **58** 450
75. V K Turchaninov, A F Ermikov, S E Korostova, et al. *Zh. Org. Khim.*, 1988 (in the Press)
76. USSR P. 1 199 757; *Byull. Izobret.*, 1985, (47)
77. A G Gorshkov, E S Domnina, A I Mikhaleva, et al. *Khim. Geterotsikl. Soedin.*, 1985, 848
78. V G Rozinov, G A Pensionerova, V I Donskikh, et al. *Zh. Obshch. Khim.*, 1986, **56** 790
79. L V Morozova, A I Mikhaleva, S E Korostova, et al. *Elektronika Organicheskikh Materialov* (Electronics of Organic Materials), Izd. Nauka Moscow, 1985, p. 305
80. B A Trofimov, A I Mikhaleva, L V Morozova, et al. *Khim. Geterotsikl. Soedin.*, 1983, 269
81. B A Trofimov, L V Morozova, M V Sigalov, et al. *Makromol. Chem.*, 1987, **188** 2251
82. M V Sigalov, E Yu Shmidt, B A Trofimov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1146
83. M V Sigalov, E Yu Shmidt, B A Trofimov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 2136
84. H J Anderson, C E Loader *Synthesis*, 1985, 353
85. J Rokach, P Hamel, M Kakushima, et al. *Tetrahedron Lett.*, 1981 4901
86. F Franco, R Greenhouse, J M Muchowski *J. Org. Chem.*, 1982, **47** 1682
87. M Kakushima, R Frenette *J. Org. Chem.*, 1984, **49** 2025
88. H M Gilow, D E Burton *J. Org. Chem.*, 1981, **46** 2221
89. K C Nicolaou, D A Clareman, D P Papahatyis *Tetrahedron Lett.*, 1981, 4647
90. H Carpio, E Galeazzi, R Greenhouse, et al. *Can. J. Chem.*, 1982, **60** 2295
91. N Ezaki, T Shomura, M Koyama, et al. *J. Antibiotics*, 1981, **34** 1363
92. N Kaneda, S Nakamura, N Ezaki *J. Antibiotics*, 1981, **34** 1366
93. S F Vasilevskii, T A Sundukova, M S Shvartsberg, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 1661
94. T A Sundukova, S F Vasilevskii, M S Shvartsberg, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 726
95. T A Prikhod'ko, Z P Trotsenko, S F Vasilevskii *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 1690
96. S F Vasilevskii, T A Sundukova, M S Shvartsberg, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 1871
97. M S Shvartsberg, S F Vasilevskii, T A Prikhod'ko *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 2524
98. T A Sundukova, S F Vasilevskii, M S Shvartsberg *VI Vsesoyuznaya Konferentsiya po Khimii Atsetilena i Ego Proizvodnykh: Tezisy Dokladov* (The VI All-Union Conference on the Chemistry of Acetylene and its Derivatives: Abstracts of Reports), Baku, 1979, Part 1, p. 57
99. S F Vasilevskii, T A Prikhod'ko, M S Shvartsberg, et al. *III Vsesoyuznyi Simpozium po Organicheskomu Sintezu: Tezisy Dokladov* (The III All-Union Symposium on Organic Synthesis: Abstracts of Reports), Moscow, 1981, p. 112
100. M S Shvartsberg, S F Vasilevskii, T A Prikhod'ko, et al. *V Vsesoyuznyi Kollokvium po Khimii, Biokhimii i Farmakologii Proizvodnykh Indola: Tezisy Dokladov* (The V All-Union Colloquium on the Chemistry, Biochemistry, and Pharmacology of Indole Derivatives: Abstracts of Reports), Tbilisi, 1984, p. 129
101. M S Shvartsberg, T A Prikhod'ko, V M Kurilenko, et al. *III Vsesoyuznaya Konferentsiya po Khimii Geterotsiklicheskikh Soedinenii: Tezisy Dokladov* (The III All-Union Conference on the Chemistry of Heterocyclic Compounds: Abstracts of Reports), Rostov-on-Don, 1983, p. 42
102. T A Prikhod'ko, S F Vasilevskii, M S Shvartsberg *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 2602
103. T A Prikhod'ko, S F Vasilevskii, M S Shvartsberg *VII Vsesoyuznaya Konferentsiya po Khimii Atsetilena: Tezisy Dokladov* (The III All-Union Conference on the Chemistry of Acetylene: Abstracts of Reports), Erevan, 1984, p. 104
104. S F Vasilevskii, A V Pozdnyakov, T A Prikhod'ko, et al. *II Vsesoyuznoe Soveshchanie po Khimii Azinov: Tezisy Dokladov* (The II All-Union Conference on the Chemistry of Azines: Abstracts of Reports), Sverdlovsk, 1985, p. 126
105. T A Prikhod'ko, Abstract of Candidate's Thesis in Chemical Sciences, Institute of the Chemistry and Kinetics of Combustion, Siberian Division of the USSR Academy of Sciences, Novosibirsk, 1987
106. M P Sammes, A R Katritzky *Advances in Heterocyclic Chemistry*, Acad. Press, New York, etc., 1982, p. 234
107. D L Boger *Chem. Rev.*, 1986, **86** 781
108. A Eddaif, A Laurent, P Mison, et al. *Tetrahedron Lett.*, 1981, 2779
109. B H Lipshutz *Chem. Rev.*, 1986, **86** 795
110. C Ortiz, R Greenhouse *Tetrahedron Lett.*, 1985, **26** 2831
111. S P Tanis, J W Raggon *J. Org. Chem.*, 1987, **52** 819
112. R A Jones, T A Saliente, J S Argnes *J. Chem. Soc., Perkin Trans. I*, 1984, 2541
113. G W Gribble, R B Perni *J. Org. Chem.*, 1985, **50** 2934
114. H Urbach, R Henning *Tetrahedron Lett.*, 1985, **26** 1839
115. G Ofsuyi, S Nakanishi, N Ohmura, et al. *Synthesis*, 1983, 390
116. D O A Garrido, G Buldain, B Frudman *J. Org. Chem.*, 1984, **49** 2619

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Syntheses of organic compounds in the presence of the fused iron catalyst and their mechanisms and kinetics

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ABSTRACT. New synthetic possibilities of the reduced promoted fused iron catalyst in intermolecular and intramolecular amination, cyanation, hydrogenation-dehydrogenation, and hydrodeoxygenation reactions and intermolecular and intramolecular dehydration, polymerisation, and isotope exchange are examined. The mechanisms and kinetics of the reactions leading to the synthesis of amines, alcohols, hydrocarbons, and other organic compunds are discussed. A laser Raman spectroscopic method is described for the investigation of heterogeneous organic catalysis *in situ*.

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I. Introduction

The problem of the development of new effective methods of synthesis of organic compounds remains, as before, of current interest in the field of organic synthesis and petrochemistry. The experimental data accumulated hitherto make it possible to differentiate the principal approaches which are most often used in the development of catalytic syntheses. By arranging the approaches in the order based on the decrease in the relative novelty of the reactions and catalysts, we obtain the following list:

(1) New reactions + new catalysts;
(2) Known reactions + new catalysts;
(3) New reactions + known catalysts;
(4) Known reactions + known catalysts.

The first approach is heuristic and the fourth involves the optimisation of known syntheses. In the present review, attention is concentrated on the second and third approaches, namely on the preparation of organic compounds of different classes using the reduced promoted fused iron catalyst (RPFIC), which is known primarily as the catalyst of the synthesis of ammonia from hydrogen and nitrogen and of organic compounds from CO and H_2. Since a large number of monographs and reviews (see, for example, Refs. 1–4) have been devoted to these two processes, they are not considered in this review.

Fused iron catalysts have a number of significant advantages, among which one should include in the first place the simplicity and ecological purity (lack of waste) in their preparation, low cost, high thermal stability permitting the use of catalysts of this type in highly exothermic processes (hydrogenation, hydrogenolysis, etc.), stability and mechanical strength which permit their use in reactors with a fluidised catalyst bed (fluid process), as well as the ease of varying their chemical composition (by employing as promoting agents various oxides or their mixtures), on which depend the activity and selectivity of the catalytic action. All the foregoing factors create, in our views, the necessary groundwork for a more comprehensive investigation of the RPFIC in order to synthesise organic compounds of different classes.

II. Fused iron catalysts: preparation, activation, and investigation

Several methods are used to prepare RPFIC. The following is most widely used under laboratory conditions. The initial mixture is made up from dry powders (60–120 mesh) comprising Fe_3O_4, whose fraction in the mixture is 90–95 wt. %, and promoting additives, which are usually Al_2O_3, SiO_2, K_2O, CaO, MgO, V_2O_5, BaO, Cr_2O_3, and MnO_2. By varying the composition of the initial mixture, it is possible to obtain catalysts with different activities, selectivities, and stabilities. The mixture of oxides is fused in a water-cooled steel crucible lined with asbestos and kaolin, fusing being effected with the aid of an electric arc generated by steel or copper electrodes, which are also water-cooled. The melting point of the mixture of oxides is 1500–1600 °C and the fusion time is 60–120 s. The ingots formed are comminuted and screened into fractions, from which the fraction with a grain size of approximately 1–3 mm is usually taken for preparative purposes in organic synthesis.

The catalyst is activated (reduced) at 400–480 °C and a hydrogen pressure of 1–50 atm, the reduction time being 4–50 h. Completion of the reduction of the catalyst is checked from the amount of water evolved, which is usually close to the stoichiometric amount. The catalyst activated in this way is pyrophoric and it is therefore stored and inserted into and removed from the reactor in a protecting gas atmosphere (CO_2, Ar, N_2). Depending on the composition and the preparation conditions, the reduced catalyst has a specific surface of 10 ± 5 m^2 g^{-1} (BET method, N_2).

The phase and elemental compositions of the RPFIC, both before and after reduction with hydrogen, have been the object of continuous study.[1,3,5–13] In the melting stage with promoting agents,

partial interaction of the components is already observed, leading to the formation of a multiphase multicomponent alloy.[5,12] When the latter is reduced with hydrogen, the iron oxides with different stoichiometries are almost quantitatively converted into α-Fe^0. At the same time, the displacement of the promoting agent and their compounds from the bulk of the catalyst onto the surface is observed. Certain other processes also occur, as a result of which the bulk phase and the surface of the RPFIC acquire different compositions.[1,5,6,13]

Thus the surface of the promoted fused iron catalyst for the synthesis of ammonia, containing (calculated relative to the non-reduced specimen) 2% Al_2O_3(Al/Fe = 0.16), 1% K_2O(K/Fe = 0.012), and 1.5% CaO(Ca/Fe = 0.015), the remainder being Fe_3O_4,† acquired, as shown by X-ray photoelectron spectroscopy, a composition‡ corresponding to the component ratios Al/Fe = 2.0, K/Fe = 0.78, and Ca/Fe = 1.2 after reduction with hydrogen.[13] Thus the fraction of Fe^0 on the surface of the given RPFIC was less than 50%.

Measurements of the fraction of Fe^0 on the surface of the RPFIC by the selective adsorption method agree with the results obtained by the X-ray photoelectron spectroscopic method.[1,5,14]

Information about the structure and properties of surface compounds directly in the course of the activation of heterogeneous catalysts and catalysis in their presence can be provided in principle by IR spectroscopy. Considerable advances have been achieved recently in the measurement of the IR spectra of adsorbed molecules.[15] However, the application of this method under real activation and catalytic conditions involves considerable experimental difficulties which become impossible to overcome for RPFIC owing to the strong absorption of IR radiation by the latter.

In this connection, the data on the activation of the RPFIC obtained by laser Raman spectroscopy *in situ* are of special interest. Despite the advantages of Raman spectroscopy over IR spectroscopy in the study of this catalyst (they have been described in detail[16]), there have so far been only two studies in which the method was applied to the RPFIC. In these studies, the interactions of H_2 and D_2 with the surfaces of RPFIC having the composition $5V_2O_5$ [17] and $3Al_2O_3 + 1K_2O$ [18] were investigated. Treatment of the RPFIC with H_2 is accompanied by the appearance of absorption bands in the region of $\sim$980 cm^{-1} [17] (Fig. 1) and $\sim$1950 cm^{-1},[18] which may indicate the presence on the surface of hydride-like forms of hydrogen having the structure

$$\overset{H^{\delta-}}{Fe^{(\delta+)}}\!\!\diagup\!\!\diagdown\!\!Fe \quad \text{and} \quad \overset{H^{\delta-}}{|}\;Fe^{\delta+}\,.$$

The surface of the RPFIC before the start of the catalytic reaction on the latter can be represented as shown[19] in Fig. 2. This scheme reproduces two significant features in the structure of the RPFIC surface. The first is associated with the presence of Fe^0 and hydride hydrogen on the surface. The second is due to the high concentration of oxide promoting agents on the surface, which suggests, in its turn, the existence on it of Brønsted and Lewis acid–base centres (pairs). Thus RPFIC can be classified as bifunctional heterogeneous catalysts which are capable of manifesting simultaneously both oxidation-reduction (hydrogenation-dehydrogenation) and acid–base properties.

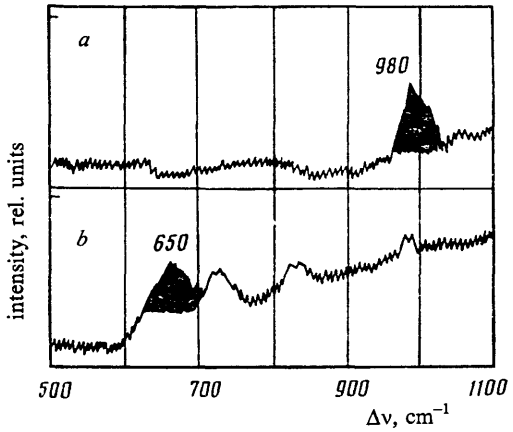


Figure 1. The Raman spectra *in situ* of the surface of an iron melted catalyst promoted with 5% V_2O_5 in the course of activation with protium or deuterium [187 °C, $p_{H_2(D_2)}$ = 0.2 MPa]:[17] *a*, H_2, $\nu_H \simeq 980$ cm^{-1}; *b*, D_2, $\nu_D \simeq 650$ cm^{-1}.

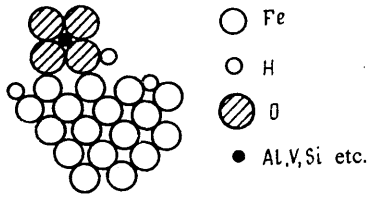


Figure 2. Schematic representation of the surface of a reduced promoted fused iron catalyst.[19]

Naturally, under the conditions of catalysis where there is direct interaction of the RPFIC with the reactants, the composition of the multiphase and multicomponent catalysts can undergo appreciable additional changes.[3,7,8,11,20–23] The effects of the reaction medium on the RPFIC have been studied in greatest detail in relation to syntheses from CO and H_2.[3,7,8,20,21,23] It has been established that, as a result of such interaction, the catalyst is enriched in iron carbides (ε-carbide, χ-carbide, etc.) and iron oxides of different composition ($Fe_{1-x}O$) both in the bulk phase and on the surface.

III. Modified Fischer–Tropsch syntheses

These include syntheses from CO and H_2 with the addition of a third component in which organic compounds belonging to different homologous series are formed. The use of a third component leads on the one hand, to new synthetic possibilities of the Fischer–

† An abbreviated formulation of the composition of the RPFIC will be used henceforth in the text, for example, $2Al_2O_3 + 1K_2O + 1.5CaO$.

‡ The composition of the RPFIC surface is understood as the composition of the surface layer 10–30 Å thick.

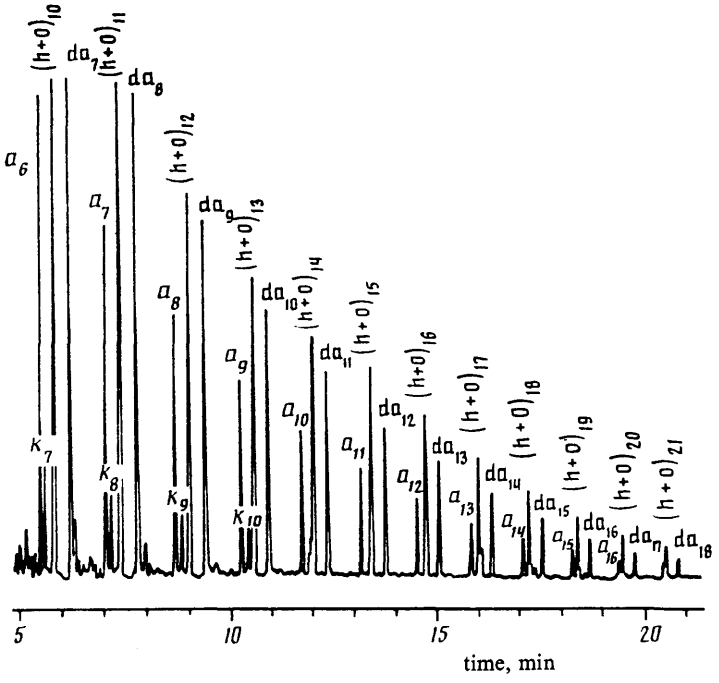


Figure 3. A fragment of the chromatogram of the products of synthesis from CO, H_2, and $(CH_3)_2NH$: h—alkanes; o—alkenes; a—alkanols; k—alkyl methyl ketones; da—dimethylalkylamines.

Tropsch reaction (FT-synthesis), associated primarily with the introduction of functional groups into individual components of the FT-product§ and, on the other hand, it makes it possible to discover and refine the mechanism of the interaction of CO and H_2. The third component, added directly to the synthesis gas, frequently plays simultaneously several functions, among which one should include, apart from those mentioned above, the functions of a chemical label, chemical trapping agent, synthesis initiating reagent, etc. As a rule, this component undergoes a wide variety of intrinsic reactions both with and without the participation of the components of the synthesis gas. Ammonia, primary and secondary amines, acetylenes and some of its derivatives, etc., are used as modifying substrates in FT-syntheses.

1. The Fischer–Tropsch synthesis modified by ammonia or alkylamines

The first example of such FT-synthesis is the preparation of alkylamines from CO, H_2, and ammonia.[24,25] In the presence of the RPFIC $5Al_2O_3 + 7BaO$ at 175–205 °C, a synthesis gas ($H_2:CO = 2$) pressure of 20 MPa, and an ammonia concentration of 8 vol. %, a product containing up to 30% of alkylamines was obtained. The alkylamines consisted of 88.5% of primary amines, 8.5% of secondary amines, and 3% of tertiary alkylamines.[26]

§ Here and henceforth the components of the FT-product are understood to be organic compounds of one class (hydrocarbons, alcohols, etc.).

In order to increase the yield of alkylamines in the FT-synthesis with participation of ammonia, catalysts of different composition have been used.[27–29] The best result (selectivity with respect to alkylamines of 50%) was achieved in the presence of a RPFIC prepared on the basis of natural magnetite.[29]

Methods have been developed for the synthesis of secondary alkylamines from CO, H_2 and n-butylamine [30] or methylamine,[31] and also for the synthesis of tertiary alkylamines from CO, H_2, and dimethylamine.[32] At 168–175 °C, a synthesis gas pressure of 10–14 MPa, and for $H_2:CO:$methylamine = 1:1:1.25 ratios, the yield of alkylamines reached 35–35 g m^{-3} in terms of the converted synthesis gas with a selectivity with respect to n-alkylmethylamines of 78%.[31]

It is noteworthy that, together with alkylamines, other components of the FT-products, especially alkanols, are formed in all cases when ammonia or alkylamines are used as modifying additives.[23–32]

Using high performance gas–liquid chromatography on quartz capillary columns and chromatograph-linked mass spectrometry, a detailed study has been made of the composition of the products of synthesis from CO, H_2, and ammonia[33] and dimethylamines[32,34,35] (Fig. 3 of Table 1).

The mechanisms of the formation of alkylamines in modified FT-syntheses have been examined[28,32–35] and it has been shown[32–35] that the mechanism proposed by Henrici-Olive,[28] which presupposes competition between CO and NH_2 for insertion in the metal–alkyl bond, does not operate when the reaction is carried out in the presence of the RPFIC. The probable pathways leading to the

formation of alkylamines in the presence of RPFIC can be represented schematically as follows:[32-35]

$$n\,CO + (2n+1)\,H_2 \xrightarrow[-(n-1)H_2O]{} [OI]_n \xrightarrow{+H_2} C_nH_{2n}O$$

$$[OI]_n \xrightarrow{-H_2O,\ +HNR^1R^2,\ H_2} C_nH_{2n+1}NR^1R^2,$$

where $[OI]_n$ is an oxygen-containing intermediate in which the number of carbon atoms is n and R^1, R^2 = H or Me.

One of the pathways in this scheme leads to the formation of amines as a result of the direct hydroamination of the surface oxygen-containing intermediate $[OI]_n$—the precursor of an aldehyde, ketone, or alcohol, while the other pathway leads to the hydroamination of the alkanals and alkyl methyl ketones $C_nH_{2n}O$—the primary components of FT-products. The scheme proposed above agrees with the data in Table 1 and with the fact that the alkanols formed under the conditions of the FT-synthesis with the addition of a third component are not aminated.[34,35]

Table 1. Composition of Fischer–Tropsch synthesis products (wt. %) with participation of ammonia and dimethylamine (RPFIC $1Al_2O_3 + 1.5BaO + 0.4SiO_2$, 176 °C, 12 MPa, $H_2 : CO = 4$).

Reaction	Alkanes	Alkenes	Alkanols	Alkyl-methyl ketones	Alkyl-amines	Unidentified components	Refs.
$CO + H_2$	26.5	9	50	3.5	—	11	[33]
$CO + H_2 + (CH_3)_2NH$ (5%)	29	8.5	18	3.5	26*	15	[32]
$CO + H_2 + NH_3$ (12%)	32	11.5	6.5	2	37**	11	[33]

* Alkylamines $C_nH_{2n+1}N(CH_3)_2$, where $1 \leqslant n \leqslant 17$.

** Alkylamines $C_nH_{2n+1}NH_3$ including 3.5% of di-n-alkylamines.

2. The Fischer–Tropsch synthesis modified by acetylene and its derivatives

The addition of acetylene or its derivatives makes it possible in the first place to increase the productivity of the FT-synthesis.

The productivity of the gas-phase synthesis from CO and H_2 with the addition of 1.5% of C_2H_2 at 170–190 °C, p_{CO} = 11 MPa, and p_{H_2} = 3.5 MPa in the presence of the RPFIC $2Al_2O_3 + 0.5V_2O_5 + (0.5-1)K_2O$, calculated relative to the product which is a liquid at 20 °C, amounted to 60–65 g h^{-1} (litre cat.)$^{-1}$ [36,37] against 40–45 g h^{-1} (litre cat.)$^{-1}$ in the usual FT-synthesis. The achievement of the acetylene-modified FT-synthesis in the liquid phase makes it possible to increase the productivity to 450 g h^{-1} (litre cat.)$^{-1}$.[38]

The study of the products of the FT-synthesis from CO, H_2, and $HC{\equiv}{}^{14}CH$ showed that the molar radioactivity of all the alkanols, starting with 1-propanol, is constant and close to the molar radioactivity of the added acetylene,[39] i.e. acetylene (or its radioactive fragment) is incorporated singly in the growing hydrocarbon chain. This fact suggests that the observed increase in productivity is caused by the initiating role of acetylene, which gives rise to a primary C_3 complex on interaction with the synthesis gas.[40,41]

The FT-syntheses modified by compounds having the general formula R–C≡CH, where R = Ph, CH_2OH, CH_2OCH_3, or $CH_2O(CH_3)_3$, have been investigated.[42-47] In the presence of the RPFIC $(3-4)(SiO_2 + Al_2O_3 + V_2O_5) + (0.5-1)K_2O$, the interaction of the synthesis gas with phenylacetylene yields mainly aromatic alkyl-substituted alcohols and hydrocarbons having the composition $Ph(CH_2)_nX$, where n = 3–8 and X = OH or H. Most of the added phenylacetylene is then hydrogenated to styrene and ethylbenzene and gives rise to oligomers. Apart from the components containing an aromatic ring, the product contains up to 25% of n-alkanes, alkanols, and alkanals. Certain characteristics of the phenylacetylene-modified FT-synthesis are presented in Table 2.

Table 2. Characteristics of the gas-phase and liquid-phase syntheses of aromatic alkyl-substituted alcohols from CO, H_2, and PhC≡CH (150 °C, 10 MPa, $CO : H_2 = 1$, $v = 10^3$ h^{-1}).[44]

Process	Productivity, g h^{-1} (litre cat)$^{-1}$			Selectivity, %			Losses, %	Conversion, %
	$\Sigma Ac_{ph} + Ad_{ph}$	H_{ph}	ΣAc, Ad, H	$\Sigma Ac_{ph} + Ad_{ph} + H_{ph}$	EB + ST	oligomers		
Liquid-phase (C_6H_6 soln)	48	21	1—1.5	21	43	1	6	29
Gas-phase	15	5	6—8	7	15	70	3	5

Notation. v is the space velocity of the synthesis gas, $\Sigma Ac_{ph} + Ad_{ph}$ the overall content of alcohols and aldehydes incorporating the $Ph(CH_2)_2$ fragment, H_{ph} hydrocarbons containing the $Ph(CH_2)_2$ fragment, ΣAc, Ad, H the overall content of alkanols, alkanals, and alkanes, EB + ST the overall content of ethylbenzene and styrene.

The synthesis of bifunctional compounds—αω-diols and alkoxyalcohols—from CO, H_2, and substituted acetylenes have also been achieved in the presence of RPFIC:[45-47]

$$CO + H_2 + HC{\equiv}CCH_2OH \rightarrow HO(CH_2)_nOH + H_2O,$$

$$CO + H_2 + HC{\equiv}CCH_2OR \rightarrow HO(CH_2)_nOR + H_2O,$$

where R = CH_3 or $C(CH_3)_3$ and n = 4–7.

In terms of their reactivity in the synthesis, the initiating reagents can be arranged in the sequence $HC{\equiv}CH > PhC{\equiv}CH > (CH_3)_3COCH_2C{\equiv}CH \simeq CH_3OCH_2C{\equiv}CH > HOCH_2{\equiv}CH$.

It has been shown[48] that oct-1-yne, hex-1-yne, and hex-3-yne participate, like acetylene, in the propagation of the hydrocarbon chain in their interaction with the synthesis gas. On the other hand, acetonitrile, butyne-1,4-diol, and the halogenoalkynes $HC{\equiv}CCH_2X$, where X = Cl or Br, do not possess the properties of initiating reagents in the FT-synthesis.

IV. Reactions of alcohols, aldehydes, and olefins under the conditions of the Fischer–Tropsch synthesis

In order to elucidate the possible involvement of oxygen-containing compounds in FT-synthesis in the presence of RPFIC of different composition, the reactions of the methanol $^{14}CH_3OH$,[49-51] the ethanols $CH_3{}^{14}CH_2OH$, $^{14}CH_3CH_2OH$, $CH_3{}^{14}CD_2OH$, and $CD_3{}^{14}CH_2OH$,[52-54] the propanols $CH_3CH_2CH_2OH$, CH_3CH_2.

.$^{14}CH_2OH$, $CH_3{}^{14}CH_2CH_2OH$, $^{14}CH_3CH(OH)CH_3$,[49,55,56] the butanols n-C_4H_9OH, $^{14}CH_3CH(CH_3)CH_2OH$, and $C_3H_7{}^{14}CH_2OH$,[49,51,55] benzyl alcohol,[57] the formaldehyde $H^{14}CHO$,[50] the ethanals $CD_3{}^{14}CHO$ [58] and $CD_2D^{14}CHO$,[59] and propanol[55,56] were investigated. It was established that the principal reactions of alkanals under the conditions of the FT-synthesis are their hydrogenation to the corresponding alcohol, decarbonylation to alkanes containing 1 carbon atom less, and oxidation to the corresponding acid.[55,58,59] On the other hand, acetaldehyde added to the synthesis gas is partly decomposed via the reaction[59]

$$2CH_3CHO+2H_2=C_4H_9OH+H_2O.$$

Under the conditions of FT-synthesis, alcohols undergo ester condensation:[55,59]

$$2C_4H_9OH=C_3H_7COOC_4H_9+2H_2$$

and enter into a homologisation reaction:[51]

$$C_4H_9OH+CO+2H_2=C_5H_{11}OH+H_2O.$$

Aromatic alkyl-substituted alcohols and hydrocarbons $Ph(CH_2)_nX$, where X = OH or H and n = 2–4, were first obtained in FT-synthesis with added benzyl alcohol. The conversion of $PhCH_2OH$ reaches 90% in the presence of the RPFIC $2Al_2O_3$ + $0.8V_2O_5$ + $0.5K_2O$. The main alcohol reaction product is then toluene, benzene and bibenzyl being formed in small amounts.[57]

Studies on syntheses from CO and H_2 with added alkenes CH_3CH_2CH = $^{14}CH_2$,[60] CH_2 = $^{14}CH_2$,[56,61,62] CH_2 = CH_2,[63] and CH_2 = $C(CH_3)CH$ = CH_2 [64] are important for the understanding of the mechanism of the FT-synthesis and ways of intensifying it. The principal reaction of olefins is their hydrogenation (to the extent of 80–90%) to the corresponding alkanes. On the other hand, but-1-ene is partly converted into n-pentane and pent-1-ene in the presence of RPFIC $2Al_2O_3$.[60]

However, under the conditions of FT-synthesis in the presence of RPFIC alkenes are capable of entering to a definite extent also into the oxo synthesis reaction,[60,62] the yield of alcohols increasing with increase in their concentration (Table 3).

Table 3. The influence of ethylene on the yield of alcohols in synthesis from CO and H_2 in the presence of the RPFIC $2Al_2O_3$ + $0.5V_2O_5$ + $0.5K_2O$ [62] (2–2.5 MPa, H_2 : CO = 3.8).

T, °C	C_2H_4 concentration, %	Relative yield of $C_nH_{2n+1}OH$ with different n				
		1	2	3	4	5
204	7	0.4	1.0	1.0	0.3	0.2
204	15	0.3	1.0	1.3	0.4	0.3
230	50	0.3	1.0	13.0	0.6	0.5
230	0	0.3	1.0	0.4	0.2	0.1

Studies on the reactions of aldehydes, alcohols, and olefins under the conditions of FT-synthesis[49–65] have shown that in the presence of the RPFIC the contribution of reactions with participation of these compounds with formation of the FT-product is as a rule low and amounts to only several per cent.

Apart from the synthesis from CO and H_2, the synthesis from CO and H_2O (the Kölbel–Engelhardt synthesis), which results in the formation of products close in composition to the FT-product, has also been achieved.[66]

The synthesis from CO and H_2O in the presence of RPFIC was first achieved in the presence of the catalyst for ammonia synthesis at a temperature of 300 °C, a pressure of 4 MPa, and for the ratio CO : H_2O = 2–2.5. Under these conditions, the conversion of CO reaches 84% and the main products are alkanes and alkenes.[67] The formation of alkanes in the Kölbel–Engelhardt synthesis (KE-synthesis) is formally regarded as a result of the combination of the water gas reaction[4] and the FT-synthesis:

$$(2n+1)CO+(2n+1)H_2O=(2n+1)CO_2+(2n+1)H_2 \quad \text{(water gas reaction)},$$
$$n\,CO+(2n+1)H_2=C_nH_{2n+2}+n\,H_2O \quad \text{(FT-synthesis)}$$
$$(3n+1)CO+(n+1)H_2O=C_nH_{2n+2}+(2n+1)CO_2 \quad \text{(KE-synthesis)}$$

Similar combinations of stoichiometric equations can be formulated also for the formation of other components of the KE-products—alkenes, alkanols, alkanals, etc.

The results obtained in the synthesis from CO_2 and H_2 in the presence of RPFIC, whose main product is ethanol, have been published.[68] At 335–370 °C and 20–40 MPa and for H_2 : CO_2 = 3 and a space velocity of the synthesis gas of $10^4(2-3)$ h^{-1}, the productivity of the process with respect to ethanol is 30–45 g h^{-1} (litre cat.)$^{-1}$. Together with ethanol, appreciable amounts of methanol, 1-propanol, and acetic acid are formed.

The products of the Fischer–Tropsch synthesis with participation of a third component, the Kölbel–Engelhardt synthesis, and the synthesis from CO_2 and H_2 are complex mixtures of organic products with a broad range of compositions in terms of different fractions. Alcohols and amines can be isolated from the products by familiar chemical methods (in the form of borates or hydrochlorides respectively). After their separation by fractionation into comparatively narrow fractions, they can find applications as raw materials for the preparation of plasticisers, surfactants, etc. The remainder of the products can be used as additives to hydrocarbon fuels or as a hydrocarbon raw materials suitable for further processing by traditional methods.

The processes examined are not at present competitive in relation to the familiar methods of synthesis of functional derivatives of hydrocarbons (alcohols, amines). However, in view of the possibility of their being carried out on the basis of virtually any hydrocarbon raw material, including a renewable raw material, the above synthesis will become increasingly more promising for practical use as the petroleum resources are exhausted.

This is why the interest in the study of syntheses from carbon oxides and hydrogen is at present growing continuously.

V. Syntheses of nitrogen-containing compounds

1. Hydroamination of oxygen-containing compounds

(a) Hydroxy-compounds. The deliberate search for effective catalysts of the reaction involving the amination of alcohols, which is prosecuted also at the present time, led at the beginning of the 1960's to development of an effective RPFIC for the synthesis of alkylamines from alkanols and ammonia in the presence of hydrogen.[69] The best yield of amines, stable in time, are attained in the presence of the RPFIC having the composition $5V_2O_5$.[70]

In the interaction of the RPFIC with a mixture of an alcohol, ammonia, and hydrogen, there is a possibility of the formation, during the amination reaction on the surface and in the bulk of the catalyst, of iron nitrides, carbonitrides, and oxides, which can influence the activity and selectivity of the catalyst. This problem has been partly considered in relation to the gas-phase reaction of 1-butanol with an ammonia–hydrogen mixture ($C_4H_9OH : NH_3 : H_2 = 1 : 8 : 24$) at 120–170 °C in the presence of three modified specimens of the RPFIC $5V_2O_5$.[22] The first specimen was enriched in iron ε-nitride, the second in iron carbonitride, and the first in iron oxides. In the presence of all three specimens, the yield of butylamines was significantly lower than in the presence of the initial RPFIC after prolonged use. This shows that, on contact between the RPFIC and the reaction mixture containing more than 70% of H_2, iron nitrides, carbonitrides, and oxides accumulate in the catalyst at least in amounts which can be detected from the change in the yield of amines.

A consequence important for the preparative gas-phase synthesis of amines, consisting in the fact that the stable activity and selectivity of the RPFIC can be maintained by retaining a high H_2 concentration in the initial gas mixture, follows from the data of the above study.[22]

In terms of their ability to enter into the amination reaction in the presence of the RPFIC $5V_2O_5$, alkanols can be arranged in the sequence[70,71] 1-octanol ≃ 2-octanol > 3-octanol > 4-octanol ≃ 2-methyl-4-heptanol ≃ 2-ethyl-1-hexanol.

On the other hand, in the amination of $C_nH_{2n+1}OH$, where $n = 5-10$, the conversion and overall selectivity with respect to alkylamines are independent of n, although the selectivity with respect to secondary alkylamines increases somewhat with increase in n.[72]

Table 4. Amination of 1-octanol in the presence of a RPFIC (210 °C, 5 MPa, space velocity of n-$C_8H_{17}OH$ 1.2 h^{-1}).[73]

State of aggregation of alcohol	$H_2:NH_3:ROH$	Conversion of ROH, %	Composition of amines, %		
			$C_8H_{17}NH_2$	$(C_8H_{17})_2NH$	$(C_8H_{17})_3N$
Gas*	15:12:1	88	75	21	4
Gas	34:3:1	45	38	50	12
Liquid	4:3:1	46	20	72	8

* 230 °C, space velocity of the alcohol 0.35 h^{-1}.

The amination of primary alcohols in the presence of RPFIC is a consecutive reaction leading to the formation of primary, secondary, and tertiary amines. In this reaction, it is always difficult to attain a high selectivity with respect to each amine separately. In order to increase the yield of secondary amines from alkanols and ammonia, a novel procedure has been proposed, consisting in carrying out the reaction in a film of the liquid alcohol.[73] In the amination of 1-octanol, this procedure makes it possible to increase the selectivity with respect to secondary amines from 21 to 72% (Table 4).

Optimum conditions have been found for the preferential synthesis of primary, secondary, or tertiary alkylamines from primary alcohol and ammonia under hydrogen pressure.[74–77] In the amination of 1-alkanols $C_{n+1}OH$, where $n = 6-12$, in the presence of the RPFIC $5V_2O_5$ at 260–295 °C, mixtures of alkylamines containing up to 96% of $C_nH_{2n+1}NH_2$, or up to 60% of $(C_nH_{2n+1})_2$, or up to 70% of $(C_nH_{2n+1})_3N$ were obtained. In all cases, amines containing the alkyl fragment of the initial alcohol are formed.[78]

Alkanols with a branched carbon skeleton (2-ethyl-1-hexanol and 2,2-dimethyl-1-propanol) are also aminated in the presence of RPFIC with high yields of the corresponding primary amines.[79,80]

Important results concerning the kinetics and mechanism of the amination of alkanols by ammonia in the presence of RPFIC have been obtained.[81–87] It has been established that the dependence of the rate of amination of the alcohol on its partial pressure at a constant rate of supply is characterised by a maximum in the region of $p_{ROH} = 0.02-0.03$ MPa.[83,85] This suggested that the kinetic equation for the reaction has a rational-fractional form, the power exponent of p_{ROH} in the denominator of the equation being greater than in the numerator.[83–85] The occurrence of the kinetic isotope effect in the amination of $CH_3(CH_2)_6CD_2OH$ and CH_3CD_2OH [82,84,85] permitted an inference about the character of the rate-limiting stage of the process. Within the framework of the Langmuir–Hinshelwood–Hogan–Watson kinetic model, a multistage amination mechanism has been proposed in which the rate-limiting stage is the dehydrogenation of the initial alcohol to the aldehyde.[84,85] The rate of amination of primary alkanols at moderate[84] and atmospheric[85] pressures is described by the equation

$$W = \frac{k \cdot b_{ROH} \cdot p_{ROH}}{(1 + b_{ROH} \cdot p_{ROH} + b_{H_2O} \cdot p_{H_2O})^2},$$

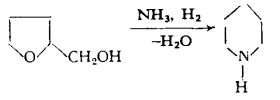
where k is the amination reaction rate constant, p_{ROH} and b_{ROH} are respectively the partial pressure and adsorption coefficient of the alcohol, and p_{H_2O} and b_{H_2O} are respectively the partial pressure and absorption coefficient of H_2O. The equation describes satisfactorily all the experimental data in the temperature range 180–270 °C and in the range of alcohol conversions 11–96%.

Fused iron catalysts exhibit an activity also in the *N*-alkylation of dimethyl- and methyl-amines.[86–88] Thus, in the reaction of 1-octanol with CH_3NH_2 in the presence of the RPFIC $1V_2O_5$ + 0.85BaO at temperatures in the range 230–240 °C, at a pressure of 2 MPa, for the ratios $H_2 : CH_3NH_2 : C_8H_{17}OH = 16 : 4 : 1$, and for a rate of supply of the alcohol at 350–400 g h^{-1} (litre cat.)$^{-1}$, the conversion of the alcohol reaches 93% and the overall selectivity with respect to amines is 93%, of which 70% corresponds to methyl-n-octylamine.[88] The kinetic equation proposed for the description of the interaction of alcohols with ammonia is also applicable to the reactions of alkanols with $(CH_3)_2NH$.[86,89]

Effective methods have been developed for the preparation of amines from alicyclic[90–92] and aromatic alkyl-substituted[93] alcohols and ammonia in the presence of RPFIC. Under conditions optimal for the synthesis of primary amines [315 °C, $p_{NH_3} = 3.2$ MPa, $p_{H_2} = 1.8$ MPa, rate of supply of cyclohexanol 36 mol h^{-1} (litre cat.)$^{-1}$] the conversion of the alcohol into amines is 88.5% for a selectivity with respect to cyclohexylamine of 95%.

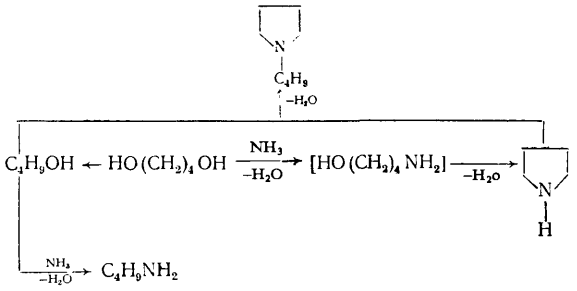
It was shown above that reactions involving the amination of alcohols with different structures take place selectively in the presence of RPFIC with formation mainly of the corresponding primary amines. In contrast to this, in the hydroamination of

tetrahydrofurfuryl alcohol (THFA) the main reaction product is not tetrahydrofurfurylamine but piperidine, whose yield is 51%:[94-96]



By virtue of the availability of the THFA, which is obtained from a renewable natural raw material, this synthesis of piperidine can be of interest for practical use.

Fused iron catalysts are used not only for intermolecular amination but also for intramolecular amination. Thus the interaction of butane-1,4-diol (BD) with an ammonia–hydrogen mixture in the presence of RPFIC results in the formation of pyrrolidine and its derivatives.[97] Under optimum conditions [260 °C, p_{NH_3} = 2, p_{H_2} = 2.8, and p_{BD} = 0.14 MPa; rate of supply of BD 560 g h^{-1} (litre cat.)$^{-1}$], the conversion of BD is 99% for a selectivity with respect to pyrrolidine above 70%.[97] The principal reactions of BD in the presence of RPFIC are illustrated schematically below:



The syntheses of piperazine from diethanolamine, of 1-alkyl- and 1,4-dialkyl-piperazines from *N*-alkyldiethanolamines, as well as morpholine from diethylene glycol have also been achieved.[97-99]

Table 5. Hydroamination of aldehydes and ketones [230 °C, p_{H_2} = 2.5 MPa, p_{NH_3} = 1.3 MPa, $p_{R^1COR^2}$ = 0.05 MPa,[102] $V_{R^1COR^2}$ = 20 mol h^{-1} (kg cat.)$^{-1}$]

Initial carbonyl compound	Amine formed	Conversion, %	Selectivity w.r.t. amine, %
2-Heptanone	2-Aminoheptane	93	95
4-Heptanone	4-Aminoheptane	92	92
2-Octanone	2-Amino-octane	92	95
2-Nonanone	2-Aminononane	90	96
Octanol	1-Amino-octane	87	90
Cyclohexanone	Cyclohexylamine	98	98
1-Phenyl-2-propanone	2-Amino-1-phenylpropane	85	93
Acetophenone*	1-Amino-1-phenyl ethane	96	70

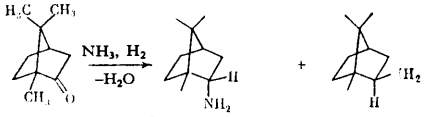
* Temperature 210 °C, rate of supply of acetophenone 9 mol h^{-1} (kg cat.)$^{-1}$.

(b) Carbonyl compounds. Aliphatic aldehydes can be hydroaminated to amines in the presence of RPFIC.[69] The kinetics of the hydroamination of carbonyl compounds have been investigated in relation to 2-octanone.[100,101] The kinetic isotope effect has been noted in the hydroamination of butanone when H_2 in the initial reaction mixture was replaced by D_2 and a multistage process mechanism, corresponding to this observation, was proposed, in which the addition of hydrogen to the ketimine is regarded as the rate-limiting stage. The kinetic equation assumes the form

$$W = \frac{k\, p_{H_2}^{0.5}}{1 + b_{H_2O} p_{H_2O}},$$

where k is the apparent hydroamination rate constant, p_{H_2} and p_{H_2O} are the partial pressures of H_2 and H_2O respectively, and b_{H_2O} is the adsorption coefficient of H_2O. The optimum conditions for the synthesis of primary amines from certain aldehydes and ketones of different structure in the presence of RPFIC $5V_2O_5$ have been determined using this equation[102] (Table 5).

In certain cases, the RPFIC exhibits a stereoselectivity unusual for metallic heterogeneous catalysts. Thus in the hydroamination of *d,l*-camphor,[103-105] its overall conversion into *endo*- and *exo*-bornylamines reaches 92% for the *endo* : *exo* = (1.4–1.8) : 1 ratio.



endo-bornylamine *exo*-bornylamine

Such stereoselectivity has been examined in a study[105] where it was shown that its most probable cause is the "imine–enamine" tautomerism on the acid–base centres of the RPFIC. However, one cannot rule out also a relation between the unusual stereoselectivity and the characteristic features of the coordination of the sterically hindered camphor molecule on the active centres of the RPFIC.

(c) Esters and ethers. In the hydroamination of aliphatic symmetrical and asymmetric esters in the presence of the RPFIC $5V_2O_5$, both the alcoholic and acid components of the ester molecule participate in the replacement of the ester group by the amino-group:[106-108]

$$R^1CH_2OOCR^2 \xrightarrow[-H_2O]{NH_3} R^1CH_2NH_2 + R^2CH_2NH_2.$$

At 280–300 °C, p_{NH_3} = 1.5–2.3, p_{H_2} = 2.6–3.5, and $p_{R^1CH_2OOCR^2}$ = 0.06–0.01 MPa and for a specific rate of supply of the ester of 200–500 g h^{-1} (litre cat.)$^{-1}$, the conversion of the latter reaches 86% for a selectivity of 70–88% with respect to primary alkylamines and 12–30% with respect to secondary alkylamines. On the other hand, ethers (diethyl ether, t-butyl methyl ether, tetrahydrofuran, and 1,4-dioxane) are not aminated in the presence of RPFIC.[108]

2. The interaction of oxygen-containing compounds with ammonia

It was shown above that alkylamines are formed from a vapour–gas mixture of an alcohol, aldehyde, ketone or ester, ammonia, and hydrogen on contact with RPFIC. The interaction of alcohol with ammonia in the absence of hydrogen in the presence of RPFIC of different composition ($2Al_2O_3 + 5Cr_2O_3$; $2Al_2O_3 + 2.5MnO_2$; $2Al_2O_3 + 0.5V_2O_5$; $5Al_2O_3 + 2.5K_2O$) has been investigated.[109,111] At 300–320 °C and for an alkanol : ammonia = 1 : 1–3 ratio and a rate of supply of the alcohol of 4–4.5 mol h^{-1} (litre cat.)$^{-1}$, $C_3H_7C{\equiv}N$, $C_5H_{11}C{\equiv}N$, and $C_8H_{17}C{\equiv}N$ are formed from 1-butanol, 1-hexanol, and 1-nonanol respectively in 80–85% yields. The rate of cyanation of alkanols to nitriles is independent of the length of the carbon chain.[109,110] Data concerning the influence of the structure of the oxygen-containing

group on its conversion into nitriles are presented in Table 6.[111]
A general mechanism of the conversion of alcohols into amines and nitriles is presented below.

Scheme 1

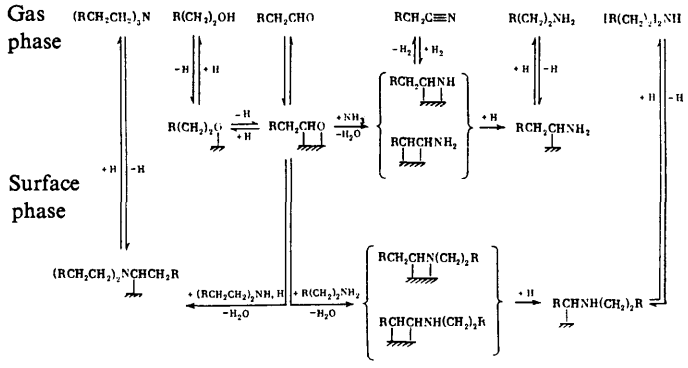


Table 6. Interaction of oxygen-containing compounds with NH_3 in the presence of the RPFIC $2Al_2O_3$ at 320 °C.[111]

Initial compound	Content of nitriles in reaction mixture, %			Content of amines, %
	$C_3H_7C{\equiv}N$	$C_2H_4C{\equiv}N$	$CH_3C{\equiv}N$	
1-Butanol	80	—	—	1-Aminobutane, 4
2-Methyl-1-propanol	73.5	1.5	0.2	1-Amino-2-methylpropane, 3.6
2-Butanol	—	3.9	2.0	—
t-Butyl alcohol	—	—	—	—
Butanone	—	2.6	1.0	—
1-Butanal	69.7	0.4	0.2	1-Aminobutane, 4.9
Ethyl acetate	—	—	51	—

Overall, RPFIC are fairly effective in the syntheses of alkylamines, certain simple saturated heterocycles, and nitriles from oxygen-containing compounds. Analysis of the literature data shows that these processes make it possible to attain higher productivities and proceed more stably than the processes involving the synthesis of the above nitrogen-containing compounds by other known preparative methods in the presence of other heterogeneous catalysts (nickel, copper–chromium, etc.). The reaction mixtures obtained as a result of the amination of individual oxygen-containing compounds in the presence of RPFIC are fairly simple in composition and as a rule contain the target products at a high concentration, which makes it possible to isolate them by means of the usual fractionation.

VI. Hydrogenation and dehydrogenation, isotope exchange, and other reactions

1. The hydrogenation of aldehydes and ketones to alcohols

Alcohols, especially aliphatic alcohols, are the most important products of preparative and industrial organic synthesis. The preparation of high-quality alcohols is in most cases based on the use of the reaction involving the hydrogenation of aldehydes and ketones.

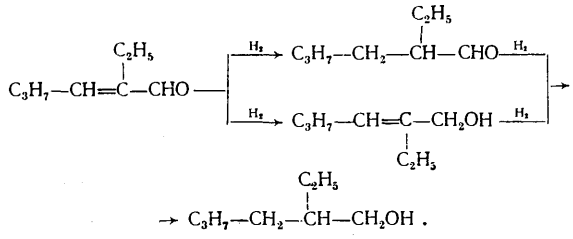
The possibility, in principle, of the formation of alcohols in the hydrogenation of aliphatic aldehydes in the presence of RPFIC has been demonstrated[112,113] but the RPFIC proposed for this purpose ($1MoO_3$ or $2Al_2O_3$) require a hydrogen pressure of 10 MPa and above.

The improvement of the method led to the development of the highly effective RPFIC $(2-5)V_2O_5$, in the presence of which carbonyl compounds were converted into the corresponding alcohols at p_{H_2} = 1–3.5 MPa [114–117] at a high rate and with a high selectivity (Table 7).

Table 7. Hydrogenation of aldehydes and ketones in the presence of a RPFIC (space velocity of H_2 2 × 10^4 h^{-1}).[114,117]

Initial carbonyl compound	Alcohol obtained	T, °C	p_{H_2}, MPa	Rate of supply, h^{-1}	Conversion, %	Selectivity w.r.t. alcohol, %
Butanol	1-Butanol	180	1.5	2	99.5	99.5
Nonanal	1-Nonanol	180	2.5	4.5	98	98.5
2-Octanal	2-Octanol	150	3.5	3	97.5	99.5
2-Ethylhex-2-en-1-al	2-Ethyl-1-hexanol	135	0.9	1.5	95	99
Cyclopentanone	Cyclopentanol	185	2.1	3.5	97	99
Cyclohexanone	Cyclohexanol	185	2.5	4.5	94	99.5

The hydrogenation of 2-ethylhex-2-en-1-al in the presence of water leads to an increase in the yield of an unsaturated alcohol 2-ethylhex-2-en-1-ol:[116]



Data on the kinetics of the hydrogenation of aliphatic and alicyclic ketones have been published.[117–121] The kinetics of the hydrogenation of 2-octanone and cyclohexanone have been investigated in the presence of the RPFIC $5V_2O_5$ under conditions where the reverse dehydrogenation reaction of the alcohols formed could be neglected. The rate of reaction increases with increase in the ketone and hydrogen concentrations and is independent of the alcohol concentration (the reaction product). A kinetic isotope effect (KIE) was observed following the replacement of H_2 by D_2 in the hydrogenation of 2-octanone.[121] A multistage reaction mechanism was proposed in which the rate-limiting stage is the addition of the first hydrogen atom to the adsorbed ketone molecule. For low conversions of ketones under isothermal conditions, the initial rate is described by a kinetic equation of the type[117,118]

$$W_0 = k \cdot p_{0(R^1COR^2)} \cdot p_{0(H_2)}^{0.5},$$

where k is the apparent reaction rate constant and $p_{0(R^1COR^2)}$ and $p_{0(H_2)}$ are the initial partial pressures of the ketone and hydrogen.

The equation holds satisfactorily over the entire experimental temperature range and the ranges of the ketone and hydrogen partial pressures.

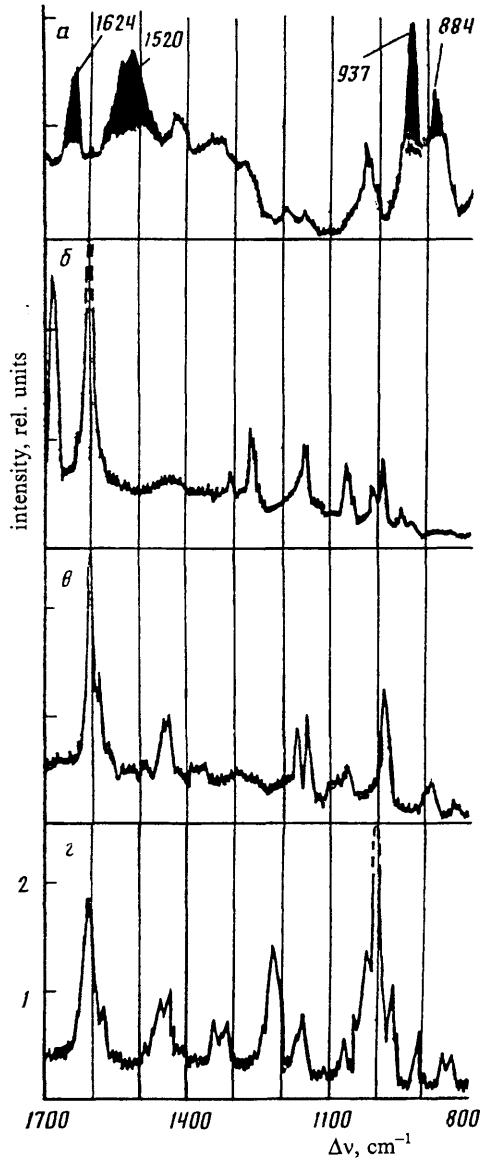


Figure 4. Raman spectra: *a*, the RPFIC surface in the hydrogenation of acetophenone *in situ* (177 °C, p_{H_2} = 0.2 MPa, p_{PhCOCH_3} = 4 kPa); *b*, acetophenone; *c*, methylphenylcarbinol; *d*, ethylbenzene.[16,122]

The kinetics of the non-isothermal hydrogenation of ketones in a tubular flow reactor up to a conversion of 0.8 are described by the equation[120]

$$1/V = (1/A \cdot p_{o(R^1COR^2)} \cdot p^{0,5}_{o(H_2)}) \int_0^x \{[1/(1-x)] \exp E/RT_0(1+\alpha x)\}\, dx,$$

where V is the specific rate supply of the ketone, T_0 the initial reaction temperature, E the apparent activation energy, A the pre-exponential factor, α a coefficient, and x the conversion of the ketone

The mechanism of the addition of hydrogen to ketones during their hydrogenation to alcohols in the presence of RPFIC has been investigated by a combined method involving laser Raman spectroscopy *in situ* and gas–liquid chromatography[16,17,122] and also by reaction chromatograph-linked mass spectrometry (RCMS).[123,124]

The Raman spectrum (Fig. 4*a*) of the surface of the RPFIC $5V_2O_5$ in the hydrogenation of acetophenone (ACP) by hydrogen (ACP conversion 6%, selectivity with respect to methylphenylcarbinol ~70%, selectivity with respect to ethylbenzene ~30%) differs significantly both from the spectrum of the initial ACP (Fig. 4*b*) and from the spectra of the reaction products (Figs. 4*c* and 4*d*). The intense lines in the region of ~1624, ~1520, ~937, ~884 cm^{-1} (Fig. 4*a*) can probably be attributed to intermediates in which there are C=O, C=C, C–C, and C–O bonds and the intermediates themselves can be interpreted as the "keto-" and "enol-forms" of the adsorbed ACP.

The question of the ratio of the "ketone" and "enolic" mechanisms in the hydrogenation of ketones in the presence of RPFIC was solved[123,124] by the RCMS method using a deuterium label and involving the analysis of the isotope composition of the trimethylsilyl ethers of the deuterioalcohols formed. The initial ketones can undergo the following reactions:

ketone mechanism

$$-CH_2-\overset{|}{C}=O \xrightarrow[RPFIC]{D_2} -CH_2-\overset{|}{C}D-OD \xrightarrow{BSTFA} -CH_2-\overset{|}{C}D-OSiMe_3 \quad (E_k)$$

"enolic" mechanism

$$-CH=\overset{|}{C}-OH \xrightarrow[RPFIC]{D_2} -CHD-\overset{|}{C}D-OH \xrightarrow{BSTFA} -CHD-\overset{|}{C}D-OSiMe_3 \quad (E_e)$$

BSTFA = *N,O*-bis(trimethylsilyl)trifluoroacetamide

It is seen from the scheme presented that, depending on the mechanism, trimethylsilyl ethers E_k and E_e with different numbers of D atoms are formed, which can be demonstrated mass-spectrometrically. A typical chromatogram, recorded in an experiment with cyclohexanone, is presented in Fig. 5, while the mass spectra of the cyclohexanone deuteriation products are illustrated in Fig. 6. Calculation of the isotope composition of the trimethylsilyl ethers E_k and E_e, taking into account the isotope composition of the unreacted cyclohexanone and its H/D exchange, established that the hydrogenation of alicyclic ketones to alcohols at 70–210 °C proceeds with equal probability via both the "enolic" and "ketone" mechanisms.

2. Dehydrogenation of alcohols and amines

It is known that the catalysts $1MoO_3$ or $2Al_2O_3 + 0.5V_2O_5 + 1K_2O$ for the hydrogenation of carbonyl compounds to alcohols can be used under appropriate conditions for the reverse alcohol dehydrogenation reaction. 1-Heptanol and ethanol have been hydrogenated in the presence of such catalysts to heptanal and acetaldehyde respectively in 30–40% yield.[113,125] The kinetics and mechanism of the dehydrogenation of alcohols in the presence of the RPFIC $5V_2O_5$ have also been investigated in other studies.[85,125] In the gas-phase dehydrogenation of CH_3CD_2OH, CD_3CH_2OH, and

CH_3CH_2OH [125] in helium at 180 °C, the rates of reaction of these ethanols are in the following proportions:

$$W_{CH_3CH_2OH}/W_{CD_3CH_2OH} \simeq 1;$$
$$W_{CH_3CH_2OH}/W_{CH_3CD_2OH} \simeq 2.5 \pm 0.1.$$

Hence it follows that the slow stage of the reaction is the abstraction of a α-hydrogen atom from the alcohol molecule. The kinetics of the dehydrogenation of the ethanols in the presence of the RPFIC $5V_2O_5$ correspond to the equation

$$W = \frac{k \cdot b_{ROH} \cdot p_{ROH}}{(1 + b_{ROH} \cdot p_{ROH} + b_{ACH} \cdot p_{ACH})^2},$$

where k is the reaction rate constant, p_{ROH} and b_{ROH} are the partial pressure and the adsorption coefficient of the alcohol respectively, and p_{ACH} and b_{ACH} are the partial pressure and the adsorption coefficient of the aldehyde respectively.

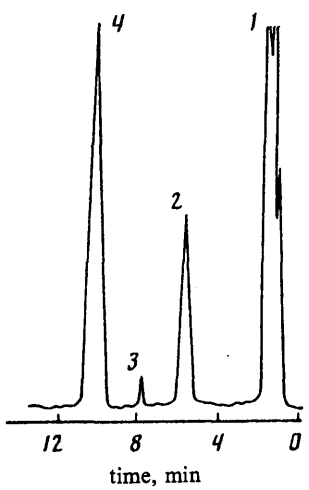
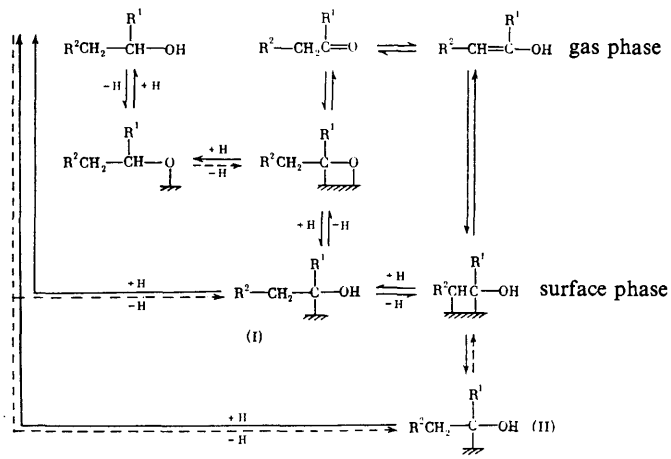


Figure 5. Chromatogram of the reaction mixture obtained in the deuteriation of cyclohexanone in the presence of a RPFIC:[124] *1*, BSTFA and its hydrolysis products; *2*, trimethylsilyl ether of deuteriated cyclohexanol; *3*, trimethylsilyl ether of deuteriated cyclohex-1-enol; *4*, deuteriated cyclohexanone.

The catalysts examined are capable of effecting the dehydrogenation of not only alcohols but also amines. Thus n-butylamine is dehydrogenated to butyronitrile in 78% yield in the presence of the RPFIC $2Al_2O_3$ at 280–320 °C.[111]

The mechanisms of the hydrogenation of carbonyl compounds to alcohols and of the dehydrogenation of the latter to aldehydes and ketones in the presence of RPFIC, based on data in Refs. 123–125, are presented below:

Scheme 2



After deuteriation, the isotope compositions of compounds (I) and (II) are different. The reactions designated by a dashed line occur only in the dehydrogenation of the alcohol.

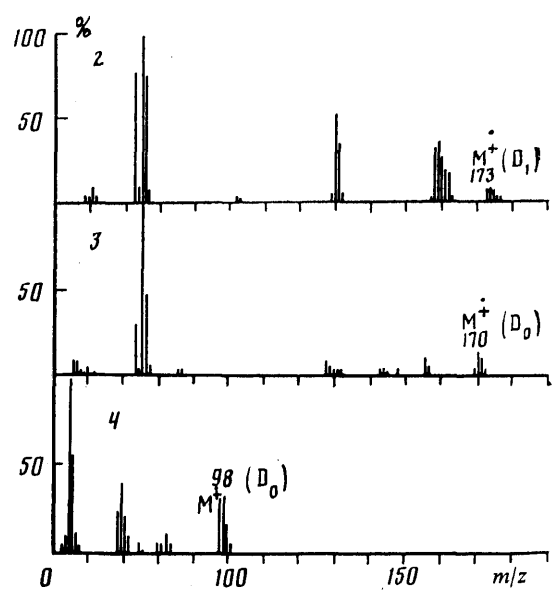


Figure 6. Mass spectra of the chromatographic bands presented in Fig. 5.[123]

3. Hydrodeoxygenation of alcohols, aldehydes, and ketones

The hydrodeoxygenation (HDO) of oxygen-containing compounds to hydrocarbons is used widely in preparative and industrial organic chemistry. Alcohols, aldehydes, and ketones with different structures are hydrodeoxygenated quantitatively to saturated hydrocarbons at 250–350 °C and p_{H_2} = 0.1–0.3 MPa in the presence of the RPFIC

$5V_2O_5$ with retention of the carbon skeleton of the initial oxygen-containing substrate.[126,127] The distribution of deuterium in the saturated hydrocarbons formed on deuteriodeoxygenation of alcohols, aldehydes, and ketones has been investigated[127] by the RCMS method.[128]

Analysis shows that the isotope compositions of the deuteriocyclopentanes obtained in the reaction of cyclopentene and cyclopentanol with deuterium (Fig. 7) are similar,[127] which suggests that the products of the deuteriation of an olefin and of the deuteriodeoxygenation of an alcohol are formed via intermediates having similar structures:

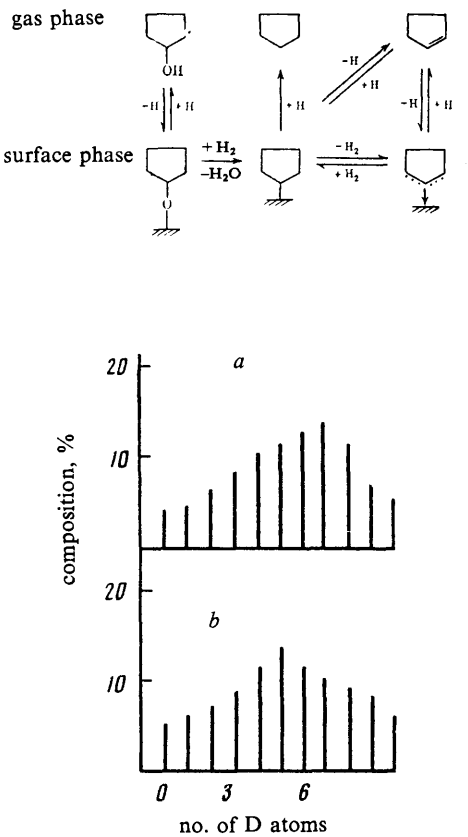
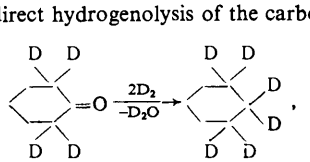


Figure 7. Isotope composition of the deuteriocyclopentanes obtained in the reactions of cyclopentene (*a*) and cyclopentanol (*b*) with D_2 (300 °C, p_{D_2} = 0.15 MPa).[127]

On the other hand, comparison of the isotope compositions of the deuteriocyclohexanes obtained as a result of the deuteriodeoxygenation of cyclohexanone and 2,2,6,6-tetradeuteriocyclohexanone (Fig. 8), according to which about 70% of all the $[D_n]$cyclohexanes is $[D_6]$cyclohexane, provides grounds for the assumption that this reaction proceeds via two pathways, the main one involving the direct hydrogenolysis of the carbonyl group:



while the other involves the hydrogenation initially of the ketone to the alcohol and then of the alcohol to the hydrocarbon.

When benzaldehyde was hydrodeoxygenated, it was observed unexpectedly that, together with toluene, up to 30% of bibenzyl and *trans*-stilbene is formed.[129] It has been suggested that one of the pathways leading to the formation of stilbene is the metathesis of benzaldehyde at the carbonyl group.

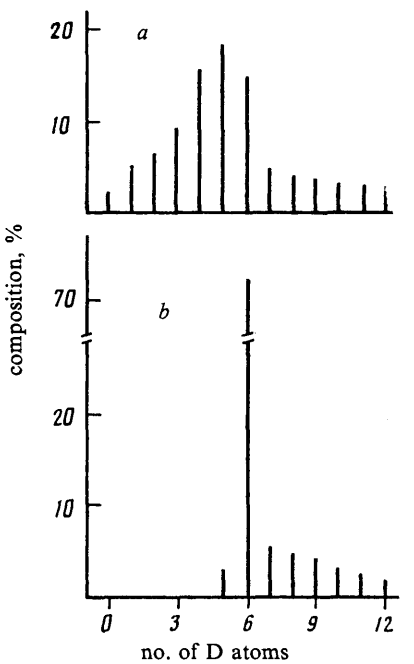
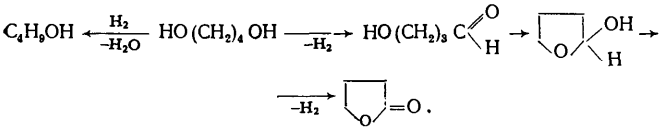


Figure 8. Isotope composition of the deuteriocyclohexanes obtained in the reaction of cyclohexanone (*a*) and 2,2,6,6-tetradeuteriocyclohexanone (*b*) with D_2.[127]

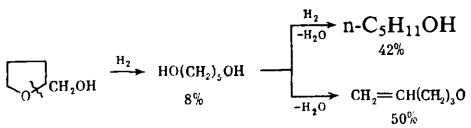
4. Hydrogenolysis of esters, diols, and other oxygen-containing compounds

The gas-phase hydrolygenolysis of esters and ethers in the presence of RPFIC has been examined.[106–108] At 200–250 °C, n-heptyl oenanthate gives rise to 1-heptanol and n-heptane in 50 and 25% yields respectively. Only heptane in 18% yield was obtained under the same conditions from di-n-heptyl ether.

On interaction with H_2 in the presence of the RPFIC (4–5)V_2O_5 + 1(Al_2O_3 + SiO_2) at 280–300 °C and p_{H_2} = 2–3 NPa, butane-1,4-diol is converted into γ-butyrolactone and 1-butanol in 20–30% and 10–20 yields respectively:[130]



The reactions of THFA in the presence of RPFIC are illustrated in the following scheme:



The hydrogenolysis of THFA to pent-4-en-1-ol is an interesting case of the conversion of a heterocyclic alcohol into an unsaturated aliphatic alcohol.

5. Hydrogenation of C=C and C≡C bonds

Only a few studies have been specially devoted to questions concerning the hydrogenation of multiple carbon–carbon bonds in the presence of RPFIC. The possibility of the hydrogenation of hexene to hexane in the presence of the ammonia synthesis catalyst has been reported.[131]

Hept-1-ene and cyclopentene are hydrogenated quantitatively in a microreactor with a fluidised bed of RPFIC $5V_2O_5$ with pulsed supply of the olefin into a stream of H_2 or D_2 at 250 °C.[127]

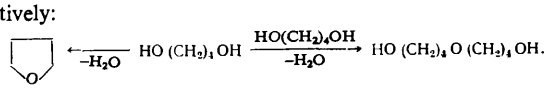
There are data for the hydrogenation of acetylene at 70 °C in the presence of the RPFIC $2Al_2O_3 + 0.5V_2O_5 + 1K_2O$. Isoprene is hydrogenated to a mixture of isopentane and isopentene in the presence of the same catalyst at 165–170 °C.[64]

Benzene is capable of being converted into cyclohexane in the presence of RPFIC, the catalyst having the composition $(5-8)Al_2O_3$ being the most active.[132,133] In its presence, the rate of hydrogenation of benzene is only several times smaller than in the presence of the nickel catalyst.[133]

6. Dehydration and polymerisation reactions

Until recently, the RPFIC was regarded exclusively as a metallic catalyst.[134] The role of stabilisers of the disperse metallic iron phase on the surface and of regulators of the particle size and of the overall surface area was attributed to the promoting agents. However, the RPFIC surface consists mainly of a non-metallic phase (see Section II). In other words, the surface layer of the RPFIC bears a formal similarity to that of traditional bifunctional catalysts, whose composition includes Group VIII metals (1–10%) on Al_2O_3, SiO_2, zeolite, etc. carriers.[135,136] The difference of the RPFIC consists primarily in the fact that, unlike the traditional catalysts, it incorporates 1–10% of promoting agents (Al_2O_3, SiO_2, V_2O_5, etc.) and 90–99% of α-Fe^0. Thus the RPFIC can be regarded as an inverted bifunctional catalyst. The manifestation of both oxidation-reduction (hydrogenation–dehydrogenation processes) and acid–base activities is characteristic of bifunctional catalysts. The efficiency of the RPFIC in oxidation–reduction reactions was demonstrated in previous Sections, but, as will be shown below, some of the results obtained in the presence of RPFIC can be treated from the standpoint of acid–base catalysis.

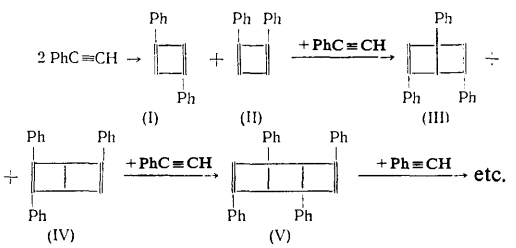
A typical acid–base catalytic reaction is the dehydration of alcohols or diols. The first such reaction carried out in the presence of the RIPMC $(4-5)V_2O_5 + 1(Al_2O_3 + SiO_2)$ was the dehydration of butane-1,4-diol.[130] It underwent both intermolecular and intramolecular dehydration in a H_2 atmosphere at 280–300 °C with formation of dibutylene glycol and tetrahydrofuran (THF) respectively:



Subsequently the intramolecular dehydration of ethylene glycol[137] and the intermolecular dehydration of t-butyl ether of propargyl alcohol[138] were achieved in the presence of RPFIC.

Compounds with the C=C and C≡C multiple bonds can enter into polymerisation reactions in the presence of RPFIC: at 220 to 230 °C, isoprene forms a solid rubber-like product, which consists of polyisoprene.[64]

The development of this approach led to the creation of a procedure for the oligomerisation of phenylacetylene (PA).[139,140] In the presence of the RPFIC $(0.5-1)K_2O + (3-4)(SiO_2 + Al_2O_3 + V_2O_5)$ at 150 °C in a nitrogen atmosphere, PA undergoes linear oligomerisation with formation of PA dimers, trimers, and tetramers and also cyclisation with formation of the diphenylcyclobutadienes (I) and (II), triphenyl-substituted Dewar benzenes (III) and (IV), and the ladder oligomer (V):



The authors[139,140] did not discuss the mechanism of the oligomerisation of PA, but, taking into account the acid–base properties of the RPFIC, presumably one of the possible pathways to the oligomerisation of PA involves a mechanism analogous to that of cationic polymerisation.

7. Isotope exchange reactions

Gaseous deuterium or a deuterium label in the molecule are frequently used in the study of the mechanisms of heterogeneous organic catalysis.[141–143] Certain examples of the employment of gaseous deuterium or a deuterium label, involving the measurement of kinetic isotope effects in syntheses of oxygen- and nitrogen-containing compounds in the presence of RPFIC, were presented above. We shall consider in greater detail a series of isotope exchange reactions occurring in the presence of RPFIC.

In the interaction of CH_3OH with D_2 in a stationary system in the presence of the RPFIC $2K_2O$ at 112 °C, p_{CH_3OH} = 4.5 GPa, and p_{D_2} = 20 GPa, methanol acquires, after 40 min, the following isotope composition (5): CH_3OH 80, CH_3OD 19, CH_2DOD 1, CHD_2OH < 0.1.[144] Hence, it is seen that in the presence of the RPFIC the most vigorous H/D exchange occurs in the hydroxy-group of the alcohol.

The exchange of n-hexane, cyclohexane, cyclohexanol, cyclopentanol, cyclohexanone, and cyclopentanone with D_2 has been investigated in the presence of the RPFIC $5V_2O_5$.[123,127] In alicyclic alcohol molecules (p_{D_2} = 0.1–0.3 MPa), as in CH_3OH molecules, only the H atom of the hydroxy-group is replaced by deuterium at 250 °C. Under these conditions, saturated hydrocarbons hardly undergo the H/D exchange. On the other hand, in ketone molecules protium is vigorously exchanged for deuterium at carbon atoms in the α-position to the carbonyl group.

In a study of deuterium distribution in the products of synthesis from CO and H_2 with added D_2O, it was established that there is no exchange between the hydrocarbons formed and D_2O.[145] On the other hand, the hydrocarbons contain a certain amount of deuterium

which was believed to pass from D_2O to gaseous hydrogen, reacting subsequently with CO. The deuterium content in the alcohols formed in the FT-synthesis is higher than in hydrocarbons.

When $^{14}C^{18}O_2$ is added to the synthesis gas in the presence of a RPFIC, the carbon label is transferred from carbon dioxide to the monoxide mainly via the reaction

$$^{14}CO_2 + H_2 \rightleftarrows {}^{14}CO + H_2O,$$

while the transfer of the oxygen label proceeds via the reaction[146]

$$C^{18}O_2 + C^{16}O \rightleftarrows C^{16}O^{18}O + C^{18}O.$$

A novel one-stage synthesis of aliphatic alcohols labelled with ^{18}O isotope consists in the vapour-phase interaction of alkanols with $H_2{}^{18}O$ in the presence of hydrogen at 150–250 °C over a RPFIC.[147,148] Thus, when a mixture of $H_2{}^{18}O$ methanol vapours is passed through the catalyst bed, $C_2H_5{}^{18}OH$ is formed in 92% yield relative to the equilibrium yield. The authors[147,148] explain the observed $^{16}OH/^{18}OH$ isotope exchange by the reversible dehydrogenation of the alkanols under the conditions indicated. Taking into account the acid-base properties of the RPFIC, such oxygen exchange can be described by the following multistage scheme in which RMC represents reduced FeH metallic centres and ABC represents POH acid–base centres (P = V, Al, Si):

$$C_2H_5OH \xrightarrow[-H_2]{RMC} CH_3CHO,$$
$$CH_3CHO + H_2^{18}O \xrightarrow{ABC} CH_3CH^{18}O + H_2O,$$
$$CH_3CH^{18}O + H_2 \xrightarrow{RMC} CH_3CH_2^{18}OH.$$

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Thus reduced promoted fused iron catalysts exhibit a high (frequently unexpected) efficiency in a whole series of hydrogenation syntheses. In some cases they are superior to the familiar catalytic systems in terms of a series of most important technological parameters such as productivity, selectivity, and stability (Fischer–Tropsch syntheses modified by ammonia or lower amines, hydroamination and hydrogenation of certain oxygen-containing compounds, etc.). In other cases, they may prove preferable, despite their lower efficiency, because of their availability, low cost, and the simplicity of their preparation. Such an unusually broad spectrum of the catalytic activity of RPFIC is probably associated with its bifunctional nature, which is manifested in the syntheses of organic compounds of different classes via a combination of oxidation-reduction (hydrogenation-dehydrogenation) and acid–base catalytic properties. By varying easily within wide limits the chemical composition of the RPFIC and hence also the nature of the catalytically active surface on which a wide variety of reactions of the initial reactants take place, it is possible to achieve deliberately the necessary ratio of these properties. This is in fact why experimental search on a broad front makes it possible in most cases to select a RPFIC best corresponding to the purposes of the synthesis of the organic compounds. The latter factor makes it extremely likely that new examples of the successful employment of RPFIC in organic synthesis will appear in the future.

Finally, the wide-scale application of RPFIC and other universal catalysts may prove a useful alternative to the approach, dominant at present in chemical research, according to which a new catalyst is developed for each specific synthesis of an organic compound.

References

1. A Nielsen *An Investigation on Promoted Iron Catalyst for the Synthesis of Ammonia*, Jul. Gjellerup's Forlag, Copenhagen, 1968
2. B Timm *Proceedings of VIIIth International Congress on Catalysis*, Verlag Chemie, Weinheim, 1984, Vol. 1, p. 7
3. H Storch, N Golumbic, R Anderson *The Fischer–Tropsch and Related Syntheses* (Translated into Russian), Inostr. Lit., Moscow, 1954, p. 516
4. R B Anderson *The Fischer–Tropsch Synthesis*, Acad. Press, Orlando, 1984, p. 301
5. L D Kuznetsov, L M Dmitrienko, P D Rabina, Yu A Soklinskii *Sintez Ammiaka* (Ammonia Synthesis), Izd. Khimiya, Moscow, 1982, p. 295
6. A Pattek-Janczyk, A Z Hrynkiewicz *Appl. Catal.*, 1983, **6** 27
7. D J Dwyer, J H Hardenbergh *Appl. Surf. Sci.*, 1984, **19** 14
8. D J Dwyer *Catalyst Characterization Science. Surface and Solid State Chemistry*, ACS Symposium Series 288 (Edited by M L Deviney et al.), Washington, 1985, p. 124
9. A Nielsen *Catal. Rev.-Sci. Eng.*, 1970, **4** 1
10. M Boudart *Catal. Rev.-Sci. Eng.*, 1981, **23** 1
11. M E Dry *Applied Industrial Catalysis*, Acad. Press, New York, 1983, Vol. 2, p. 161
12. A Pattek-Janczyk, A Baranski, A Kotarba, et al. *Appl. Catal.*, 1988, **39** 169
13. S M Davis *Catal. Lett.*, 1988, **1** (4) 85
14. E V Slivinskii, A Ya Rozovskii, Yu B Kagan, et al. *React. Kinet. Catal. Lett.*, 1975, **3** 455
15. O V Krylov, L D Bernam *Usp. Khim.*, 1986, **55**(3) 371 [English translation in *Russ. Chem. Rev.*, 1986(3)]
16. A V Bobrov, L S Glebov, G A Kliger, et al. *IV Vsesoyuznaya Konferentsiya po Mekhanizmu Kataliticheskikh Reaktsii* (The IVth All-Union Conference on the Mechanisms of Catalytic Reactions), Izd. Akad. Nauk SSSR, Moscow, 1986, Part 2, p. 420
17. A V Bobrov, Ya M Kimel'feltd, L S Glebov, et al. *Chem. Phys. Lett.*, 1985, **118** 156
18. H B Zhang, G L Schrader *J. Catal.*, 1985, **95** 325
19. L S Glebov, G A Kliger, A N Shukin, S M Loktev *Neftekhimiya*, 1988, **28** 674
20. S M Loktev, L I Makarenkova, E V Slivinskii, S D Entin *Kinet. Katal.*, 1972, **13** 1042
21. S M Loktev, A N Bashkirov, E V Slivinskii, et al. *Kinet. Katal.*, 1973, **14** 217
22. R A Fridman, G A Kliger, E I Bogolepova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 744
23. A Ya Rozovskii *Katalizator i Reaktsionnaya Sreda* (The Catalyst and the Reaction Medium), Izd. Nauka, Moscow, 1988, p. 303
24. A N Bashkirov, Yu B Kagan, G A Kliger *Dokl. Akad. Nauk SSSR*, 1956, **109** 774
25. A N Bashkirov, Yu B Kagan, G A Kliger, USSR P. 133 890; *Byull. Izobret.*, 1960, (23)
26. A N Bashkirov, Yu B Kagan, G A Kliger *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1958, 504
27. P M Brown, J M Maselli US P. 3 726 926; *Chem. Abs.*, 1973, **79** 18 038
28. G Henrici-Olivé, S Olivé *J. Mol. Catal.*, 1978, **4** 379
29. L S Glebov, G A Kliger, S M Loktev, et al., USSR P. 1 187 867; *Byull. Izobret.*, 1985, (40)

30. Yu B Kagan, A N Bashirov, G A Kliger, Yu I Ermakov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1959, 1345
31. Yu B Kagan, A N Bashkirov, G A Kliger, Kuang-Yu Lui *Neftekhimiya*, 1964, **4** 106
32. L S Glebov, G A Kliger, T P Popova, et al. *J. Mol. Catal.*, 1986, **35** 335
33. G L Kliger, L S Glebov, T P Popova, et al. *J. Catal.*, 1988, **111** 418
34. G A Kliger, L S Glebov, V P Ryzhikov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1875
35. L S Glebov, G A Kliger, V P Ryzhikov, S M Loktev *Tezisy Dokladov Vsesoyuznoi Konferentsii 'Khimicheskie Sintezy na Osnove Odnouglerodnykh Molekul'* (Abstracts of Reports at the All-Union Conference on 'Chemical Syntheses Based on One-carbon Molecules'), Izd.Nauka, Moscow, 1987, p. 135
36. Yu B Kagan, S M Loktev, G A Nizov et al., USSR P. 386900; *Byull. Izobret.*, 1973, (27)
37. S M Loktev, A N Bashkirov, Yu B Kagan, et al. *Dokl. Akad. Nauk SSSR*, 1973, **211** 1126
38. S M Loktev *J. Mol. Catal.*, 1982, **17** 225
39. Yu B Kagan, G V Isagulyants, V A Zhilin, et al. *Kinet. Katal.*, 1974, **15** 1518
40. Yu B Kagan, A Ya Rozovskii, S M Loktev, A M Bashkirov *Dokl. Akad. Nauk SSSR*, 1980, **250** 1151
41. E V Slivinskii, S M Loktev, Yu P Voytsekhovskii, V Yu Rumyantsev *Dokl. Akad. Nauk SSSR*, 1987, **297** 620
42. Yu B Kagan, E V Slivinskii, S M Loktev, et al. *Kinet. Katal.*, 1985, **26** 1018
43. Yu B Kagan, S M Loktev, Yu P Voytsekhovskii, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1839
44. Yu B Kagan, E V Slivinskii, Yu P Voytsekhovskii, et al. *Neftekhimiya*, 1986, **26** 533
45. S M Loktev, Yu B Kagan, E V Slivinskii, et al., USSR P. 1097594; *Byull. Izobret.*, 1984, (22)
46. E V Slivinskii, V Yu Rumyantsev, Yu B Kagan, S M Loktev *Neftekhimiya*, 1986, **26** 642
47. Yu B Kagan, V Yu Rumyantsev, E V Slivinskii, S M Loktev *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2141
48. V Yu Rumuyantsev, E V Slivinskii, S M Loktev *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 2503
49. J T Kummer, P H Emmett *J. Am. Chem. Soc.*, 1953, **75** 5177
50. W K Hall, R J Kokes, P H Emmett *J. Am. Chem. Soc.*, 1957, **79** 2983
51. Yu B Kryukov, A N Bashkirov, V K Butyugin, et al. *Dokl. Akad. Nauk SSSR*, 1958, **119** 1152
52. P H Emmett *J. Am. Chem. Soc.*, 1951, **73** 564
53. R J Kokes, W K Hall, P H Emmett *J. Am. Chem. Soc.*, 1957, **79** 2989
54. Yu B Kryukov, A N Bashkirov, R A Fridman, et al. *Neftekhimiya*, 1965, **5** 62
55. Yu B Kagan, Yu B Kryukov, V V Kamzolkin, A N Bashkirov *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1952, 649
56. W K Hall, R J Kokes, P H Emmett *J. Am. Chem. Soc.*, 1960, **82** 1027
57. Yu B Kryukov, A N Shuikin, Z T Shumaeva, A N Bashkirov *Neftekhimiya*, 1970, **10** 83
58. Yu B Kryukov, E G Simon'yants, L G Liberov, A N Bashkirov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1966, 1871
59. Yu B Kruukov, A N Bashkirov, E G Simon'yants, et al. *Kinet. Katal.*, 1969, **10** 135
60. Yu B Kryukov, A N Bashkirov, L G Liberov, et al. *Kinet. Katal.*, 1961, **2** 780
61. Yu B Kryukov, A N Bashkirov, V K Butyugin, et al. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1958, 642
62. A N Bashkirov, Yu B Kryukov, E G Simon'yants, L G Liberov *Dokl. Akad. Nauk SSSR*, 1966, **171**, 609
63. C N Satterfield, G A Huff, R Summerhayes *J. Catal.*, 1983, **80** 486
64. S M Loktev, N B Sokratova, A N Bashkirov, Yu B Kagan *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1972, **17** 465
65. L M Tau, R Robinson, R D Ross, B H Davis *J. Catal.*, 1987, **105** 335
66. H Kölbel, F Engelhardt *Angew. Chem.*, 1952, **64** 54
67. I F Bogdanov, N V Lavrov, G V Grebenshchikov *Trudy Inst. Goryuchikh Iskopaemykh Akad. Nauk SSSR*, 1962, **18** 94
68. A N Bashkirov, V V Kamzolkin *Dokl. Akad. Nauk SSSR*, 1958, **118** 293
69. A N Bashkirov, Yu B Kagan, G A Kliger, USSR P. 133889; *Byull. Izobret.*, 1960, (23)
70. Yu B Kagan, A N Bashkirov, G A Kliger *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1961, 469
71. Yu B Kagan, A N Bashkirov, G A Kliger, et al. *Neftekhimiya*, 1961, **1** 403
72. Yu B Kagan, A N Bashkirov, G A Kliger, et al. *Neftekhimiya*, 1961, **1** 555
73. Yu B Kagan, G A Kliger, A N Bashkirov, et al. *Neftekhimiya*, 1967, **7** 619
74. G A Kliger, A N Bashkirov, L S Polak, et al. *Neftekhimiya*, 1980, **10** 907
75. G A Kliger, A N Bashkirov, O A Lesik, E V Marchevskaya *Neftekhimiya*, 1971, **11** 80
76. G A Kliger, A N Bashkirov, L S Polak, et al. *Neftekhimiya*, 1973, **13** 116
77. G A Kliger, A N Bashkirov, L S Polak, et al. *Neftekhimiya*, 1973, **13** 265
78. G A Kliger, A N Bashkirov, O A Lesik, et al. *Neftekhimiya*, 1975, **15** 441
79. G A Kliger, A N Bashkirov, L S Polak, et al. *Neftekhimiya*, 1969, **9** 433
80. G A Kliger, A N Bashkirov, E V Marchevskaya, et al. *Kinet. Katal.*, 1980, **21** 1086
81. G A Kliger, A N Bashkirov, P Schneider, et al. *Neftekhimiya*, 1968, **8** 283
82. R A Fridman, E I Bogolepova, R M Smirnova, et al. *Neftekhimiya*, 1972, **12** 91
83. G A Kliger, L F Lazutina, R A Fridman, et al. *Kinet. Katal.*, 1975, **16** 660
84. G A Kliger, L F Lazutina, R A Fridman, et al. *Kinet. Katal.*, 1975, **16** 665
85. R A Fridman, E I Bogolepova, Yu B Kryukov, A N Bashkirov *Neftekhimiya*, 1975, **15** 426
86. V P Ryzhikov, G A Kliger, L S Glebov, et al. *Neftekhimiya*, 1986, **26** 609
87. G A Kliger, A N Bashkirov, Kuang-Yu Lui, Yu B Kagan *Neftekhimiya*, 1962, **2** 384
88. Yu B Kagan, A N Bashkirov, G A Kliger, Kuang-Yu Li *Neftekhimiya*, 1962, **2** 391
89. A Baiker, J Kijenski *Catal. Rev. Sci. Eng.*, 1985, **27** 653
90. A N Bashkirov, G A Kliger, O A Lesik, Yu B Kagan, USSR P. 165 172; *Byull. Izobret.*, 1964, (18)

91. G A Kliger, A N Bashkirov, O A Lesik, Yu B Kagan *Neftekhimiya*, 1965, **5** 569
92. G A Kliger, A N Bashkirov, L S Polak, et al. *Neftekhimiya*, 1973, **13** 723
93. G A Kliger, A N Bashkirov, O A Lesik, et al. *Neftekhimiya*, 1966, **6** 769
94. A N Bashkirov, G A Kliger, E V Marchevskaya, et al., USSR P. 715 576; *Byull. Izobret.*, 1980, (6)
95. A N Bashkirov, G A Kliger, O A Lesik, et al. *Kinet. Katal.*, 1983, **24** 392
96. G A Kliger, O A Lesik, V P Ryzhikov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 2847
97. G A Kliger, O A Lesik, E V Marchevskaya, et al. *Khim. Geterotsikl. Soedin.*, 1987, (2) 195
98. G A Kliger, H Fidler, O A Lesik, et al. *IV Vsesoyuznyi Simpozium 'Geterogennyi Kataliz v Khimii Geterotsiklicheskikh Soedinenii'* (The IVth All-Union Symposium on 'Heterogeneous Catalysis in the Chemistry of Heterocyclic Compounds'), Riga, 987, p. 80
99. G A Kliger, H Fidler, O A Lesik *Neftekhimiya*, 1988, **28** 684
100. G A Kliger, L S Glebov, R A Fridman, et al. *Kinet. Katal.*, 1978, **19** 615
101. G A Kliger, L S Glebov, R A Fridman, et al. *Kinet. Katal.*, 1978, **19** 619
102. G A Kliger, L S Glebov, A N Bashkirov *Neftekhimiya*, 1977, **17** 599
103. A N Bashkirov, G A Kliger, B A Krentsel', et al., USSR P. 810 671; *Byull. Izobret.*, 1981, (9)
104. A N Bashkirov, G A Kliger, B A Krentsel', et al., USSR P. 956 004; *Byull. Izobret.*, 1980, (33)
105. L S Glebov, G A Kliger, V D Oppengeim, et al. *Neftekhimiya*, 1988, **28** 800
106. A N Bashkirov, G A Kliger, E V Marchevskaya, O A Lesik, USSR P. 522 173; *Byull. Izobret.*, 1976, (27)
107. G A Kliger, A N Bashkirov, E V Marchevskaya, et al. *Neftekhimiya*, 1978, **18** 433
108. G A Kliger, O A Lesik, E V Marchevskaya, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2598
109. Yu B Kryukov, A N Bashkirov, N S Zakirov, F I Novak *Dokl. Akad. Nauk SSSR*, 1966, **170** 852
110. F I Novak, N S Zakirov, Yu B Kryukov, A N Bashkirov *Neftekhimiya*, 1966, **6** 297
111. Yu B Kryukov, N S Zakirov, F I Novak, et al. *Neftekhimiya*, 1967, **7** 124
112. A N Bashkirov, S M Loktev, G V Sabirova *Khim. Tekhnol. Topl. Masel* 1958, (7) 39
113. A N Bashkirov, S M Loktev, Yu B Kagan, G V Sabirova *Tr. Inst. Elektrokhim., Ural Nauchn. Tsentr. Akad. Nauk SSSR*, 1959, **13** 180
114. A N Bashkirov, G A Kliger, L S Glebov, et al., USSR P. 789 477; *Byull. Izobret.*, 1980, (47)
115. A N Bashkirov, L S Glebov, G A Kliger, et al. *Khim. Promst. (Moscow)*, 1979, (7) 393
116. L S Glebov, G A Kliger, G A Korneeva, A N Bashkirov *Neftekhimiya*, 1982, **22** 34
117. L S Glebov, G A Kliger, A N Bashkirov *Neftekhimiya*, 1978, **18** 803
118. L S Glebov, G A Kliger, A N Bashkirov, et al. *Kinet. Katal.*, 1978, **19** 1339
119. G A Kliger, L S Glebov, A Ya Rozovskii, et al. *Kinet. Katal.*, 1982, **23** 1014
120. Yu A Kolbanovskii, L S Glebov, G A Kliger, et al. *Kinet. Katal.*, 1983, **24** 1010
121. L S Glebov, G A Kliger, A A Levitskii, S M Loktev *Neftekhimiya*, 1985, **25** 750
122. A V Bobrov, L S Glebov, Ya M Kimel'fel'd, et al. *Dokl. Akad. Nauk SSSR*, 1985, **284** 1158
123. L S Glebov, A I Mikaya, V I Smetanin, et al. *J. Catal.*, 1985, **93** 75
124. A I Mikaya, A E Yatsenko, L S Glebov, et al. *IV Vsesoyuznaya Konferentsiya po Mikhanizmu Kataliticheskikh Resktsii* (The IVth All-Union Conference on the Mechanisms of Catalytic Reactions), Izd. Akad. Nauk SSSR, Moscow, 1986, Part I, p. 333
125. Yu B Kryukov, A N Bashkirov, R A Fridman, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1971, 563
126. L S Glebov, A I Mikaya, A E Yatsenko, et al. *Tetrahedron Lett.*, 1985, **26** 3373
127. L S Glebov, A I Mikaya, V G Zaikin, et al. *Neftekhimiya*, 1987, **27** 423
128. A I Mikaya, V G Zaikin *Usp. Khim.*, 1986, **55**(8) 1390 [English translation in *Russ. Chem. Rev.*, 1986(8)]
129. L S Glebov, A N Shuikin, A I Mikaya, et al. *Izv. Akad. Nauk SSSR*, 1988, 1343
130. L S Glebov, G A Kliger, A E Yatsenko, et al. *Dokl. Akad. Nauk SSSR*, 1986, **290**, 1140
131. A N Bashkirov, V V Kamzolkin, S A Lodzik *Trudy Inst. Elektrokhim., Ural Nauchn. Tsentr. Akad. Nauk SSSR*, 1955, **6** 142
132. R Badilla-Ohlbaum, H J Neuburg, W F Graydon, M J Phillips *J. Catal.*, 1977, **47** 273
133. M J Phillips, P H Emmett *J. Catal.*, 1986, **101** 268
134. R B Anderson *The Structure of Metallic Catalysts* (Translated into Russian), Izd. Mir, Moscow, 1978, 482 pp
135. P Weiz *Adv. Catal.*, 1962, **13** 137
136. K G Ione *Polifunktsional'nyi Kataliz na Tseolitakh* (Polyfunctional Catalysis on Zeolites), Izd. Nauka, Novosibirsk, 1982, p. 268
137. Yu B Kagan, E V Slivinskii, V Yu Rumyantsev, et al. *Kinet. Katal.*, 1986, **27** 1017
138. V Yu Rumyantsev, E V Slivinskii, S M Loktev *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1208
139. E V Slivinskii, Yu P Voitsekhovskii, L I Zvezdkina, et al. *Neftekhimiya*, 1985, **25** 199
140. Y P Voicechovsky, E V Slivinsky, B B Fichte, S M Loktev *J. Polym. Sci.*, 1985, **23** 1641
141. A Ozaki *Isotopic Studies on Heterogeneous Catalysis* (Translated into Russian), Atomizdat, Moscow, 1976, p. 232
142. K Tanaka *Studies in Surface Science and Catalysis*, Elsevier, Amsterdam, 1986, Vol. 27, p. 79
143. B S Gudkov *Usp. Khim.*, 1986, **55**(3) 517 [English translation in *Russ. Chem. Rev.*, 1986(3)]
144. J R Anderson, C Kemball *Trans. Faraday Soc.*, 1955, **51** 966
145. Yu B Kryukov, A N Bashkirov, R A Fridman, et al. *Neftekhimiya*, 1965, **5** 226
146. Yu B Kryukov, A N Bashkirov, L G Liberov, et al. *Kinet. Katal.*, 1970, **11** 1069
147. A N Bashkirov, Yu B Kryukov, R M Smirnova, R A Fridman, USSR P. 315 423; *Byull. Izobret.*, 1971, (36)
148. R M Smirnova, R A Fridman, Yu B Kryukov, A N Bashkirov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1971, 662

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Self-diffusion in solutions and melts of flexible-chain polymers

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ABSTRACT. The review deals with the characteristic features of the molecular motion of flexible chain macromolecules and oligomers associated with the multisegmental nature of the chain and topological limitations. The dependence of the self-diffusion coefficients of chain molecules in polymer melts and solutions, including a weakly cross-linked gel, is analysed. Attention is concentrated on data for self-diffusion where there is a change not only in the molecular weight (MW) of the diffusing molecule but also in the molecular weight of the macromolecules surrounding the specified molecule. Both model ideas and approaches based on the scaling theory, including the concept of the curvature of the trajectories of the "reptation tube", are used for the theoretical analysis. The "inhomogeneity" of the segmental mobility in the chain has made it possible to describe specific features of the behaviour of oligomers. The dependence of the self-diffusion coefficient on the MW of the chain and the matrix and on the concentration in the region of dilute, moderately concentrated, and concentrated solutions and melts has also been described quantitatively.

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I. Introduction

The problems of molecular mobility in polymeric materials have continually attracted the attention of both theoreticians and specialists in applied chemistry. Self-diffusion processes occupy a major place in this problem. Firstly, the principal features and characteristics of the mobility in polymeric materials are manifested most clearly in self-diffusion phenomena. Secondly, together with the chemical potential gradient, self-diffusion coefficients determine the rate of mass transfer in polymeric bodies. Thirdly, self-diffusion processes can affect significantly the rates of chemical reactions (diffusion-controlled chemical reactions). Despite the importance of the problem under discussion, these questions have not been solved appropriately because of the difficulty of experimental measurement of the self-diffusion coefficients (D) of chain molecules.

Together with further improvement of the "tracer" atom and NMR "spin echo" methods,[1,2] during the last ten years there has been a development of other methods for the investigation of self-diffusion processes based on the use of the laser technique.[3–5] The results of studies of self-diffusion processes up to 1983 have been surveyed in two books.[1,2] However, in recent years fundamentally new experimental data have been obtained for the mobility of polymers and theoretical equations describing satisfactorily the experimental behaviour have been proposed. Indeed, previously it was believed that the scaling theory is adequate for the understanding of the concentration dependence of D.[6] However, in the latest studies (see below) it was found that the predicted relations hold only over a limited concentration range. The predictions of the scaling theory concerning the dependence of D on the molecular weight M also failed to come true. Indeed, the scaling theory predicted a broken line (with a jump at a certain concentration) dependence of D on M. However, it has been shown in studies carried out in 1984–1986 that these results of the scaling theory are applicable only within a restricted concentration range. There are data which cannot be in any way reconciled with the previously proposed theoretical relations.

The aim of the present study is the analysis of both experimental and theoretical results for the self-diffusion coefficients of macromolecules, obtained mainly in recent years, and the establishment of a correlation of these results with one another.

II. Characteristic features of the molecular motion of flexible chain polymers

The characteristic features of the molecular motion of flexible chain macromolecules in polymer solutions and melts are determined by their structure.[6,7] Indeed a flexible chain macromolecule consists of a large number of segments N capable of being oriented independently of one another and of executing definite types of motion. Thus, in constructing a molecular picture of the motion of chain molecules, it is essential to take into account the "duality" of the thermal motion. The displacement of a flexible chain macromolecule takes place as a result of the displacement of its elements (kinetic segments). The set of such displacements of the chain sections leads to the displacement of the centre of gravity of the entire macromolecule. The mobility of the chain segments is determined in its turn by the mobility of the elements of the system (their interaction): the segments of other chains (for a melt) or solvent molecules and chain segments (for a solution).

For the simplest chain model, where the motion of the chain is regarded as the motion of N non-interacting chain segments with a coefficient of friction of the segments ζ, the following expression has been obtained † for the self-diffusion coefficients D_R (motion of the Rouse type):[8]

$$D_R = kT/N\zeta, \quad (1)$$

where k is the Boltzmann constant and T the temperature.

It was postulated previously (and is still postulated in certain studies) that the coefficient of friction of the segments ζ is proportional to the macroscopic viscosity of the medium η. This is true only for low-molecular-weight substances and dilute polymer solutions.

Analysis of numerous experimental data[11] for low-molecular-weight liquids has shown that the following relation holds for them:

$$D\eta = \frac{N_A kT}{4\sqrt{2}}\left(\frac{\rho}{MN_A}\right)^{1/3},$$

where ρ is the density of the liquid and N_A the Avogadro number. The dependence of $D\eta$ on $M^{-1/3}$ is characteristic of molecular models in the form of a sphere moving in a medium having a viscosity η.

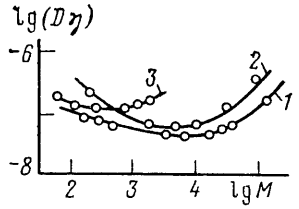


Figure 1. Dependence of $\lg(D_\eta)$ on $\lg M$ for polydimethylsiloxane (curve *1*), poly(ethylene oxide) (curve *2*), and polyethylene (curve *3*) according to the results of Budtov and Konsetov[16] and Tanner et al.[29]

However, with increase in the polymer concentration and in the molecular weight (M) of the chain (for solutions and for the melt), the quantity ζ is no longer determined by the macroscopic viscosity η. Fig. 1 illustrates the dependence of $D\eta$ on M for certain polymers.[12–14] Evidently, $D\eta$ varies with increasing M in a complex manner, although it follows from the simplest relation (1) that it should only decrease with increase in M (or N). Thus the classical ideas of the hydrodynamics of a continuous medium are inapplicable in the interpretation of the diffusion phenomena in flexible chain macromolecules.‡

† An analogous model has been proposed by Kargin and Slonimskii independently of Rouse.[9,10] The viscoelastic properties of polymeric materials have been calculated on the basis of this model.

‡ This apparently evident assertion was nevertheless not recognised for a long time, which led to a significant retardation of the development of ideas about the diffusional mobility of macromolecules.

We shall consider the displacement of an element X of a diffusing macromolecule.[15,16] Suppose that the medium surrounding the polymer chain consists of low-molecular-weight substances (a low-molecular-weight solvent) (Fig. 2*a*). Having received momentum from a certain section of the selected chain, the solvent molecule can move away from the initial position sufficiently "far" and "fast". The mean square of the displacement of the solvent molecule is $\langle X_S^2 \rangle = 2D_S t$, where D_S is the diffusion coefficient of the solvent molecule and t is the time. Nothing inhibits its motion apart from the natural viscous retardation determined by the viscosity of the solvent η_S.

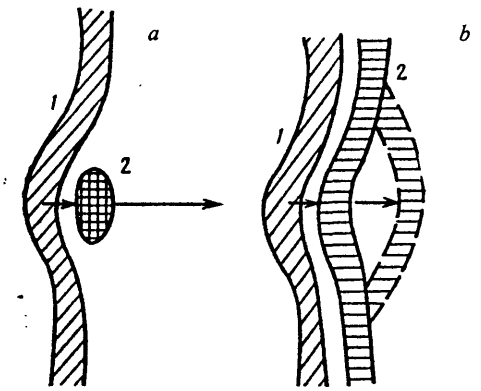


Figure 2. Schematic representation of the molecular picture of the motion of a chain molecule in a low-molecular-weight solvent (*a*) and in the melt (*b*).

Another situation arises if the medium consists of long flexible chain macromolecules (melts) (Fig. 2*b*). When a unit of a selected molecule is displaced, an elementary unit of the chain molecule surrounding the specified molecule is also displaced. However, this elementary unit cannot move away from the initial position sufficiently "far" and "fast", since it is bound to the macromolecule "at rest". The rate of displacement of this section is determined not only by its local characteristics (the size of the segment and the local viscosity of the medium) but also by its elastic linkage with the entire macromolecule and by its overall displacement. Fig. 3 presents the time variation of $\langle X_A^2 \rangle$ of an elementary unit of a chain macromolecule for the simplest Kargin–Slonimskii–Rouse model. It is seen that the longer the time of the observation, the smaller the contribution of the displacement of the element of the polymer chain compared with the displacement of the solvent molecule $\langle X_S^2 \rangle$. Fig. 3 illustrates this in a generalised form: $\langle X_A^2 \rangle / \langle X_S^2 \rangle = f(t/t_A)$.

Thus we cannot speak of the "constraint" of the transverse motion of a chain macromolecule, or about the anisotropy of the diffusional motion of a chain, or about topological limitations of the diffusional mobility, for which an attempt has been made to describe them in terms of the so called "quasi-network".

A molecular model for the diffusional motion in such systems has been proposed by de Gennes[17,18] (see also Gotlib et al.[6]). It has been shown that the square of the displacement of the elementary unit is

specified by the relation

$$\langle X_A^2 \rangle = 2A\sqrt{D_A t/\pi}, \quad t_A < t < \tau, \tag{2}$$

where D_A is the diffusion coefficient of the segment, $t_A = A^2/2DA$, τ is the relaxation time of the entire chain, and A is the size of the segment.

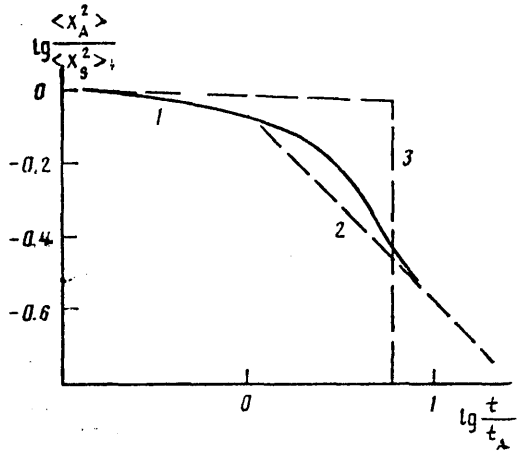


Figure 3. Dependence of $\lg(\langle X_A^2\rangle/\langle X_S^2\rangle)$ on $\lg(t/t_A)$ calculated for the Kargin–Slonimskii–Rouse model (curve *1*) and for the reptation model (curve *2*) [Eqn. (2)]; curve *3* represents the corresponding dependence of the transverse displacement for the "tube" model.

Thus a radical alteration of the mobility of the elements of the medium is characteristic of concentrated polymer solutions and melts. The displacement of the specified macromolecule by changing places with solvent molecules, observed previously for dilute solutions in a low-molecular-weight solvent, is no longer attainable for melts. The diffusional motion in a viscoelastic medium takes place in two ways. On the one hand, this is a specific motion of a section of a specified macromolecule, which involves only "local" changes in the conformation of the surrounding medium. On the other hand, this is the motion of the segment over long distances (owing to topological limitations, such motion occurs in only one direction) along the chain. The terminal chain element moves "ahead" and drags behind it the entire chain, i.e. a "snake-like" type of motion is observed—the reptation type of motion. The molecular theory of this type of motion, applied to the calculation of the viscoelastic properties of polymeric materials, has been developed in a number of studies.[17–19] In later studies, it has been used widely to develop a molecular theory of liquid-phase polymers.[6]

We shall consider below in greater detail the application of reptation motion to the description of the diffusion of chain molecules. Here one would wish to note that the reptation type of motion can be readily modelled by considering the motion of the chain in a "tube", whose configuration resembles the configuration of a flexible chain macromolecule[20,21] (Fig. 4).

Indeed in Fig. 3 we can replace the smooth decrease in $\langle X_A^2\rangle$ with increase in t by a stepwise decrease (curve *3*). This means that, for long times, one no longer observes a transverse displacement of the segment ($\langle X_A^2\rangle = 0$), i.e. an "impermeable" wall is thereby introduced. This limit in fact determines the "tube" diameter. It amounts to several segments (t/t_A at the boundary is ~ 5).

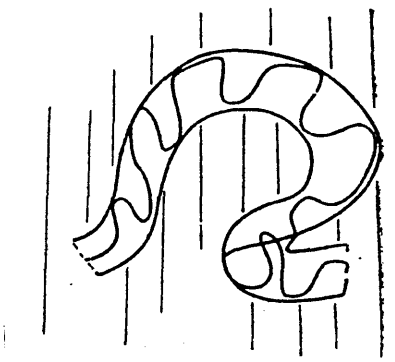


Figure 4. The "tube" model for the study of the reptation motion of the chain.

In order to characterise the configuration of the "tube", the parameter b, which is an analogue of the persistent length of a chain macromolecule, has been introduced.[22] The mean square of the distance between the ends of the "tube" is then given by

$$B^2 = Lb - \frac{b^2}{2}[1 - \exp(-2L/b)], \tag{3}$$

where L is the contour length of the "tube", i.e. the length of the fully straightened "tube". The quantity b characterises the degree of twist of the configuration of the "tube": the smaller the value of b, the more twisted is the "tube". For $L < b$, we have $B^2 = L^2$, i.e. the "tube" has the configuration of a rod, while for $L > b$, we obtain $B^2 = Lb$,[17–19]§ whereupon $b > A$. Whereas the size of the chain segment A is determined by the chemical structure of the chain, the quantity b depends on the structure of the molecules of the medium surrounding the specified macromolecule. For example, b may depend on the deformation, degree of cross-linking, and concentration of the polymer in the matrix through which the labelled macromolecule diffuses.

The introduction of the concept of curvature of the tube (or curvature of the reptation path of the diffusing macromolecule) is of fundamental importance, since it permits a molecular interpretation of concepts widely used in the physical chemistry of polymers such as the critical molecular weights M_c. For $M < M_c$ (or $L < b$), the chain behaves as a Rouse chain, whereas for $M > M_c$ (or $L > b$), the twisting of the chain and the topological limitations of the mobility of the macromolecule are fully manifested.

An attempt is usually made to interpret M_c as the distance between the nodes of a "quasi-network". For solutions, such a representation is possible. However, it is clearly inapplicable to melts, since in a melt it is impossible to specify the characteristic

§ The case $L \gg b$ was also considered in the above studies.[17–19]

point of the interaction between the specified chain and other chains, since this interaction is uniformly distributed along the chain. If a "node" with a definite lifetime τ_c is introduced into the model for the melt as a characteristic of the interaction,[22] then naturally the number of nodes N_c, hindering diffusion, will depend on the velocity of the motion v:

$$N_c = \frac{N_c(0)}{\exp(A/v\tau_c) - 1}.$$

Hence it follows that the translational friction coefficient $\Lambda = \Lambda_0(1 - N_c)$, where $N_c(0) = N_c(v \to 0)$ and $\Lambda_0 = \Lambda(v \to 0)$. Estimates have shown[22] that, for self-diffusion processes, the quantity $A/v\tau_c$ ranges from 10 to 10^6 and the influence of the nodes arising in the system can be disregarded.

We shall consider below the application of the above ideas to the analysis of experimental results obtained in recent years.

III. Self-diffusion coefficients of chain macromolecules in the melt

1. General relations

The dependence of the self-diffusion coefficient D on the molecular weight M has been investigated for a fairly large number of flexible chain polymers (PE, PDMS, PEO, PI, BSR)¶ (Fig. 5). These data have been analysed.[16] The data published subsequently[23–27] confirmed the earlier relations. The dependence of D on M can be described empirically by the relation

$$D = KM^{-\alpha}, \qquad (4)$$

where the numerical coefficient α is in the range from +1.3 to +2.0 and K is an empirical constant. These relations were confirmed in subsequent studies and the upper limit of α reached 2–2.4.[3–5]

However, the most interesting data were obtained when self-diffusion processes were investigated with variation of the molecular weight M_m of the surrounding medium.[28–30] The dependence of D on the molecular weight of the diffusing macromolecule (M) and on the length of the macromolecule in the surrounding medium (P) makes it possible to elucidate the characteristic features of the diffusional behaviour in such complex systems.

Fig. 6 illustrates the dependence of P for "labelled" PS macromolecules in a matrix comprising PS macromolecules on the molecular weight M_m of the matrix as far as weakly cross-linked gels ($M_m = \infty$).[28] Evidently, with increase in the molecular weight of the diffusing chain (M) and of the matrix (M_m), D diminishes. However, for sufficiently large values of M_m (up to weakly cross-linked gels—see also Zakharov[31]), the quantity D no longer depends on M_m. Similar data have been obtained also for PDMS,[29] PS,[30] and polyisoprenes.[31] An interesting result of Zakharov's study has been the establishment of the fact that the variation of D as a function of M depends on the method of preparation of the matrix (the method used for its deformation and annealing). The dependence of D on the deformation of the medium is clearly manifested: with increase in deformation, D fell.[31,32] However, for non-annealed elastomers, the coefficient D could actually increase on extension of the material.

¶ The following notation has been adopted: PE = polyethylene, PDMS = polydimethylsiloxane, PEO = poly(ethylene oxide), PI = polyisoprene, and BSR = butadiene–styrene rubber.

The dependence of D on M and M_m makes it possible to determine not only the values of α but also the differential indices α_N and α_P, i.e.

$$\alpha_N = d\lg D/d\lg M;$$
$$\alpha_P = d\lg D/d\lg M_m,$$

which will be analysed below.

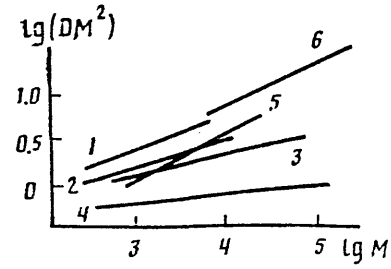


Figure 5. Dependence of $\lg(DM^2)$ on $\lg M$ for melts of certain polymers:[16] *1*, PE; *2* and *3*, PDMS; *4*, PEO; *5*, PI; *6*, BSR.

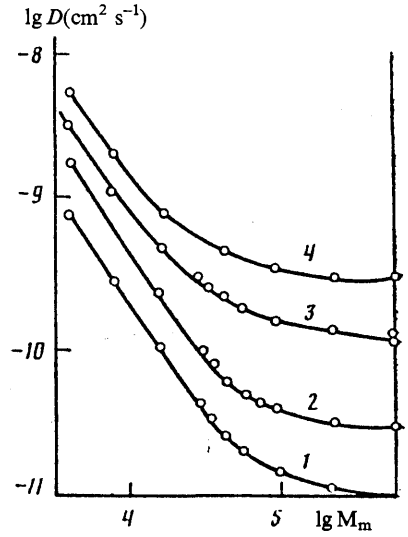


Figure 6. Dependence of $\lg D$ for a trial chain on $\lg M_m$ of the surrounding medium for PS molecules in a polystyrene matrix (T = 212 °C); 10^{-4} M: *1*, 10; *2*, 5.8; *3*, 3.0; *4*, 1.8. The points on the right-hand axis represent diffusion in a weakly cross-linked gel.

2. The motion of a chain through a weakly cross-linked gel

We shall consider the motion of a chain through a matrix with infinitely large molecules, i.e. a weakly cross-linked gel.[20] Suppose that the "local" molecular motion has developed fairly strongly and is characterised by a segment diffusion coefficient D_A. This is the

most direct instance of the manifestation of the reptation motion of a macromolecule: the chain can move only via the terminal element. Suppose that the length of the macromolecule is L ($L = NA$). Using the distance between the nodes of the quasi-network (N_c is the number of segments between quasi-cross-links), one can write the following formula for the overall length of the axial line of the tube:[17]

$$L_\tau = NA/N_c^{0.5} = L/N_c^{0.5}.$$

It follows from Eqn. (1) that the diffusion coefficient of the macromolecule within the tube is $D_T = D_A/N$. The time τ required for the chain to leave the initial tube is given by

$$\tau = \frac{l_\tau^2}{2D_\tau} = \tau_A \frac{N^3}{2N_c}, \quad (5)$$

where τ_A is the relaxation time of the segment. Although the chain migrates along the tube over a distance L during the time τ, nevertheless in space this migration is much smaller, since the tube is strongly bent [see Eqn. (3)]. The mean square of the displacement of the chain† during the time τ is $<X^2> = LA$. The following relation can then be obtained for the self-diffusion coefficient:[20]

$$D_{DG} = \frac{LA}{2\tau} = \frac{D_A N_c}{N^2} = D_R \frac{N_c}{N}. \quad (6)$$

Thus, for a very long chain, we have $D \propto N^{-2}$ in contrast to $D \propto N^{-1}$ for a short chain [see Eqn. (1)], i.e. Eqns. (1) and (6) yield the limiting laws governing the dependence of D on N.

Real macromolecules have a finite molecular weight. Calculations of the dependence of D on N for chains with a finite molecular weight have been performed.[22] The mean square of the displacement of the terminal chain element B^2 along the tube is specified by Eqn. (3). Since the relaxation time of the chain in this tube is $\alpha_T = L^2/2D_T$, we obtain finally

$$D_B = \frac{B^2 D_A}{L^2 N} = \frac{D_A}{N}\frac{B^2}{L^2}. \quad (7)$$

When $L < b$, we have $B^2 = L^2$ [see Eqn. (3)] and $D_B \propto D_A N$, i.e. the Rouse formula is obtained, whereas in the case where $L > b$ we obtain $B^2 = Lb$ and $D_B \propto D_A b/NL$, which corresponds to the de Gennes formula if it is assumed that $b = N_c A$. In the general case $D \propto N^{-1}$—N^{-2} [between N^{-1} and N^{-2}] and α is in the range from 1 to 2 [see Eqn. (4)].

We shall compare quantitatively the theoretical and experimental data. Here, we shall consider only the results of the study of the diffusion coefficients of a "trial" macromolecule diffusing in a matrix with an infinite molecular weight. We shall designate this value of D by D_∞. It is convenient to analyse the values of $D_\infty M$, whereupon Eqn. (7) is transformed into

$$D_\infty M = D_A M_A (B^2/L^2). \quad (8)$$

Fig. 7 illustrates the dependence of $\lg(D_\infty M)$ on $\lg M$ for PDMS [29] and PS [28,30] melts and also the dependence of $\lg(B^2/L^2)$ on $\lg(L/b)$ calculated by Eqn. (3). Evidently the theoretical curves reproduce correctly all the characteristic features of the experimental curves. A quantitative agreement can be obtained if the following values are selected: $D_A M_A = 4 \times 10^{-4}$ cm^2 s^{-1} and $M_b = 5 \times 10^3$ for PDMS and $D_A M_A = 6.3 \times 10^{-6}$ cm^2 s^{-1} and $M_b = 1.2 \times 10^4$ (D = 212 °C) for PS, M_b being the molecular weight of a chain section with a length b. The quantities M_b are close to the "critical" molecular weights obtained from rheological data. The quantities $D_A \simeq 10^{-6}$ cm^2 s^{-1} (PDMS) and $D_A \simeq 10^{-8}$ cm^2 s^{-1} (PS) have reasonable values. For example, for M = 746, the experimental D is 2.2 × 10^{-6} cm^2 s^{-1}. The data obtained permit the claim that a quantitative agreement is observed between the theoretical and experimental results for melts with $M_m = \infty$.

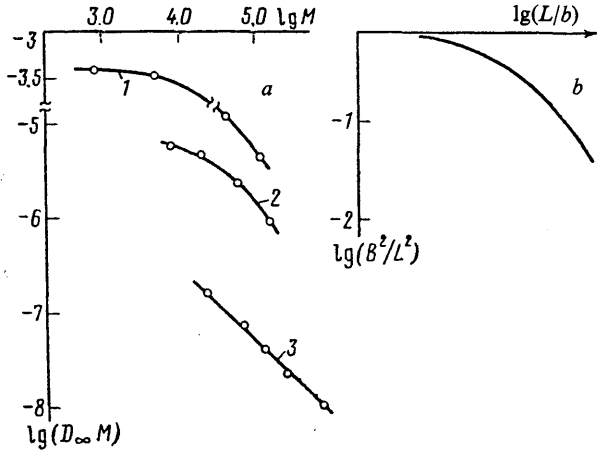


Figure 7. Dependence of $\lg(D_\infty M)$ on $\lg M$ (*a*) and of $\lg(B^2/L^2)$ on $\lg(L/b)$ (*b*) [the curve was calculated by Eqn. (3)]: *1*, PDMS;[29] *2* and *3*, PS.[28,30]

It is seen from the above analysis that, when $M < 10^3$ (PDMS) or $M < 10^4$ (PS), the diffusional motion of the macromolecule is of the Rouse type ($D \propto M^{-1}$). Only when $M > 10^4$ (PDMS) and $M > 10^5$ (PS) can one claim that the reptation type of motion is fully achieved. This means that, when $M > 10M_b$, the topological limitations by the surrounding medium on the mobility of the macromolecular chain are decisive. In view of such "diffuse" transition from one type of motion to another (a $10M_b$ range), the different literature values of "critical" molecular weights determined by different methods become understandable. Here it is essential to note that the study of the self-diffusion of "labelled" macromolecules provides a unique possibility for varying separately both the molecular weight of the diffusing chain and the molecular weight of the surrounding medium. In the usual rheological studies these two parameters are varied simultaneously, which hinders a quantitative interpretation (see the next Section).

3. Motion through a matrix with a finite molecular weight

Together with the diffusion of a chain along the tube, the process involving the renewal (relaxation) of the tube itself, as a result of the motion of other chains constituting the tube, take place.[17] The self-diffusion coefficient of the macromolecule in the melt (D_1) is then given by

$$D_1 = D_R + D_P, \quad (9)$$

where D_P is the component of D associated with the relaxation of

† The mean square of the distance between the ends of a chain with a length L is $NA^2 = LA$.

the tube and D_B is specified by Eqn. (7). The existing model theories have shown that D_P is proportional to N_c/P, N_c^2/P^2, and $N^{0.5}(N_c^2/P^3)$ [20,33,34] (here P is the number of segments in the matrix macromolecule surrounding the trial chain with a length N). Unfortunately the question of the selection of a particular dependence is so complex that fairly arbitrary hypotheses concerning the nature of the phenomenon are put forward in the studies mentioned above. One cannot therefore give preference at the present time to any one model and we therefore used the approach of the scaling theory for the description of the dependence of D_P on N.[35,36] We adopt the following functional relation for D_P (when $P > N_c$):

$$D_P = \frac{D_A}{N}(\gamma N_c/P)^n Z, \qquad (10)$$

where γ and n are empirical coefficients and Z is the probability that the molecule is located in the tube, i.e. is subjected to topological limitations by the surrounding medium as regards motion across the contour line:

$$Z = 1 - \exp[-(P - N_c)/N_c].$$

When $P < N_c$, we have $Z = 0$ and, when $P > N_c$, we have $Z = 1$.

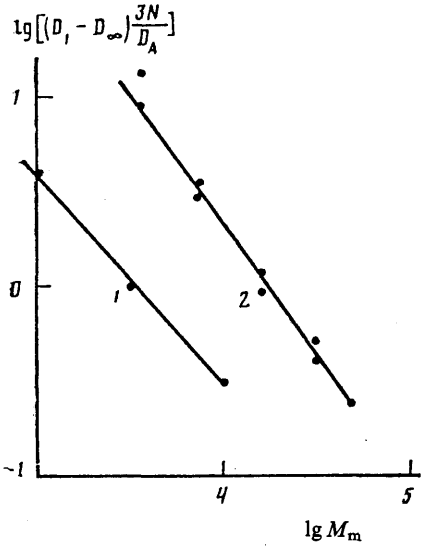


Figure 8. Dependence of $\lg[(D_1 - D_\infty)(3N/D_A)]$ on $\lg M_m$ for PDMS (curve *1*) and PS (curve *2*) according to different data.[28-30]

The coefficients γ and n can be found by analysing the experimental data. Suppose that $P > N_c$ ($Z = 1$). We then examine the variation of $(D_1 - D_\infty)(3N/D_A)$ as a function of M_m. Fig. 8 illustrates the dependence of $\lg[(D_1 - D_\infty)(3N/D_A)]$ on $\lg M_m$ for PDMS [29] and PS.[28] The quantities n (1.1 for PDMS and 1.4 for PS) and γ (0.28 for PDMS and 0.12 for PS) can be determined from the straight lines presented. The similarity of the empirical coefficients n and γ obtained for different objects shows that the hypotheses put forward are reasonable.

Thus we obtain finally for the self-diffusion coefficients of the melt[35,36]

$$D_1 = \frac{D_A}{N}\left[\frac{Lb - \frac{b^2}{2}[1 - \exp(-2L/b)]}{L^2} + Z\left(\gamma\frac{N_c}{P}\right)^n\right]. \qquad (11)$$

Fig. 9 presents the theoretical dependences of D_1M/D_AM_A on M_m/M_b for different values of M and n. Evidently the self-diffusion coefficients presented decrease with increase in M_m and tend to a limit which is independent of M_m (cf. Fig. 6). The observed relations are consistent with experimental data.

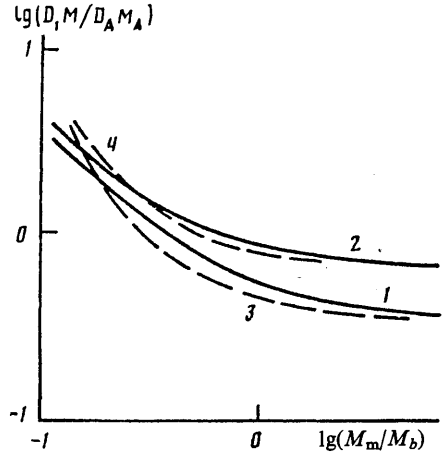


Figure 9. Dependence of $\lg(D_1M/D_AM_A)$ on $\lg(M_m/M_b)$ calculated by Eqn. (11) for $n = 1$ (curves *1* and *2*) and $n = 1.5$ (curves *3* and *4*) ($\gamma = 0.2$) with $N/N_c = 2.5$ (curves *1* and *3*) and $N/N_c = 0.5$ (curves *2* and *4*).

In the study of the dependence of D on M, the molecular weights of both the moving chain and of the surrounding medium are usually varied, i.e. $N = P$. Fig. 10 illustrates the dependence of D_1M/D_AM_A on M/M_b for $N = P$ calculated by Eqn. (11). In the range where $N > N_c$, the contribution of the second term in brackets is insignificant, i.e. the role of the "tube" renewal processes is the self-diffusion phenomenon is insignificant in this range of N. For $N \simeq N_c$, the "tube" renewal process can already play a definite role and when $N < N_c$ the very concept of the "tube" and reptation loses physical significance. Thus the second term in Eqn. (11) is significant only in the region where $N \simeq N_c$. Fig. 10 also illustrates the $D \propto N^{-2}$ relation, which gives rise to the $D(N)$ limiting law at $N \to \infty$. Evidently the straight line obtained in terms of logarithmic coordinates is close to the curve calculated from Eqn. (11). Allowance for the second term in Eqn. (11) then expands the region of applicability of the $D \propto N^{-2}$ law to cover also the region of low molecular weights. Fig. 10 also presents the dependence of D_∞ on M plotted in terms of the approximate formula

$$D_\infty = \frac{D_A}{N}\frac{1}{1 + L/b}. \qquad (12)$$

This relation is more convenient for analysis and actually agrees with the more accurate relation (7).

Thus it is seen that the relations obtained describe quantitatively the behaviour observed for self-diffusion coefficients in melts.

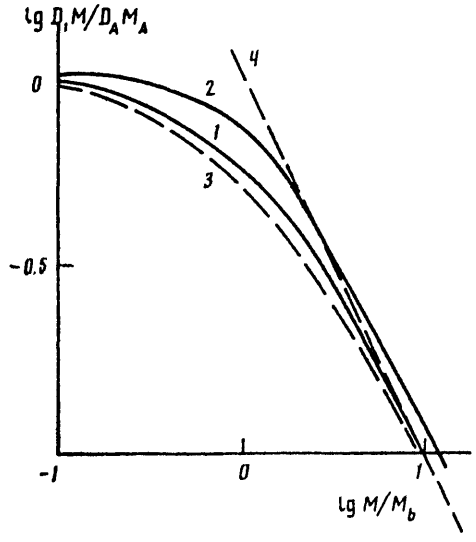


Figure 10. Dependence of $\lg(D_1M/D_AM_A)$ on $\lg(M/M_b)$ calculated by Eqns. (8) (curve *1*) and (11) (curve *2*) for $N = P$. Curve *3*, calculated from the approximate formula (12), and curve *4*, representing the limiting law governing the variation of D with M ($D \propto N^{-2}$), are presented for comparison.

IV. Self-diffusion in concentrated polymer solutions

1. General relations

In the region of dilute solutions, the theory of the translational mobility of macromolcules has been developed using Kirkwood's ideas about intermolecular hydrodynamic interactions between the elements of a chain macromolecule. The simplest relation for D when $c \to 0$ (D_0) is

$$D_0 = \frac{kT}{N\zeta}(1 + 1.843\sqrt{N}), \qquad (13)$$

where c is the concentration in g cm^{-3}. For more accurate and complex relations, see Rafikov et al.[7] All the available experimental data indicate a satisfactory agreement between the theoretical and experimental relations in the region of very dilute solutions.

The concentration dependence of D in the region of moderate concentrations has been investigated for certain systems in fair detail.[1,2] In the first studies, the authors concluded[37–39] that the scaling relations hold fairly well for the $D(c, M)$ function. It is essential to note tht the studies were performed in a restricted concentration and molecular weight range. However, in later investigations[40–45] a discrepancy between the predictions of the scaling theory and experimental relations was noted. The range of experimental concentrations of the solutions was greatly extended by Sundukov et al.[43] Fig. 11 [43] presents the dependence of D on c for solutions of poly(ethylene oxide) in dioxan.

Proceeding to the analysis of the dependence of D on c (or the volume concentration φ), it is necessary to take into account in the first place the variation of D_A (or ζ) as a function of φ. Failure to take into account the variation of the segmental mobility with increases in concentration has led in some of the early studies to incorrect conclusions. The variation of D_A (or ζ) with φ is usually described by a relation obtained on the basis of the free volume theory [see Eqn. (22) below]. The variation of D_A with φ can be taken into account more rigorously by an experimental procedure. The determination of the dependence of the self-diffusion coefficient of the solvent D_S on φ appears to be most correct.[16] In some investigations, it has been suggested that the spin–lattice relaxation times,[13,46] the monomeric friction coefficients determined from the viscoelastic properties of solutions,[44] etc. can be used to determine the dependence of D_S on φ. Below, we shall consider the reduced self-diffusion coefficient $\tilde{D} = D/D_A$. The quantity $\tilde{D}$ no longer depends on the variation of the local mobility with increasing concentration of the polymer solution.

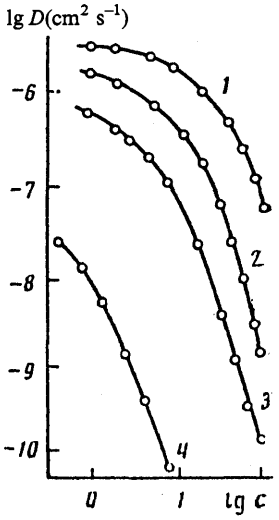


Figure 11. Dependence of $\lg D$ on $\lg c$ for PEO solutions in dioxane; 10^{-4} M: *1*, 0.2; *2*, 2; *3*, 4; *4*, 30.[43]

As in the analysis of the dependence of the viscosity of polymer solutions on concentration,[16] it has been suggested in some studies that generalised coordinates be employed for the representation of the dependence of D on c for solutions of different fractions. Thus the present author[15,47] proposed the generalised coordinates $\tilde{D}-c[\eta]$ (Fig. 12), while Sundukov et al.[43] proposed $D-(c/c_p)$, where c_p is an empirical quantity selected for each solution with a given molecular weight (Fig. 13).‡ In terms of these coordinates, it is possible to obtain a generalised dependence of D on c and M for solutions having different molecular weights in solvents of different kinds

‡ Here it is essential to note that the dependence of c_p on M is close to that of $[\eta]$ on M.

(differing in the interaction between the solvent and polymer molecules) and for polymers with different chemical structure of the chain.[47]

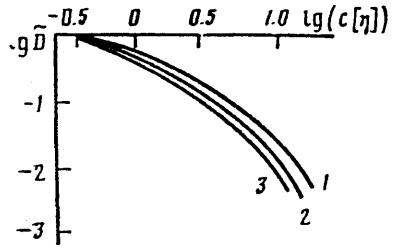


Figure 12. Dependence of $\lg \tilde{D}$ on $\lg\{c[\eta]\}$ for PS (curve *1*), PDMS (curve *2*), and PEO (curve *3*) solutions.

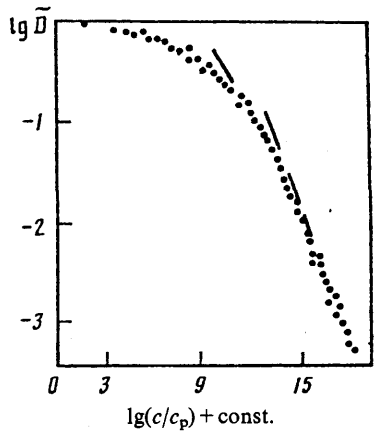


Figure 13. Dependence of $\lg \tilde{D}$ on $\lg(c/c_p)$ for PEO solutions in dioxane.[43] Data for different fractions are presented (see the caption to Fig. 11).

2. Theoretical relations for D in concentrated solutions

The main experimental relations between D and M have been explained by the present author.[36,47] Indeed, in the analysis of data for moderately concentrated solutions it is necessary to take into account the presence of the units of other macromolecules whose interaction with the units of the main chain diminishes the intramolecular hydrodynamic interactions of the selected macromolecule. There is no rigorous solution of this type of problem. However, the use of the "effective hydrodynamic field" model for the description of the hydrodynamic interactions of elements moving in a viscous liquid[48,49] proved successful. An equation for the dependence of D on M and φ was obtained:[47]

$$D(\varphi) = \frac{kT}{N\zeta}[1 + 1.843\sqrt{N}\exp(-1.27\sqrt{c[\eta]})]. \qquad (14)$$

Eqn. (14) is valid in the following concentration ranges: $1 < c[\eta] < c^*[\eta]$, where $c^*[\eta] = 0.64(\ln 2\sqrt{N})^2$. For the usual values of N, the upper limit is $c^*[\eta] \simeq 10-15$.

Fig. 14 illustrates the dependence of $\lg \tilde{D}$ on $\sqrt{c[\eta]}$ for PS, PDMS, and PEO. In terms of these coordinates, linear $D = f\{c[\eta]\}$ relations are observed and can be described by the following empirical equation:

$$\ln(\tilde{D}/\tilde{D}_0) = -(1.15-1.4)\sqrt{c[\eta]}. \qquad (15)$$

The slopes of these relations (1.15 – 1.4) are close to 1.27 [see Eqn. (14)].

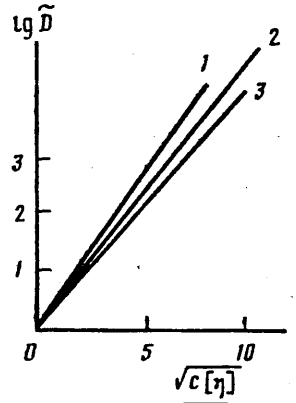


Figure 14. Dependence of $\lg D$ on $\sqrt{c[\eta]}$ for solutions of different polymers: *1*, PDMS; *2*, PS; *3*, PEO.

The values of α in Eqn. (4) vary continuously with c from +0.5 to 1 in contrast to the stepwise variation, predicted by the scaling theory, from $1(c < c^*)$ to $2(c > c^*)$. The dependence of α on $c[\eta]$ then differs somewhat for different values of N (Fig. 15*a*).

The influence of the molecular weights of the moving macromolecule and of the surrounding medium on the $D(c)$ relation have been considered separately.[35] In conformity with the notation adopted for the specified macromolecule and the macromolecules of the surrounding medium (N, P), the following equation can be written for the $D = f(c)$ relation:

$$D = \frac{D_A}{N^{0.5}}\left[\frac{1}{1.843N^{0.5}} + \exp(-1.27\sqrt{c[\eta]})\right].$$

Here $[\eta] = 0.6\bar{\nu}P^{0.5}$, where $\bar{\nu}$ is the specific partial volume. In these equations, the exponents of N and P are 0.5 (θ-conditions).

3. Self-diffusion in concentrated polymer solutions

In this concentration range, there are in fact no experimental data for the dependence of D on c and M. However, the existence of experimental and theoretical data for moderate concentrations and for polymer melts makes it possible to obtain reasonable relations also for high concentrations. The scaling theory can be used conveniently to describe the dependence of $\tilde{D}$ on φ.[35,36,47] The dependence of $\tilde{D}$ on φ is usually considered in the form

$$\tilde{D} = \tilde{D}_R(\varphi/\varphi_{th})^{\beta}(\varphi > \varphi_{th}), \qquad (16)$$

where φ_{th} is the threshold concentration proportional to $[\eta]^{-1}$ and β is a numerical coefficient. β is found from the condition $D(\varphi \to 1) \propto N^{-2}$.

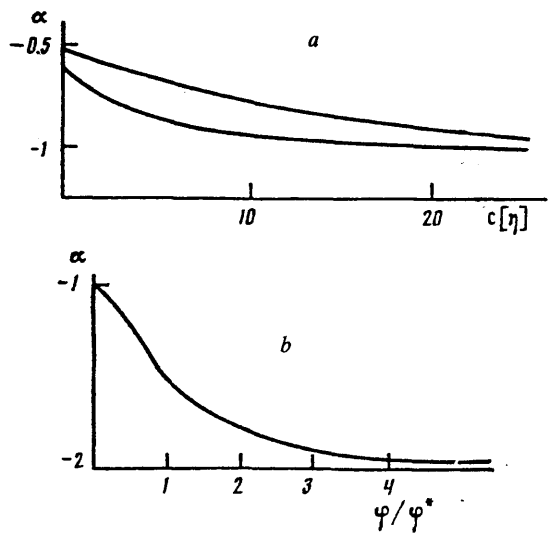


Figure 15. Dependence of α on $c[\eta]$ (*a*) and on φ/φ^* (*b*): *1*, $N = 10^3$; *2*, $N = 10^2$.

The scaling theory was first used to describe the $D(\varphi, M)$ function by Daoud and Jannink.[50] Since here we consider only the region of concentrated solutions (the θ-region), we have for the latter $\beta = -2$,[47] i. e.

$$\tilde{D} = \tilde{D}_R(1/\varphi^2 N). \tag{17}$$

However, the relations obtained in this way[47,50] suffer from one significant disadvantage. By analysing the $D \propto N^{-\alpha}$ relation [Eqns. (16) and (17)] we see that $\alpha = 1$ when $\varphi < \varphi_{th}$, $\alpha = 2$ when $\varphi > \varphi_{th}$ and α has no significance at the point φ_{th} when $\varphi = \varphi_{th}$. Naturally, there is in reality no such discontinuity in the dependence of α on φ.[37–45] This inaccuracy of the scaling theory has been removed[35] by invoking the concept of the reptation character of the motion of the macromolecule in the region of high concentrations.

We shall consider Eqn. (12). The quantity b (or N_c) is known to increase with decrease in concentration. Since the region of high concentrations is the region of the θ-solvent, it follows that, according to the scaling theory, we have

$$N_c(\varphi) = N_c/\varphi^2. \tag{18}$$

Substitution of Eqn. (18) in Eqn. (12) yields the following relation for the component D_∞ (when $\varphi > \varphi^*$):

$$D_\infty = \frac{D_A}{N} \frac{1}{1 + \varphi^2 N/N_c}. \tag{19}$$

The quantity φ^* is determined from the equation

$$\varphi^* = \sqrt{N_c/N}. \tag{20}$$

For the usual polymers, $N_c \simeq 100$, whereupon $\varphi^* = 0.2-0.3$.

Evidently Eqn. (19) gives rise to a continuous transition from $D \propto N^{-1}$ to $D \propto N^{-2}$. Omitting the intervening stages, we quote the final relation:

$$\tilde{D} = \tilde{D}_R\left[\frac{1}{1 + \varphi^2 N/N_c} + Z_\varphi\left(\gamma \frac{N_c}{\varphi^2 P}\right)^n\right], \tag{21}$$

where Z_φ is the probability that the macromolecule is in a tube at a specific concentration φ. For $\varphi < \sqrt{N_c/P}$, we then have $Z = 0$ [see also the explanation of Eqn. (10)]. The dependence of α on φ can be calculated from Eqn. (21) [see Eqn. (4)] (Fig. 15). Evidently, α varies continuously from 1 to 2. The $\alpha(\varphi)$ relation depends somewhat on the molecular weight of the surrounding medium.

The general dependence of D on φ (and not only the dependence of $\tilde{D}$ on φ) should take into account also the dependence of D_A (or D_S) on φ. The most generally accepted approach to the analysis of $D_S(\varphi)$ is associated with the "free volume" theory.[16] The simplest relation for the dependence of D_S on φ is

$$D_S = D_S(0) \exp\left\{-\frac{B_1\beta_1\varphi}{f_S(f_S - \beta_1\varphi)}\right\}, \tag{22}$$

where B_1, β_1, and f_S are parameters of the free volume theory.[12] For more complex relations governing $D_S(\varphi)$, see Budtov and Konsetov[16] and Budtov.[51] For a wide class of flexible chain polymers without specific interactions (hydrogen bonds, ionic bonds), the limits of the variation of the ratios B_1/f_S and β_1/f_S have been obtained: from 3 to 5 and from 0.25 to 0.4 respectively.[16] Interesting results concerning the influence of the size of the solvent molecules on these coefficients have been given.[52] For $d \lg D/d \lg \varphi$, we obtain

$$\frac{d \lg D}{d \lg \varphi} = \beta(\varphi) + \frac{B_1\beta_1^2\varphi}{f_S(f_S - \beta_1\varphi)^2}. \tag{23}$$

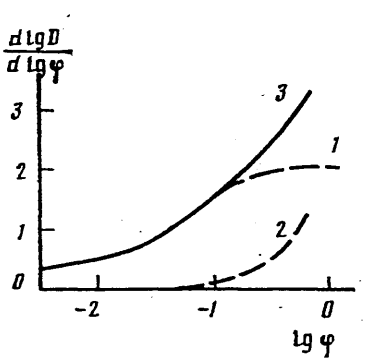


Figure 16. Dependence of $d \lg D/d \lg \varphi$ on $\lg \varphi$ calculated by Eqn. (23): *1*, the contribution of the first term in Eqn. (23); *2*, the contribution of the second term; *3*, the overall contribution.

Fig. 16 presents the dependence of $d \lg D/d \lg \varphi$ on the most typical representative of PS polymers (with toluene as the solvent). Evidently, when $\varphi \simeq 0.1$, the second term in Eqn. (23) constitutes an insignificant proportion of the first, while under conditions where $\varphi > 0.3$ it has to be taken into account.

Interesting studies have been initiated on self-diffusion processes during phase separation in polymer solutions.[53,54] Special methodological procedures have been proposed, which make it possible to estimate the self-diffusion coefficients in different phases from the non-exponential decay of the spin echo in NMR.

V. Characteristic features of the self-diffusion in oligomer melts and solutions

The relations discussed above are valid for fairly long chain molecules. When the self-diffusion of oligomers is investigated, other unusual dependences of D on M are observed.[55]§ The dependence of D on M for oligomers can be conveniently analysed in terms of the coordinates $(D_1/L_0)L - L$ (Fig. 17).¶ Evidently, in terms of these coordinates, D_1/D_0 for ethers and esters and also for n-alkanes initially diminishes with increase in L, but, when $L \simeq 30$ Å, the quantity D_1/D_0 no longer depends on L. If the end groups or other specific groups in the chain are in groups of atoms characterised by a strong interaction with the surrounding molecules, then the dependence of D_1/D_0 on L is different: the quantity increases with increase in L and subsequently attains a plateau. When the influence of the inhomogeneity of the chain structure can be disregarded ($L > 30$ Å), the ratio D_1/D_0 assumes the same value for all the systems investigated.

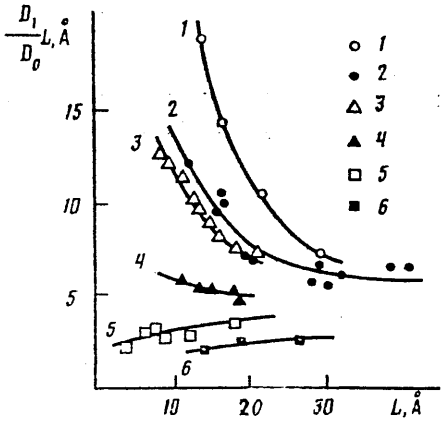


Figure 17. Dependence of $(D_1/D_0)L$ on L for different substances: *1*, ethers; *2*, esters; *3*, n-alkanes; *4*, phthalates; *5*, alcohols; *6*, acids.

The above effects can be accounted for using the free volume theory without resorting to the concept of aggregation. Indeed, it is well known that $f = f_0 + \Delta/N$, where f_0 is the fraction of the free volume for a homogeneous chain, N is the number of chain elements, and Δ is the increment in the ratio of the free volumes of the characteristic group and the repeating chain element. Then the diffusion coefficient of the oligomer D_{ol} depends on M in a complex manner:

$$D_{ol} = D_{hom}(M)\exp\left(\frac{\beta_L}{f_0}\frac{\Delta}{N}\right), \quad (24)$$

where D_{hom} is the diffusion coefficient for a homogeneous chain.

Indeed, in terms of the coordinates $\lg[(D_{hom}/D_0)L] - 1/L$, a set of curves, arranged fanwise, is observed and from their slopes it is possible to determine Δ for particular functional groups:

Group of atoms (or atom)	—O—	$-CH_3$	$-CH_2-$	C_6H_5-	>C=O	—OH	
Δ	5.4	1.7	0	—3.3	—3.5	—4.3	—11.5

The negative values of Δ indicate the retardation of the "local" motion of the corresponding group compared with the motion of the $-CH_2-$ group. These results make it necessary to treat with caution the interpretation of the dependence of D on M when low-molecular-weight polymers ($M < 10^4$) are considered. Unfortunately these effects are not taken into account in the majority of studies discussed.

VI. Numerical modelling of the translational mobility of macromolecules

The modelling of the mobility of macromolecules by means of direct computer simulation of molecular models by Monte Carlo (MC) and molecular dynamics (MD) methods has come to be widely used in recent years.[6] The first studies on the analysis of small scale movements of generalised polymer chains by the MD method were carried out Balabaev et al.[58] Subsequently this approach was widely employed for the solution of specific problems. However, the majority of calculations were limited to the consideration of lattice systems idealised to the maximum extent, while for a microscopic description of the system it is essential to take into account explicitly the interactions between all the species (atoms). This imposes significant limitations on the number of species and their dimensions (molecular weights) and also on the time of observation of the species.[59]

A significant achievement of the dynamic calculations in the study of condensed systems has been the demonstration of the fact that the widely held hypothesis that the diffusion of species in a simple monotonic liquid has a jump (activation) mechanism does not correspond to the real picture of molecular motion.[60] The molecular flux of species in such a liquid involve successive small displacements of the molecules. A negligibly small contribution of "large jumps" to the overall diffusional flux is observed. An appreciable influence by attraction forces on the relaxation of large chain fragments has also not been discovered.[61] This type of motion has in fact been taken into account by the "free volume" theory[16] [see Eqn. (22)].

It has been shown[62] that the mobility of the terminal chain elements differs from the mobility of the central elements, which is consistent with the observations made for oligomers (see Section V). The question of the anisotropy of the motion of the chain unit has been considered[63] for a liquid polymer. It was shown that for short observtion times, the tangential component of the mobility is smaller than the transverse component. However, for large observation

§ Similar effects have been observed also both for the viscosity η and for $[\eta]$ of oligomers.[56,57]

¶ Here D_1 and D_0 are the self-diffusion coefficients of oligomers for $\varphi = 1$ and $\varphi = 0$.

times, the units are able to diffuse over a distance close to the average distance between the nearest neighbouring macromolecules in the system. The surrounding chains hinder the motion of the chain considered and force the units to move preferentially along the chain contour, i.e. the anisotropy of the mobility is significant. For a dilute solution, the anisotropy of the mobility is manifested to the least extent. It is essential to note that attempts to observe reptation processes (the anisotropy of mobility) yielded a negative result in the studies of Baumgartner and Binder[64] and Evans and Edwards[65] due to the small chain length and the short observation time.[66]

Within the framework of the pseudostochastic Verdier–Stockmayer model, the dynamics of an assembly of particles has been investigated.[57,58] It was shown that $D \propto N^{-\alpha}$, increasing with increasing concentration (Fig. 15). The $<X^2> \simeq t^g$ relation also varies with increasing concentration: g diminishes to 0.2 (see above).

The diffusion of a chain macromolecule in a matrix with stationary elements which the diffusing chain cannot cross has been modelled on a computer.[69] The distance between such obstacles is d. It was found that[22] the dependence of $D(d)/D(\infty)$ on N^2/d is represented by a single curve regardless of the value of d. It coincides with the dependence of D on L/b specified by Eqn. (7) if it is assumed that $bA = 2d^2$. This relation ($bA = 2d^2$) resembles the familiar formula for the square of the length of a chain whose contour length is b.

Thus it is seen that the principal results of numerical modelling have been reflected in analytical models and have been observed experimentally. An important feature of computer modelling is that it is possible to obtain unique information about the local structure of the material.

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The experimental and theoretical results presented in this study show that the dependences of the self-diffusion coefficient on concentration and on the molecular weights of the diffusing macromolecule and of the surrounding medium have been fairly thoroughly investigated and can be described quantitatively. The influence of the interaction of the chain with the solvent on the self-diffusion coefficient has been discovered. The characteristic features of the diffusion of oligomers have been examined.

The relations obtained can be used to solve a wide range of problems in the physical chemistry of polymers.

References

1. A E Chalykh *Diffuziya v Polimerykh Sistemakh* (Diffusion in Polymer Systems), Izd. Khimiya, Moscow, 1987, 312 pp
2. A I Maklakov, V D Skirda, N F Fatkullin *Samodiffuziya v Rastvorakh i Rasplavakh Polimerov* (Self-diffusion in Polymer Solutions and Melts), Izd. Kazan. Gos. Univ., Kazan, 1986, 206 pp
3. N Nemoto, M Landry, L Noh, et al. *Macromolecules*, 1985, **18**(2) 308
4. J Wesson, L Noh, T Kitano, H Yu *Macromolecules*, 1984, **17**(4) 782
5. M Antonietti, J Coutandin, R Grutter, H Sillescu *Macromolecules*, 1984, **17**(4) 798
6. Yu Ya Gotlib, A A Darinskii, Yu E Svetlov *Fizicheskaya Kinetika Makromolecul* (The Physical Kinetics of Macromolecules), Izd. Khimiya, Leningrad, 1986, 272 pp
7. S R Rafikov, V P Budtov, Yu B Monakov *Vvedenie v Fizikokhimiyu Rastvorov Polimerov* (Introduction to the Physical Chemistry of Polymer Solutions), Izd. Nauka, Moscow, 1978, 326 pp
8. J Rouse *J. Chem. Phys.*, 1953, **21**(6) 1273
9. V A Kargin, G L Slonimskii *Zh. Fiz. Khim.*, 1949, **23**(3) 563
10. V A Kargin *Dokl. Akad. Nauk SSSR*, 1948, **62**(2) 239
11. G M Panchenkov, N N Borisenko, V V Erchenko *Zh. Fiz. Khim.*, 1969, **43**(9) 2369 [English translation in *Russ. J. Phys. Chem.*, 1969(9)]
12. V P Budtov *Vysokomol. Soedin., Ser. B*, 1976, **18**(1) 19
13. V A Sevryugin *Abstract of Candidate's Thesis in Chemical Sciences*, Kazan State University, Kazan, 1985
14. J Klein, D Fletcher, L Fetter *Nature (London)*, 1983, **304** 526
15. V P Budtov *II Vsesoyuznoe Soveshchanie 'Matematicheskie Metody dlya Issledovaniya Polimerov'* (The IInd All-Union Conference on 'Mathematical Methods for the Investigation of Polymers'), Pushchino, 1981, Preprint
16. V P Budtov, V V Konsetov *Teplomassoperenos v Polimerizatsionnykh Protsessakh* (Heat and Mass Transfer in Polymerisation Processes), Izd. Khimiya, Leningrad, 1983, 256 pp
17. P G de Gennes *Scaling Concepts in Polymer Physics* (Translated into Russian), Izd. Mir, Moscow, 1982, 312 pp
18. P De Gennes *J. Chem. Phys.*, 1971, **55**(3) 572
19. M Doi, S Edwards *J. Chem. Soc., Faraday Trans. II*, 1978, (8) 1789
20. P De Gennes *Macromolecules*, 1976, **9**(3) 587
21. S Edwards, J Grant *J. Phys. A*, 1973, **6**(5) 1169
22. V P Budtov *Vysokomol. Soedin., Ser. A*, 1983, **25**(2) 493; 1978, **20**(12) 2675
23. A E Chalykh, I N Sapozhnikova *Vysokomol. Soedin., Ser. A*, 1979, **21**(7) 1664
24. A E Chalykh, I N Sapozhnikova, A D Aliev *Vysokomol. Soedin., Ser. B*, 1980, **22**(11) 835
25. A Bartels *J. Polym. Sci., Polym. Lett.*, 1983, **21** 495
26. R Bachus, R Kimmich *Polymer*, 1983, **24**(8) 964
27. A Smith *Bull. Am. Phys. Soc.*, 1983, **28**(3) 546
28. M Antonietti, J Coutandin, H Sillescu *Macromolecules*, 1986, **19**(3) 793
29. J E Tanner, K-J Liu, J E Anderson *Macromolecules*, 1971, **4**(5) 585; (6) 748
30. P Green, P Mills, G Palmstrom, et al. *Phys. Rev. Lett.*, 1984, **53**(10) 2146
31. G M Zakharov *Vysokomol. Soedin.*, 1965, **7**(3) 458
32. V P Budtov *Vysokomol. Soedin., Ser. A*, 1981, **23**(1) 193
33. J Klein *Macromolecules*, 1978, **11**(6) 852; 1981, **14**(2) 460
34. M Daoud, P De Gennes *J. Polym. Sci., Polym. Phys. Ed.*, 1979, **17**(11) 1971
35. V P Budtov *Vysokomol. Soedin., Ser. A*, 1988, **30**(10) 2153
36. V P Budtov *Macromol. Chem.*, 1987, **188** 2353
37. P Callagham, D Pinder *Macromolecules*, 1980, **13**(5) 1085
38. P Callagham, D Pinder *Macromolecules*, 1984, **17**(3) 431
39. L Leger, H Hermit, F Rondelez *Macromolecules*, 1981, **14**(6) 1732
40. V D Skirda, N F Fatkullin, V I Sundukov, A I Maklakov *Vysokomol. Soedin., Ser. A*, 1987, **29**(10) 2035
41. A I Maklakov, V A Sevryugin, V D Skirda, N F Fatkullin *Vysokomol. Soedin., Ser. A*, 1984, **26**(12) 2502
42. A I Maklakov, I K Dvoyashkin *Vysokomol. Soedin., Ser. B*, 1983, **25**(6) 424

43. V Sundukov, V Skirda, A Maklakov *Polym. Bull.*, 1985, **14** 153
44. E Von Meerwall, E Amis, J Ferry *Adv. Polym. Sci.*, 1985, **55**(10) 1078
45. E Amis, C Han *Polymer*, 1982, **23**(10) 1403
46. O F Bezrukov, V O Budtov, V P Fokanov *Vysokomol. Soedin., Ser. A*, 1972, **14**(12) 2531
47. V P Budtov *Vysokomol. Soedin., Ser. A*, 1986, **28**(12) 2575
48. H Brinkman *Proc., K. Ned. Acad. Wet.*, 1947, **50**, 618
49. F Wang, B Zimm *J. Polym. Sci., Polym. Phys. Ed.*, 1974, **12**(8) 1619
50. M Daoud, G Jannink *J. Phys. (Paris)*, 1976, **37**(10) 1845
51. V P Budtov *Vysokomol. Soedin., Ser. B*, 1975, **17**(3) 339
52. G G Pimenov, O E Zgadzai *Vysokomol. Soedin., Ser. B*, 1985, **27**(12) 899
53. A I Maklakov, V D Skirda, T A Serebrennikova *Dokl. Akad. Nauk SSSR*, 1986, **288**(4) 922
54. O E Zgadzai, A I Maklakov, V D Skirda, A E Chalykh *Dokl. Akad. Nauk SSSR*, 1987, **297**(3) 1407
55. O F Bezrukov, V P Budtov, B P Nikolaev, V P Fokanov *Vestn. Leningr. Univ.*, 1972, (16) 60
56. V P Budtov, V V Aref'eva *Vysokomol. Soedin., Ser. A*, 1976, **18**(6) 1353
57. V P Budtov, G K Romanovskii *Vysokomol. Soedin., Ser. A*, 1980, **22**(4) 700
58. N K Balabaev, A G Grivtsov, E E Shnol' *Dokl. Akad. Nauk SSSR*, 1975, **220**(5) 1096
59. R Fox *Phys. Rev. A*, 1983, **25**(5) 1096
60. B Older, W G Hoover *Physics of Simple Liquids* (Edited by M Temperley) (Translated into Russian), Izd. Mir, Moscow, 1971, p. 81
61. M Bishop, M Kolos, H Frisch *J. Chem. Phys.*, 1983, **79**(7) 3500
62. N K Balabaev, A G Grivtsov *Vysokomol. Soedin., Ser. B*, 1981, **23**(2) 121
63. P G Khalatur, A S Pavlov, G N Marchenko, et al. *Dokl. Akad. Nauk SSSR*, 1985, **282**(5) 1186
64. A Baumgartner, K Binder *J. Chem. Phys.*, 1981, **75**(6) 2294
65. K Evans, S Edwards *J. Chem. Phys., Faraday Trans.*, 1981, **77**(10) 1891
66. P G Khalatur, S G Pletneva, G I Marchenko *Usp. Khim.*, 1986, **55**(4) 679 [English translation in *Russ. Chem. Rev.*, 1986(4)]
67. A Kolinski, L Romiszowski *J. Chem. Phys.*, 1983, **79**(3) 1523
68. A Kolinski, J Skolnick, R Jaris *Polym. Flow Interact. Workshop., La Jolla, 1985*, New York, 1985, p. 241
69. M Doi *Polym. J.*, 1973, **5** 297

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Isoprenoids as natural products with a wide variety of functions†

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ABSTRACT. The available information about certain biological properties of isoprenoid is surveyed. Their role in the regulation of the vital activity of plants and insects as well as their ecological importance, consisting in ensuring the coexistence of organisms of different classes, are demonstrated. Certain structural elements essential for the manifestation of antifeedant activity are indicated.

The bibliography includes 47 references.

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I. Introduction

The enormous strides which isoprenoid chemistry and biology have made in the recent decades necessitate a survey of the present state of our knowledge of the importance of isoprenoids as biologically active compounds. The information explosion resulting from the current vigorous research into this topic can be illustrated by two examples: (1) the Glasby Encyclopaedia of Terpenoids (edited in 1982) which still contains not less than 10 000 compounds after the exclusion of all data on natural steroids. (2) The present author's illustration by a graph of the enormous rise of the number of natural sesquiterpenoids found hitherto (Fig. 1). Fig. 1 shows the number of compounds of this single class of terpenoids, which was more than 7500 by the end of 1987, over half being sesquiterpene lactones. The curve has a consistently exponential shape. During 1970 and 1971,[1] the author attempted to summarise the data available at the time on the biological activities of (1) all isoprenoids[1] (one chapter comprising 50 pages of concentrated information) and (2) all data concerning sesquiterpenoids[2] (a 37 page chapter). However, it was already evident that we obtain information about the structures of newly described natural products much faster than data on different types of their biological activity. The latter are often combined nowadays with data on their ecological importance.

† Lecture delivered by Prof Herout at the Czechoslovak-Polish Meeting on Isoprenoids (1987), the relevant data being presented at the Zelinskii Institute of Organic Chemistry, Moscow, in 1988.

The version printed here is based largely on the English text kindly supplied by the author and partly on the Russian translation by N Ya Grigor'eva (edited by A M Moiseenkov) (Ed. of Translation).

II. Secondary isoprenoid metabolites as biologically important compounds

The question which the author put as early as 1970, namely "are secondary metabolites (in our case isoprenoids) present in plants only as waste products?", is being solved nowadays more or less unambiguously. Of course they are biosynthesised as "secondary" metabolites, but many (if not all) are essential for the life and/or survival of plants. It is now known that similar "secondary products" are not produced exclusively by the plant kingdom but are used in a wide variety of different ways also in other domains: insects and diverse marine organisms are producers of typical isoprenoids and steroids. They are not only important regulators of life functions but their presence in intracellular membranes is essential for the complex functions of living cells. This is typical, with some differences, for all classes of organisms, for example, the most primitive of the existing micro-organisms, the so called archeobacteria, have the membranes in their unicellular bodies "fixed" or "reinforced" with the aid of α,ω-bisphytanol ethers (I). The more advanced "true bacteria" contain in their membrane triterpene derivatives, for example, of the hopane type (II) (cf. Ourisson[3]). At present most advanced organisms, such as plants, fungi, and animals, make use exclusively of sterols. These are phytosterols, such as sito-, stigma-, or campe-sterols for plants and ergosterol, for example, in the case of fungi, and cholesterol (III) for animals.

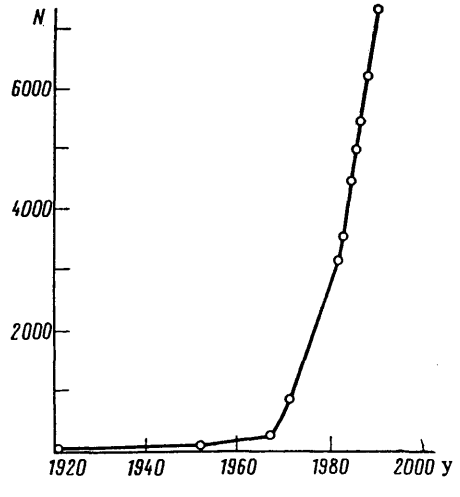
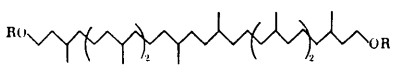
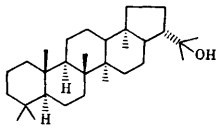


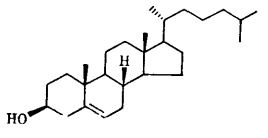
Figure 1. Growth as a function of time of the number of sesquiterpenoids (N) discovered in natural sources.



(I)

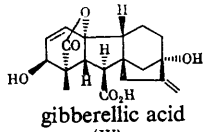


hopanol (II)



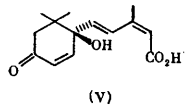
(III)

Djerassi's recent work[4] on the widely differing side chains in the sterols of marine organisms demonstrates that our knowlege of these facts remain far from perfect. The important place which hormones and vitamins as well as a number of other regulators and transferring agents occupy among secondary metabolites and which is closely related to the regulatory functions is noteworthy. Such substances have to be examined in greater detail. Certain vitamins are typical products derived from isoprenoids or steroids (A, D, E, K). Carotenoids, which are tetraterpene derivatives, have in addition important functions participating together with the chlorophylls in photosynthesis; phytol is an important component of the molecules of different chlorophylls. Steroid hormones are typical hormonal regulators in vertebrates, functioning as sexual hormones, corticoids, etc. We now have a deeper understanding of the function of ecdysteroids and juvenile hormones in the class of Arthropoda (insects, crustaceans) and probably worms (Annelida) as well. In the plant kingdom other isoprenoids function as hormones, for example, diterpenoids such as gibberellins (IV) (about 70 naturally occuring compounds of this type are known)[5] and the sesquiterpenoid abscisic acids (V) together with some of its metabolites.



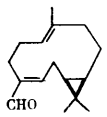
gibberellic acid

(IV)

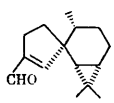


(V)

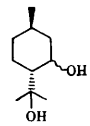
The function of the "prolongation factor" has been discovered, in addition to gibberellins, also in other compounds, especially brassinoids[6,7] during recent decades. The list of compounds of isoprenoid character able to influence the germination or growth of plants is also large. This influence, mostly in a negative sense, represents the known "allellopathic activity" of many plants in their fight against competing plants belonging to other species. Here mention will be made only of some components of liverworts discovered quite recently, for example, (–)-lepidozenal (VI) [8] and (+)-vitrenal (VII).[9] Monoterpene derivatives with the same mode of action are known in certain higher plants, such as the eucalyptus, for example *p*-menthane-3,8-diols (VIII) and (IX).[10]



(VI)



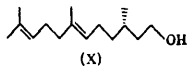
(VII)



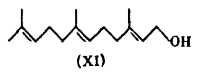
(VIII), (IX)

The important role of "secondary metabolites" in the coexistence with organisms belonging to different domains and hence their ecological importance have been traced during recent decades. In view of the manifold activity of isoprenoids, the above studies were concentrated on the latter. The activity of isoprenoids is frequently encountered in the interactions of different organisms belonging to all existing domains: Mabry and Gill[11] attempted to list the different types of activity of terpenoids in 1979 but today the list would have to be much larger. Only certain striking examples will be selected, since a detailed description would require several books. For example, the relatively recently discovered group of sesterpenoids (with 25 carbon atoms in their molecules)—not yet mentioned by Mabry and Gill—includes, according to a more recent review,[12] more than 160 compounds, mostly with functions of a defensive character. They are not restricted to plants but occur as metabolites of insects and especially of diverse marine organisms.

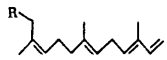
Isoprenoids do not by any means serve solely as deterrent substances. On the contrary, they frequently possess attractant properties. The scent of flowers has its value in attracting pollinators and many simple derivatives of the monoterpene series are generally known. Some of them have been adopted by insects as their own "pheromones", which is particularly interesting: a single example may be quoted: orchid (*Ophrys* sp.) pollinators are attracted from a distance to orchid flowers (and to flowers of similar, mainly tropical species) by scents of a sesquiterpene character (the name of the Swedish entomologist Kullenberg[13,14] may be mentioned in this connection), which are identical with the sexual pheromones of their females (such pollinators may be, for example, the solitary bees *Aculeate Hymenoptera*). The spectrum of the activity of simple aliphatic sesquiterpenoids is broad—for example, the dihydrofarnesol derivative terrestrol (X) [15] is a "territory marker" for the male bumble bee. Farnesol (XI) is a typical scent of certain flowers, while the basic hydrocarbon farnesene (XII) and its geometrical isomers are known "alarm"pheromones in certain Aphids.[16] Homo-derivatives of this series, for example homofarnesene (XIII) constitute[17] a "trail marker" for an ant (*Solenopsis invicta*).



(X)

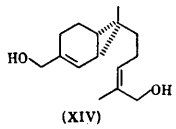


(XI)

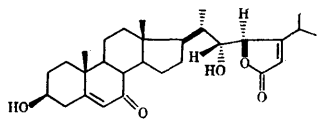


R = H (XII), R = CH_3 (XIII)

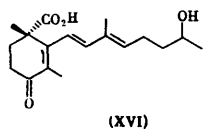
The sesquiterpenoid derivative sirenin (XIV) is known as a "sperm attractant" in the water-mould *Allomyces* sp., a fairly primitive organism on the evolutionary scale. Other examples where isoprenoids play a similar role in the sexual reproduction of fungi[18] are the steroid antheridiol (XV) and the nor-carotenoid derivative trisporic acid (XVI).



(XIV)

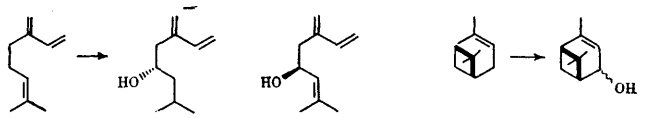


(XV)



(XVI)

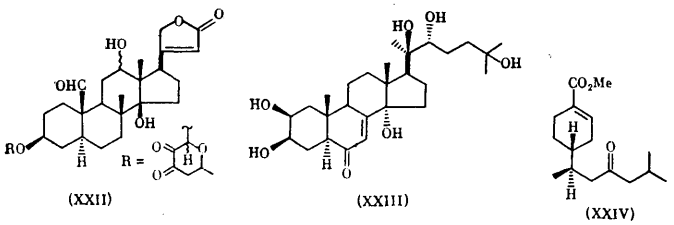
Certain compounds ingested with food and modified somewhat during their assimilation are frequently converted into derivatives with a new property, which is an entirely normal process. For example, the aggregation pheromones of certain bark beetles (*Ips* sp., *Dendroctonus*, etc.) convert some of the terpenoid derivatives in their food [for example, myrcene (XVII), α-pinene (XX)] into their own aggregation pheromone ipsenol (XVIII), ipsdienol (XIX), and/or *cis*- and *trans*-verbenols (XXI)—cf. Fergusson and Metcalf;[19] naturally, they usually contribute "another component", arising from their own biosynthetic capacity, to the mixtures of their pheromones.



(XVII) (XVIII) (XIX) (XX) (XXI)

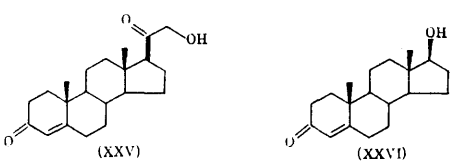
Our "human" interest is concerned at present mainly with "deterrent" activities and we are therefore much more familiar with the latter. Individual monoterpene compounds, contained in most of the essential oils of the needles or barks of conifers, play, according to their quantity or concentrations, a decisive role in determining whether these plants will or will not be resistant to the attack of herbivores. The influence of myrcene, limonene, Δ^3-carene, α- and β-pinenes, and α-phellandrene has been frequently found to be a decisive factor in the animals' choice of food. They are probably not "toxic" in the narrow sense but are unpleasant and therefore deter. This is exemplified by the fact, discovered some years ago in our laboratories, that a mixture of this kind, resembling "turpentine oil", is used by the soldiers of certain *Nasutitermes* as a deterrent against their usual natural enemies—ants.[20] In this case the terpenoids do not originate from their food but are biosynthesised in their bodies.

If we follow the activities of secondary metabolites, we can conclude that their function can often vary. The necessity to limit the active potential of any "secondary product" results in its being sequestered in some place in the body (for example, in the case of plants, in vacuoles, glandular trichomes, and resin- or milk-ducts) in such a way that it cannot disturb the vital functions of the organism producing it. It can of course be present in the form of a harmless precursor as well. By possessing such a "latent" active principle, organisms have secured a weapon against their enemies. Consider cardenolides as an example. The plants producing them are protected against many phytophages (as well as vertebrates, molluscs, and insects), since these compounds are toxic in the true sense—can be regarded as "antifeedants", since they deter most enemies. These compounds (or at least many of them), applied in appropriate doses, are used in human medicine as valuable stimulators of the heart's activity. Some insect species have discovered, during their coevolution with plants, how to "sequester" these noxious compounds in their own body, usually in the larval stage; however, cardenolides [for example, uzaridin (XXII)] are also maintained in pupae and later in adults. They thus gain a double advantage: firstly they secure a competitive advantage in being able to feed on plants with cardenolides in their tissues and, secondly, they are now toxic to their natural enemies such as lizards, birds, and others.[21] This is a rare but by no means a unique case, as we have recently discovered in a series of similar adaptations (not only for isoprenoids but also for alkaloids, cyanogens, etc.). A similar situation can be traced in other seemingly non-toxic compounds—hormones. Plants which were able to develop during their phylogeny the production of insect hormones [ecdysteroids, for example, ecdysterone (XXIII), or juvenile hormone simulators, for example, juvabione (XXI)], whose only importance according to present knowledge involves their ecological function, are protected from any insect phytophages, since the presence of their hormones in their food or in contact with their food can disturb the normal evolution of these organisms.



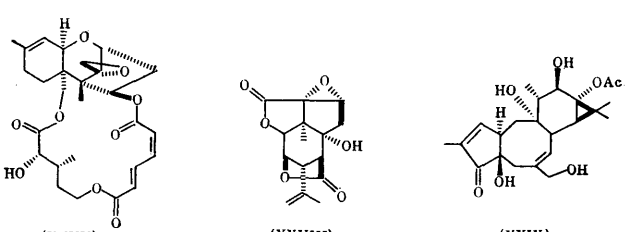
(XXII) (XXIII) (XXIV)

On the other hand, some insects produce relatively large quantities of vertebrate steroid hormones for their defense (for a series of these studies, we are indebted to Schildknecht[22]). Certain water beetles produce, for example, cortexone (XXV), testosterone (XXVI), etc. which protect them against vertebrates such as predatory frogs, fish, etc. The vertebrate hormones are probably useless against insects.



(XXV) (XXVI)

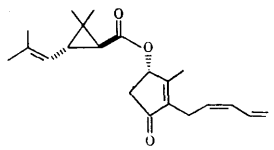
If we attempt to follow the complexity of compounds produced in nature as "secondary products", we encounter a distinct tendency—during the phylogeny of many taxa (especially in the plant kingdom), many complicated structures are biosynthesised successively and many "elaborate" molecules are also the most active. The author does not wish to develop a definition of the "toxic" principle in these terms, since very simple compounds such as HCN are toxic enough, but the isoprenoids which can be designated as "truly toxic" usually have a more complex structure. Trichothecenes are a good example[23] [see, for example, verrucarin A (XXVII)] of typically very active but very toxic antibiotics with a sesquiterpenoid moiety. Here one may include picrotoxinin (XXVIII), a compound isolated for its toxic properties, and phorbol (XXIX), a well known toxic component of plants belonging to the family *Euphorbiaceae* (cf. Evans and Taylor[24]).



(XXVII) (XXVIII) (XXIX)

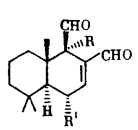
Other also relatively complex molecules, protecting their parent organisms, need not be toxic in the usual sense. We know of compounds which we simply designate as insecticidal, since they are relatively harmless to classes of organisms other than insects. It may be that they simply penetrate the special sort of chitin cuticle

which is important for arthropods. We shall mention as the only example pyrethrins (XXX) [25] with an isoprenoid component (chrysanthemic acid) in their molecules.



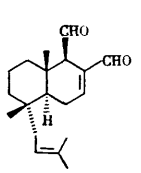
pyrethrin A (XXX)

We find that the physiological activity of secondary products is mostly not so specialised and their activity is then expressed in different ways—we speak of their bactericidal, fungistatic, and molluscicidal activities. As a result of the coevolution of plants (as the main source of food, directly or indirectly, of most other classes of organisms), their secondary metabolites represent a broad array of components with similar activities. Their phytophagous enemies have to develop sensory systems to protect themselves against feeding on noxious food. Such compounds are classified nowadays as deterrent compounds or antifeedants. These apparently include the vast majority of the known isoprenoids (naturally on the basis of the data published hitherto, although only a limited fraction of the compounds indicated have been investigated on these lines). However, certain rules concerning the structural prerequisites for "deterrents" can be derived from the limited number of examples available. The author's favourite examples are certain groups[26] which are found repeatedly in isoprenoid structures, in the first place a vicinal dialdehyde group, usually conjugated with a double bond, as in polygodial (XXXI) and in the related drimanes [warburganal (XXXII), ugadensidial (XXXIII)]. They are all very pungent to the human tongue and are deterrent to many insect herbivores. Polygodial was first encountered in *Polygonaceae* (*P. hydropiper*) and later in *Magnoliales* and independently in some liverworts (*Marchantiopsida*).

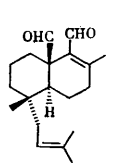


R = R' = H (XXXI)
R = OH, R' = H (XXXII)
R = R' = OH (XXXIII)

To complete the list, it also occurs in animals—molluscs (certain nudibranchs[27]). All these organisms are protected against their predators, although the latter are very different. For nudibranchs, it represents a unique weapon against fish. The same "model" is repeated in the diterpenoid series in liverworts, for example, in sacculatal (XXXIV) [28] and in perottetianal (XXXV).[29]

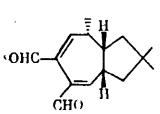


(XXXIV)

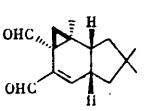


(XXXV)

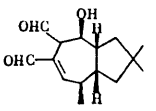
A similar pungent taste and protecting properties are known for the fruit bodies of many fungi which contain, for example, velleral (XXXVI), isovelleral (XXXVII), piperdial (XXXVIII), and merulidial (XXXIX).[30]



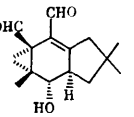
(XXXVI)



(XXXVII)

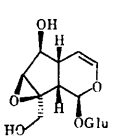


(XXXVIII)

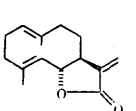


(XXXIX)

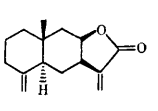
In the case of velleral, an interesting aspect of its deterrent activity was noted: in the fruit body, only a precursor (velutinol) is present. After mechanical damage to the fruit body's cells, it gives rise to the pungent velleral as a result of an enzyme reaction. Velleral, being unstable, later changes into another more stable compound. The idea of a parallel effect—the interaction with receptors on the human tongue and deterrent activity—was originally proposed by Kubo.[31] This is probably a much wider phenomenon and we believe that not only compounds giving rise to a "hot" or "pungent" perception but all bitter compounds act similarly. This concerns, for example, alkaloids, since the latter are mostly quite bitter, as well as other classes of compounds. Among isoprenoids, we know very many groups of bitter derivatives, for example, all iridoids[32] and especially their glycosides [for example, catalpol (XL)]. There is at present much evidence that they exhibit a common antifeedant activity. Furthermore, this concept agrees well with the properties of the large group of sesquiterpene lactones which have been investigated in the author's Prague laboratories for more than 40 years. In the author's research, the principal indication of their presence in a plant belonging to the family Compositae was a "sensory" one: the pungent taste indicated the presence of certain simple γ-lactones having a typical structure usually with an exocyclic methylene group and the lactone ring formed as a result of the oxidation of the methyl component of the isopropyl residue of the acyclic precursor and the subsequent ring closure at the hydroxyl in the α-position relative to this residue; typical examples are costunolide (XLI), isoalantolactone (XLII); for more information, see one of the latest reviews.[33]



(XL)



(XLI)

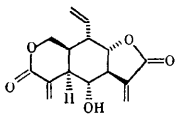


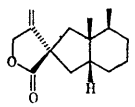
(XLII)

Compounds with a large number of oxygen-containing functional groups are usually bitter. The typical α,β-unsaturated γ-lactone group is believed to constitute the active principle, since it is capable of interacting with cysteine and of inducing cytotoxicity—a typical property in many kinds of biological activity.[34,35] This is the reason why many of these compounds were studied as possible anticancer agents. Vernolepin (XLIII) [36] was found to be the most active; its molecule contains two such lactone groups at once. More than 20 syntheses of this compound or its simplified derivatives have been described.

Dozens of the more than 3700 sesquiterpene lactones known at present have now been tested and found active in many respects (as antifeedants, not only for insects but also for mammals, bacteriostatic agents, fungicides, vermifuges, etc.). In many cases they induce human dermatitis. They are not in practical use and α-santonin is very obsolete today as a vermifuge. Nevertheless, in the plant kingdom they represent a good example of an antifeedant group which occurs repeatedly in classes which are distant on the evolutionary scale—mostly in *Compositae* (nearly 3500), *Umbeliferae* (more than 100), Magnoliales, and finally liverworts (more than 50

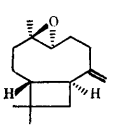
compounds). In our experiment, we demonstrated together with Dr Nawrot that the antifeeding effect for some insects **is not** necessarily combined with the α,β-unsaturation in the lactone ring [cf. the activity of bakkenolide (XLIV); cf. Harmatha and Nawrot[37]].

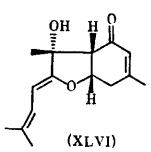

(XLIII)


(XLIV)

The antifeeding activity is not limited to lactones, since many other active sesquiterpene compounds are known. An interesting compound is caryophyllene epoxide (XLV), which has been repeatedly identified as the antifeedant for leaf-cutting ants (*Atta* sp.); because of its fungistatic properties, caryophyllene epoxide stops the growth of a special fungus which is cultivated by these ants as food.[38]

Compound (XLVI), a very potent antifeedant which is the main component of the seeds of *Angelica sylvestris*,[39] was discovered during our studies on bisabolangelone.

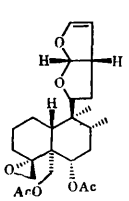

(XLV)

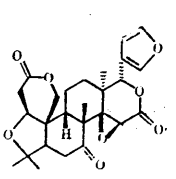

(XLVI)

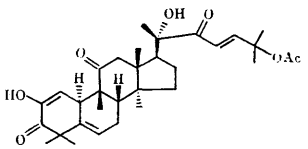
Diterpenoid derivatives are feeding deterrents as well. This concerns not only the many relatively simple diterpenic acids but especially two groups of bitter compounds—quassinoids[40] and clerodanes [as an example, see clerodin (XLVII)]. Clerodanes are the largest group of compounds tested hitherto for their antifeedant activities—more than 100 compounds (see the recent review of Van Beek and de Groot[41]).

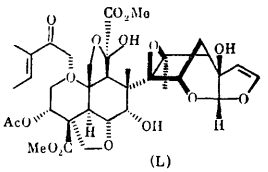
In the triterpene series, the same situation is repeated as in diterpenoids: apart from the relatively simple triterpenoids, certain groups of bitter compounds of this class are known, for example, cucurbitacins, limonoids, and/or meliacins. All their names are derived from the names of plant families [*Cucurbitaceae*; limonoids from the lemon; *Meliaceae*; for example, see limonin (XLVIII) and cucurbitacin E (XLIX)].

The most thoroughly studied compound until now, namely the tetranortriterpenoid azadirachtin, is a meliacin. It is the characteristic compound found in the neem tree (*Azadirachte indica*) and its very complex final structure (L) was established only recently by Kraus et al.[42] Three symposia and several books[43,44] have been devoted to this special antifeedant—still probably the only one in practical use in the form of alcoholic seed extracts. Rembold called it a "blessing for the developing countries", since in tropical areas it is readily available even to simple farmers.

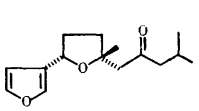

(XLVII)

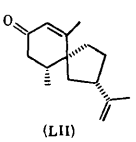

(XLVIII)


(XLIX)


(L)

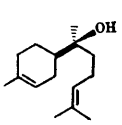
This is a brief resumé of the antifeedant history. It is incomplete since new groups with deterrent activity are being discovered, for example, saponins of triterpenoid and/or steroid origin. Whole books have been devoted to phytoalexins—compounds which are produced by plants only after they have been damanged, for example, by pathogenic fungi.[45] One fact must be emphasised as remarkable, namely plants of the family *Solanaceae*, which contain no sesquiterpenoids when in a healthy condition, produce exclusively the sesquiterpene derivatives ipomeamarone (LI) and solavetivone (LII) as phytoalexins for their protection.

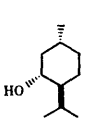

(LI)


(LII)

III. Conclusion

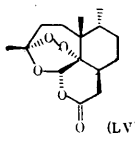
An attempt has been made to comment very briefly on the broad spectrum of the biological activities of isoprenoids known at the present time. Owing to their important functions, they are used in many branches of human activity. Their importance in medicine is well known. They serve as medicaments in the form of natural products (hormones, vitamins, etc.) or as products of organic synthesis as well. They have retained their importance in perfumery and in the cosmetic industry at the time when synthetic materials have clearly come to the fore. However, as models, natural products remain irreplaceable. We shall consider two characteristic examples as an illustration. The author's studies of the common European medicinal plant camomile in the early 1950s led to the discovery of *l*-α-bisabolol (LIII)—its most important component with anti-inflammatory properties. At the present time, tonnes of synthetic dl-α-bisabolol are being produced by the BASF company, since it is one of the five most valued components of cosmetics. (–)-Menthol (LIV), an important product of the food industry (sweets, chewing gum, and, of course, cigarettes) is also made synthetically.


(LIII)

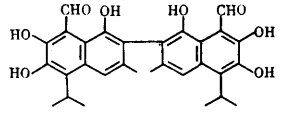

(LIV)

New compounds are being added to the contemporary medicinal preparations on the basis of recent studies on substances listed in the old "Materia Medica", i.e. traditional drugs of different nations. In China, where this is a very old tradition and recent research has been very active and fruitful, two preparations of isoprenoid origin have been discovered. Qinghaousu (LV) and its derivatives have been found[46] in *Artemisia annuua L.* They are also known as arteannuins or artemisimins. They are rare sesquiterpene lactones

with a cadinane carbon skeleton. These compounds constitute a very useful remedy against some forms of malaria—also in cases where the classical drug quinine is not successful. Furthermore, gossypol (LVI), a cadinane type of dimeric sesquiterpenoid, is now undergoing clinical experimental tests[47] as a chemosterilant for men (but not for women, since steroid derivatives are still normally employed for the latter).



(LV)



(LVI)

In agriculture and forestry novel means for the integrated fight against insect pests may be expected to be added to the hitherto most effective pyrethrin and the insecticides derived from this model substance, known as pyrethroids and constituting at the present time a major proportion of the agents used in practice. However, hitherto azadirachtin, mentioned above, is the only substance suitable for practical application; none of the others meet the rigorous criteria imposed on compounds of this kind. However, certain new (non-isoprenoid) natural products may prove to be more promising. I therefore end with a hopeful thesis: "Nature possesses much more potent means than we, humans, have been able to discover hitherto".

References

1. V Herout *Progress in Phytochemistry* (Edited by L Reihold and Y Liwschitz), Acad. Press, New York, 1968, p. 144
2. V Herout *Aspects of Terpenoid Chemistry and Biochemistry* (Edited by T W Goodwin), Acad. Press, London, 1971, p. 53
3. G Ourisson *Chimia*, 1988, **41** 7
4. C Djerassi *Steroids*, 1984, **43** 351
5. S C Dolan, J MacMillan *J. Chem. Soc., Perkin Trans. 1*, 1985, 2741
6. L Kohout *Chem. Listy*, 1984, **78** 1129
7. K Z Gamburg *Usp. Sovr. Biol.*, 1986, **102** 314
8. A Matsuo, H Nozaki, N Kubota, et al. *J. Chem. Soc., Perkin Trans. 1*, 1984, 203
9. A Matsuo, S Uto, H Nozaki, et al. *J. Chem. Soc., Perkin Trans. 1*, 1984, 215
10. H Nishimura, T Nakamura, J Mizutani *Phytochemistry*, 1984, **23** 2777
11. T J Mabry, J E Gill *Herbivores* (Edited by J N Harborne), Acad. Press, New York, 1979, p. 501
12. P Crews, S Naylor *Progress in the Chemistry of Organic Natural Compounds* (Edited by W Herz, et al.), Springer-Verlag, Vienna, 1985, Vol. 48, p. 203
13. B Kullenberg *Zoon Suppl.*, **1** 9
14. B Kullenberg *Zoon Suppl.* **1** 31
15. S Stallberg-Stenhagen *Acta Chem. Scand.*, 1970, **24** 358
16. W S Bowers, C Nishino, M E Montgomery, et al. *Science*, 1977, **196**(4290) 680
17. T M Alvarez, R K Van der Meer, C I Longfren *Tetrahedron*, 1987, **43** 2897
18. A W Barksdale *Science*, 1969, **166** 831
19. J E Fergusson, R L Metcalf *J. Chem. Ecol.*, 1985, **11** 311
20. J Vrkoc, K Ubik, L Dolejs, I Hrdy *Acta Entomol. Bohemosl.*, 1977, **70** 343
21. M Rothschild *Insect–Plant Relationship* (Edited by H P van Emden), Blackwell Sci. Publ., Oxford, 1972, p. 59
22. H Schildknecht *Endeavour*, 1971, **30** 136
23. P G McDougal, N R Schmuff *Progress in the Chemistry of Organic Natural Compounds* (Edited by W Herz, et al.), Springer-Verlag, Vienna, 1985, Vol. 47, p. 153
24. F J Evans, S E Taylor *Progress in the Chemistry of Organic Natural Compounds* (Edited by W Herz, et al.), Springer-Verlag, Vienna, 1985, Vol. 44, p. 1
25. J E Cassida *Pyrethrum. The National Insecticide*, Acad. Press, New York–London, 1973
26. V Herout *Frontiers of Bio-organic Chemistry and Molecular Biology* (Edited by S N Ananchenko), Pergamon Press, Oxford, 1980, p. 265
27. G Cimino, S De Rosa, S De Stefano *Science*, 1983, **219** 1237
28. Y Asakawa, T Takemoto *Tetrahedron Lett.*, 1977, 1407
29. Y Asakawa, M Toyota, T Takemoto *Phytochemistry*, 1979, **18** 1681
30. J B Harborne *Nat. Prod. Rep.*, 1986, 323
31. I Kubo, Y-W Lee, M Pettei *J. Chem. Soc., Chem. Communs.*, 1976, 1013
32. H Inouye, S Uesata *Progress in the Chemistry of Organic Natural Compounds* (Edited by W Herz, et al.), Springer-Verlag, Vienna, 1986, Vol. 50, p. 167
33. F Seaman *Bot. Rev.*, 1982, **48** 121
34. S M Kupchan, D C Fessler, M A Eakin, et al., *Science*, 1970, **168** 376
35. R L Hanson, H A Lardy, S M Kupchan *Science*, 1970, **168** 378
36. K Yoshida, P A Grieco *J. Org. Chem.*, 1984, **49** 5257
37. J Harmatha, J Nawrot *Biochem. Syst. Ecol.*, 1985, **12** 95
38. J J Howard, J Cazin, Jr., D F Wiemer *J. Chem. Ecol.*, 1988, **14** 59
39. L Novotny, Z Samek, F Sorm *Tetrahedron Lett.*, 1966, 3341
40. J Polonsky *Progress in the Chemistry of Organic Natural Compounds* (Edited by W Herz, et al.), Springer-Verlag, Vienna, 1985, Vol. 47, p. 221
41. T A Van Beek, A de Groot *Recl. Trav. Chim. Pays-Bas*, 1986, **105** 513
42. W Kraus, M Bokel, H Pöhnl, A Klenk *Tetrahedron Lett.*, 1985, **26** 6435
43. H Schmutterer, et al. (Editors), *Proceedings of 1st International Neem Conference*, German Agency for Technical Cooperation, Eschborn, 1981
44. H Schmutterer, et al., *Proceedings of 2nd International Neem Conference*, German Agency for Technical Cooperation, Eschborn, 1984
45. J A Bailea, et al. (Editors), *Phytoalexins*, Blackie, Glasgow, 1982
46. D L Klayman *Science*, 1985, **228** 1049
47. Z D Kai, S Y Kang, M J Ke, et al. *J. Chem. Soc., Chem. Communs.*, 1985, 168

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The use of $^{15}N-X$ (X = ^{29}Si, ^{73}Ge, $^{117/119}Sn$, ^{207}Pb) spin–spin coupling constants in structural studies on Group IV organoelement compounds

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ABSTRACT. Data for the $^{15}N-X$ spin–spin coupling constants and their relation with the structure of Group IV organoelement compounds are surveyed. The ^{15}N and X chemical shifts are quoted. The experimental and theoretical aspects of the spin–spin coupling are briefly considered. It is shown that the possibility of measuring the given constants for the natural abundance of the isotopes and also of their sensitivity to the nature of the N–X chemical bond and various aspects of the electronic and steric structures of the molecules, which has arisen recently, has given rise to new prospects in strucural research on nitrogen-containing Group IV organoelement compounds.

The bibliography includes 80 references.

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I. Introduction

The spin–spin coupling constants (SSCC) are a valuable source of information about the steric and electronic structures of molecules.[1–4] Almost all Group IV elements (with the exception of germanium) have natural isotopes with spin $I = 1/2$ (Table 1). This creates favourable conditions for the investigation of SSCC with participation of these nuclei X and provides a unique possibility for tracing the periodicity in the variation of SSCC for Group IV elements.

Until recently, the $^{15}N-X$ (X = ^{29}Si, $^{117/119}Sn$, ^{207}Pb) SSCC were measured only for individual compounds. One of the causes of this is the extremely low natural abundance of molecules with two magnetically active isotopes—^{15}N and X. Therefore all the data were obtained in the early stages of this research for isotopically enriched specimens, which required a considerable expenditure of time and resources for the synthesis of the labelled compounds. Nevertheless, the first investigations already showed that the $^{15}N-X$ SSCC (J_{NX}) can be used successfully in structural research.

Table 1. The NMR parameters of the nuclei of nitrogen and Group IVA elements.[16]

Nucleus	Natural abundance, %	Spin	$\gamma \cdot 10^{-7}$	$\lvert\psi_{ns}(0)\rvert^2$, a.u. (Ref.66)	Sensitivity* $\times 10^3$
^{13}C	1.10	$^1/_2$	6.7263	2.772	15.90
^{14}N	99.63	1	1.9331	4.775	1.01
^{15}N	0.37	$^1/_2$	−2.7116	4.775	1.04
^{29}Si	4.70	$^1/_2$	−5.3146	3.811	7.84
^{73}Ge	7.76	$^9/_2$	−0.9331	9.543	1.40
^{117}Sn	7.61	$^1/_2$	−9.5319	12.680	45.20
^{119}Sn	8.58	$^1/_2$	−9.9756	12.680	51.80
^{207}Pb	22.60	$^1/_2$	5.5797	20.53	9.13

* Relative to protons for the same number of nuclei and in a constant field B_0.

The $^{15}N-^{13}C$ spin–spin coupling constants were investigated in much greater detail than the constants involving other elements of this Group, which is undoubtedly due to the important role which the N–C bond plays in bioorganic chemistry. The $^{15}N-^{13}C$ spin–spin coupling constants have been examined in other reviews[5–7] and therefore will not be considered here. Furthermore, the chemistry of the remaining Group IV elements differs significantly from the chemistry of carbon. For example, such compounds are characterised by a greater tendency towards the formation of coordinate bonds and by a lower stability in the case of unsaturated compounds. The fields involving research into the SSCC differ correspondingly and their comparison is not always possible. Nevertheless, the principal conclusions and regularities observed in the study of the $^{15}N-^{13}C$ SSCC indicate the most promising aspects of such research. Thus the popularity and success of the empirical relations between the $^{15}N-^{13}C$ SSCC ($^1J_{NC}$) and different structural parameters, such as the hybridisation of the N and C atoms (the Binsch relation[8]), i.e.

$$80\,{}^1J(^{15}N—^{13}C) = \alpha_N^2\alpha_C^2 \qquad (1)$$

(where α is the amount of s character of the localised hybrid bond

expressed as a percentage), the pyramidality of the nitrogen atom,[7,9] the atomic charges, etc., demonstrates the usefulness of studies of this kind.

After superconducting magnets had been devised and a method had been developed for increasing the sensitivity of the NMR of heavy nuclei via polarisation transfer from protons, the measurement of the $^{15}N-X$ SSCC became possible for the natural abundance of isotopes. The amount of experimental data which have become available hitherto is so large that their systematic arrangement and survey are required. This communication is the first attempt on these lines. Together with the SSCC, we quote also the chemical shifts (CS) of the ^{15}N nuclei (relative to $MeNO_2$) and X (relative to XMe_4), since this usually makes it possible to achieve a more reliable interpretation of SSCC which have been little investigated hitherto. We hope that this review will promote the expansion of the field of research into $^{15}N-X$ SSCC and will facilitate the interpretation of new data.

II. Fundamentals of the theory

According to Ramsey's theory,[10] the spin–spin coupling in a liquid can be regarded as a result of the contribution of three components: spin–orbital (SO), spin–dipole (SD), and Fermi-contact (FC). The spin–orbital coupling can also be subdivided into two components—diamagnetic (OD) and paramagnetic (OP). The contributions of the SO and SD components are relatively small and tend to diminish with increase in the degree of π-bonding between the atoms of the interacting nuclei.[11] If the interacting nuclei are linked by a multiple chemical bond, then the SSCC is as a rule determined by the FC interaction. This simplifies significantly the interpretation of the experimental data within the framework of the analytical relations obtained from the quantum-chemical theory of spin–spin coupling.

The observed SSCC $^1J_{NX}$ depend significantly on the gyromagnetic ratio γ of the N and X nuclei. In order to exclude from consideration the individual properties of the nuclei, the concept of the reduced SSCC ^1K, which depends only on the electronic environment of the nuclei, has been introduced:

$$^1K_{NX} = 4\pi^2\, {}^1J_{NX}/h\gamma_N\gamma_X. \quad (2)$$

According to Pople and Santry,[12] in terms of the approximation of the LCAO-MO theory, the contribution of the FC interaction is described by the equation

$$^1K_{NX}^{FC} = -\frac{16e^2h^2}{9M_p^2c^2} |\psi_N(0)|^2 |\psi_X(0)|^2 \cdot \sum_i^{occ} \sum_j^{unocc} (^3\Delta E_{i\to j})^{-1} \cdot c_{is_N} c_{js_N} c_{is_X} c_{js_X}, \quad (3)$$

where $|\psi_N(0)|^2$ and $|\psi_X(0)|^2$ are the valence s electron densities at the N and X nuclei, $^3\Delta E_{i\to j}$ the energy of the excitation of the electronic transitions, and c_{is} and c_{js} are the LCAO coefficients of the s orbitals of the N and X atoms, while the remaining constants have the usual significance. In the extended Hückel method, $^3\Delta E_{i\to j} = e_j - e_i$ (e_i and e_j are the energies of the occupied and unoccupied orbitals respectively), which makes it possible to simplify Eqn. (3):

$$^1K_{NX}^{FC} = \frac{4e^2h^2}{9M_p^2c^2} |\psi_N(0)|^2 |\psi_X(0)|^2 \pi_{NX}, \quad (4)$$

$$\pi_{NX} = 4 \sum_i^{occ} \sum_j^{unocc} (e_i - e_j)^{-1} c_{is_N} c_{js_N} c_{is_X} c_{js_X}, \quad (5)$$

where π_{NX} is the mutual polarisability of the s orbitals of the N and X atoms.

In terms of the average excitation energy (ΔE) approximation, the contribution of the FC interaction can be represented by Eqn. (6), which reflects the relation between $^1K_{NX}$ and the s order of the N–X bond ($P_{s_Ns_X}$):

$$^1K_{NX}^{FC} = \frac{4e^2h^2}{9M_p^2c^2} |\psi_N(0)|^2 |\psi_X(0)|^2 P_{s_Ns_X}^2/\Delta E. \quad (6)$$

A modification of this equation within the framework of the valence bond theory [Eqn. (7)], using the concept of the s character of the localised hybrid bonds [see, for example, Eqn. (11)], is also frequently employed:

$$^1K_{NX}^{FC} = \frac{4e^2h^2}{9M_p^2c^2} \alpha_N^2\alpha_X^2 |\psi_N(0)|^2 |\psi_X(0)|^2/\Delta E. \quad (7)$$

In the interpretation of the SSCC, it is usually assumed that the quantities $|\psi_X(0)|^2$ and $|\psi_N(0)|^2$ are constant (in reality they depend on the atomic charge). This makes it possible to explain the observed changes in the SSCC by the differences in the nature of the chemical bond.

Eqns. (6) and (7), based on the ΔE approximation, presuppose that the FC interaction makes a positive contribution to the SSCC. In fact, negative contributions to the ^1K are frequently observed, especially for Group V–VII nuclei. This arises from the fact that the ΔE approximation is not always valid.

Jameson and Gutowsky[11] showed that the quantities ^1K obey periodicity laws and proposed a model for the prediction of the sign of ^1K for the nuclei of any elements in the Periodic System. According to this model, the nuclei involved in spin–spin coupling can be divided into three types.

A. Elements having an open s shell in the ground configuration. The s orbitals participate directly in the formation of the chemical bond (Group I in the Periodic System).

B. Elements having open s shells in an accessible configuration. The involvement of valence s orbitals in the formation of a chemical bond is possible as a result of the mixing of these configurations with the ground configurations (Groups II–VI).

C. Elements which do not have open s shells. In this case, the s electrons do not participate in the formation of a chemical bond (Groups VI and VII) and spin–spin coupling occurs mainly via the mechanism involving the polarisation of outer s shells, which leads to a negative sign of the FC interaction.

For Group IV elements, the valence s and p electrons have fairly close energies, so that, as a result of their mixing, the s electrons become available for the formation of a chemical bond. For this reason, the elements X should be assigned to type B. However, with increase in the radius of the atoms X their polarisability increases greatly. This can lead to an increase in the negative contribution of the polarisation of the inner s shells and hence to more negative values of $^1K_{NX}$.

For compounds of divalent X, mainly the p electrons participate in the formation of a chemical bond and the properties of the valence s electrons resemble those of closed s shells, which makes it possible to assign them to type C.

Jameson and Gutowsky assigned the Group V elements to a type intermediate between types B and C. The nitrogen(III) atom has a lone electron pair (LEP) and the difference between the energies of the valence $2s$ and $2p$ electrons is relatively large. For this reason, the use of the ΔE approximation is in general unreliable. Nevertheless, the observed correlation between $^1J_{NC}$ and the s character of the N–C bond in carbon compounds shows that in this instance the ΔE approximation is valid.

Equations describing the spin–spin coupling in liquids have been derived for a non-polar covalent bond. At the present time, there are no analogous equations describing the SSCC for coupling via a coordinate bond. Therefore in the interpretation of such SSCC, it is usually assumed that the equations obtained for the FC interactions are valid for the covalent component of the coordinate bond. Here we have in mind Eqn. (8), describing the nature of the coordinate bond within the framework of the valence bond theory:[13]

$$\psi_{N\to X} = \psi_{NX} + \lambda\psi_{N^+X^-}, \qquad (8)$$

where λ is a coefficient. However, the question how this interaction takes place and how to predict the sign of ^1K is not entirely clear. The coordinate bond has also been examined in Jameson and Gutowsky's model.[11] Certain considerations concerning this topic can be deduced from the study of the ionic bond by the above workers. In particular, it has been shown[11] that for ionic bonds there is a possibility of a small positive contribution to the FC coupling component. The overlap of the occupied *s* and *p* orbitals with the unoccupied *d* orbitals of the metal and also any kind of their mixing (covalence) give rise to a positive contribution to the spin density on the X nuclei. Consequently, in the case of a coordinate bond (at least in σ-bonding) the FC interaction should make a positive contribution to the SSCC.

III. Experimental aspects

1. The ^{14}N–X spin–spin coupling

The ^{14}N–X spin–spin coupling constants can be observed directly relatively rarely because of the effective relaxation of the ^{14}N nuclei via a quadrupolar mechanism. The merging of the components of the multiplet is then observed in the spectra of the X nuclei as a consequence of the scalar relaxation of the second kind.[14,15]

In principle, the ^{14}N–X SSCC can be determined by analysing the line form in the spectra of the X nuclei. Neglecting the natural width of the signal, the line form can be described analytically with the aid of the equation

$$I(x) = \frac{2\eta}{\pi J}\,\frac{45+\eta^2(5x^2+1)}{225x^2+\eta^2(34x^4-2x^2+4)+\eta^4(x^6-2x^4+x^2)}. \qquad (9)$$

Here $x = \Delta\nu/J$, where $\Delta\nu = \Delta\omega/2\pi$; $\eta = 10\pi T_{qN}J$, T_{qN} being the quadrupolar relaxation time. The description of the line form taking into account the natural width of the signal is more difficult. This problem has been described in detail.[15] It follows from Eqn. (9) that the line form in the spectra of the nuclei X is determined by the dimensionless parameter η. The quadrupolar relaxation time of the ^{14}N nuclei can be determined from the ^{14}N spectrum using the relations $T_2 \simeq 1/\pi\Delta\nu_{1/2}$ and $T_{qN} \simeq T_2$, where $\Delta\nu_{1/2}$ is the width of the signal at half its height.

The ^{14}N–X SSCC can be obtained directly in this case if $\eta \geqslant 10$. A clearer criterion is the relation $J \geqslant \Delta\nu_{1/2}(^{14}\mathrm{N})$, provided that the line half-width in the ^{14}N spectra does not exceed the ^{14}N–X SSCC. Consequently, the probability of finding directly these SSCC increases with increase in $^1J_{NX}$ (Fig. 1). For this reason, the ^{14}N–X SSCC for the heavy nuclei ^{117,119}Sn and ^{207}Pb are observed more frequently than for the ^{29}Si nuclei.

On the other hand, $\Delta\nu_{1/2}(^{14}\mathrm{N})$ diminishes (T_{qN} and ν increase) with increase in the symmetry of the charge distribution around the ^{14}N nuclei. Molecules with a tetrahedral or linear configuration of the nitrogen atom as well as quasi-linear molecules (isocyanates, isothiocyanates) usually have relatively long times T_{qN} because of the rapid (on the NMR time scale) exchange. In certain cases, this makes it possible to determine the ^{14}N–X SSCC from the satellites of the X nuclei in the ^{14}N spectra.

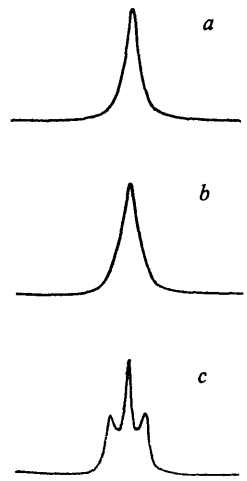


Figure 1. Dependence of the line form in the spectra of the X nuclei on the SSCC $^1J(^{14}\mathrm{N}-\mathrm{X})$ for a constant relaxation time of the ^{14}N nuclei (T_{qN} = 1.6 ms). The spectra were calculated by Eqn. (9): *a*, J = 50 Hz; *b*, J = 100 Hz; *c*, J = 200 Hz.

However, the ^{14}N–X SSCC can be found directly relatively rarely. Furthermore, the accuracy of the ^{14}N–X SSCC determined directly depends significantly on η, since the distance between the components of the multiplet in the spectra of the X nuclei (but not the ^{14}N nuclei) diminishes with decrease in η. For these reasons, preference is usually given to the study of the ^{15}N–X SSCC.

2. The ^{15}N–X spin–spin coupling

As a consequence of the extremely low natural abundance of the ^{15}N isotope, the ^{15}N–X spin–spin coupling constants were initially measured for enriched specimens. In this case, an accurate measurement of the ^{15}N–X SSCC presents no problems, provided that the ^{15}N and X nuclei form a first order spectrum. Furthermore, there is a possibility of determining the sign of ^1K.

The high sensitivity of modern NMR spectrometers makes it possible to measure ^{15}N–X SSCC for the natural abundance of the isotopes. This can be achieved in two ways: on the basis of the satellites of the X nuclei in the ^{15}N spectra and on the basis of the satellites of the ^{15}N nuclei in the spectra of X nuclei. In most studies, the ^{15}N–X SSCC have been determined from the ^{15}N spectra because the satellites are in this case more intense. It is noteworthy that the sensitivity of the measurements is in this case limited by the low natural abundances of both isotopes. However, from the standpoint of the limitations associated with the dynamic range of the spectrometer,[16] the use of ^{15}N NMR is preferable (see the reviews on ^{15}N NMR [5,7,17,18]).

The intensity of the useful signal in the measurement of the ^{15}N–X SSCC depends in the first place on the NMR sensitivity of

the observed nuclei (Table 1). A number of other factors are also significant—the Overhauser nuclear effect and the increase in signal intensity when methods involving the transfer of polarisation from protons are used (INEPT, DEPT, etc.[19,20]). Since the NMR sensitivity of the X nuclei is in all cases appreciably higher than that of the ^{15}N nculei, in principle the $^{15}N-X$ SSCC can be more conveniently determined from the spectra of the X nuclei.

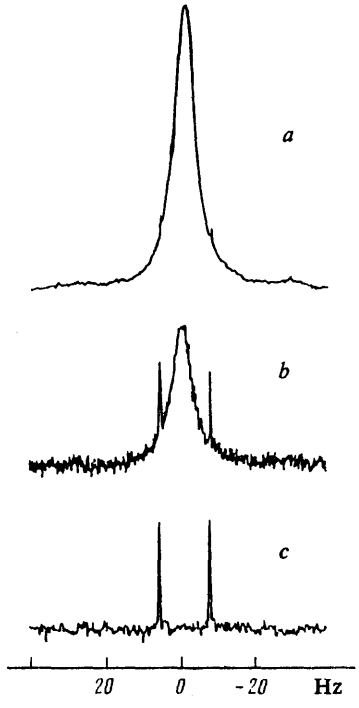


Figure 2. The ^{15}N satellites in the ^{29}Si NMR spectra of hexamethyldisilazane. The spectra were obtained by the INEPT (*a*), DEPT (*b*), and INEPT + Hahn's spin-echo (*c*) methods. Working frequency 71.55 MHz, temperature 303 K, number of accumulations 16 (*a* and *b*) and 64 (*c*).[22]

We have shown that[21] the detection of the ^{15}N satellites in the ^{29}Si NMR spectra facilitates significantly the broadening of the central line and of the ^{13}C satellites as a result of the $^{14}N-X$ spin–spin coupling and relaxation of the second kind (Fig. 2*a*). Using polarisation transfer from protons, it is usually possible to measure the $^{15}N-^{29}Si$ SSCC in the ^{29}Si NMR spectra after only a few accumulations. It has been shown[22] that the DEPT method is preferable to INEPT, since it decreases appreciably the intensity of the central line and of the ^{13}C satellites (Fig. 2*b*). The difference between the relaxation times of the central signal and of the ^{15}N satellites can be used to suppress completely the central line[22] (Fig. 2*c*). If several nitrogen atoms are attached to the silicon atom, then the ^{15}N satellites are also broadened as a result of the quadrupolar relaxation in the $^{14}N-^{29}Si-^{15}N$ fragments. In this case, the $^{15}N-^{29}Si$ SSCC can be more usefully determined from the ^{15}N spectra.

The observation of the ^{15}N satellites in the $^{117/119}Sn$ and ^{207}Pb NMR spectra is difficult.[23] This is apparently associated with the fact that the above nuclei have relatively short relaxation times.[24,25] For this reason, the difference between the widths of the central line and of the ^{15}N satellite is less pronounced, which leads to their merging as a consequence of the low intensity of the latter.

In the case of the protonated nitrogen atom, the satellites of the X nuclei in the ^{15}N NMR spectra can be observed after accumulation for 1–2 h [23,26] using the usual polarisation transfer methods (INEPT, DEPT, etc.),[19,20] provided that there is no rapid intramolecular or intermolecular exchange of NH protons. It has been shown[23,27] that, for a non-protonated nitrogen atom, it is also possible to employ the INEPT method, assuming that the long-range $^{15}N-^{1}H$ SSCC are 1–2.5 Hz. The best results have been achieved on the assumption that J_{NH} = 2.5 Hz for the NR (R = alkyl) group, 1.5 or 2 Hz for the Me_3SnN group, and 1 or 1.5 Hz for the Me_3SiN group.[23] In this case, the measurement of the $^{15}N-X$ (X = ^{29}Si, $^{117/119}Sn$) SSCC required accumulation for 6–12 h. It has been observed that[27] the main INEPT sequence (without the suppression of the spin–spin coupling with protons) is most suitable, since the use of refocussing (of the longer DEPT sequence) for such low values of the $^{15}N-^{1}H$ SSCC diminishes appreciably the signal intensity due to relaxation effects.

Table 2. The $^{15}N-^{29}Si$ SSCC for the silazanes (I)–(XVIII) (solvent—$CDCl_3$).[31]

Compound	$^1J_{SiN}$, Hz	$\delta(^{15}N)$, p.p.m.	$\delta(^{29}Si)$, p.p.m.
(I)	6 [28]	—	−39.9
(II)	12* [29]	—	−64.3 (SiH_2), −41.4 (SiH_3)
(III)	7.6 [23]	−342.0	—
(IV)	13.4	−354.2	2.1
(V)	14.4	−334.3	13.3
(VI)	17.4	−335.7	−11.9
(VII)	14.3 (NSi_2), 9.8 (NSi_3) [47]	—	−6.8 [47]
(VIII)	15.4	−347.3	−4.6
(IX)	15.8	−345.4	−4.0 (NSiN)
	15.8	—	−4.3 (NSiO)
(X)	15.5	−342.9	−3.4
(XI)	15.7	−341.9	−1.2
(XII)	16.9	−341.7	−8.2
(XIII)	17.4 [47]	−345.8 [47]	−15.5 [47]
(XIV)	15.9	−334.9	−11.3
(XV)	15.9	−334.9	−10.9
(XVI)	17.1	−335.1	−12.6
	17.3	—	−13.2
(XVII)	17.7	−336.7	−8.3 (NSiN)
	17.7	—	−12.6 (NSiO)
(XVIII)	17.2	−334.8	−12.3

* It is not indicated to which of the non-equivalent silicon atoms the SSCC amounting to 12 Hz corresponds.

Note. Here and in other tables the numerals in square brackets denote references (Ed. of Translation).

IV. Silicon-29

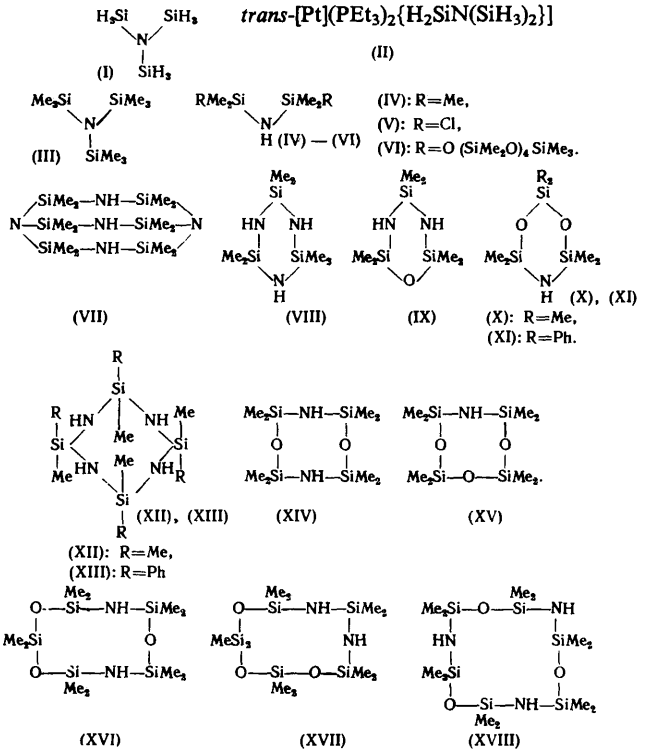
1. Coupling across a covalent bond

(a) Silazanes

Historically the $^{15}N-^{29}Si$ SSCC were first measured for compounds (I) and (II) enriched in the ^{15}N isotope.[28,29] It was established that $^1K_{NSi} > 0$. During the next 10 years, these SSCC

were scarcely measured. Systematic studies on the $^{15}N-^{29}Si$ SSCC began in 1983 [30] after polarisation transfer methods, permitting measurements for the natural abundance of the isotopes, became available.

It has been found that the $^{15}N-^{29}Si$ SSCC for the silazanes (I)–(XVIII) increase with increasing electronegativity (EO) of the substituents at the Si atom in the sequence H < Me < Cl < NR, OR (Table 2).[31] A similar trend has been observed also for substituents at the nitrogen atom. Thus, when the silyl group is replaced by the more electronegative hydrogen atom, the $^{15}N-^{29}Si$ SSCC increase. On this basis, it has been suggested that $^1K_{NSi} > 0$ for the silazanes (I)–(XVIII). However, in the presence of only electropositive substituents at the nitrogen atom (for example, Li), negative values of $^1K_{NSi}$ may be expected.[22]



The cyclosilazane and cyclosiloxazane $^{15}N-^{29}Si$ SSCC are virtually the same for the N–Si–N and N–Si–O fragments, whereas the $^{29}Si-^{13}C$ SSCC differ significantly (63 ± 1 Hz and 69 ± 1 Hz respectively). This was explained on the basis of Bent's rules[32] by the more significant change in the *s* character of the bonds involving the Si atom with the most electropositive substituents, i.e. Si–C.

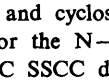
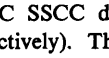
The tendency towards a decrease in the $^1J_{NSi}$ on passing to smaller rings has been explained by the increased polarity of the N–Si bonds (decrease in $d_\pi-p_\pi$ conjugation), which agrees well with the conclusions reached for the ^{15}N and ^{29}Si chemical shifts. A decrease in the Si–N–Si valence angle in smaller rings reduces the *s* character of the N–Si bonds and hence reduces $^1J_{NSi}$.

(b) Silylamines

Higher values of $^{15}N-^{29}Si$ SSCC have been observed for silylamines (Table 3) compared with silazanes (Table 2). This is associated with the increase in the electronegativities of the substituents at the nitrogen atom in the sequence $SiMe_3$ < H < alkyl.

The $^{15}N-^{29}Si$ SSCC increase systematically with increase in the electronegativities of the substituents at the Si atom in the sequence Me < Ph < NR < OR.[22,26] Consequently $^1K_{NSi} > 0$ in the given sequence. A similar conclusion was reached from a comparison of the SSCC $^1J_{NSi}$ and $^1J_{PSi}$ for isostructural nitrogen(III) and phosphorus(III) compounds,[22] which revealed the opposite dependences of these SSCC on the electronegativities of the substituents. Since it is known that $^1K_{PSi} < 0$,[33,34] it follows from the foregoing that $^1K_{NSi} > 0$.

Table 3. The $^{15}N-^{29}Si$ SSCC for silylamines, silylamides, azasilatranes, and other compounds with a covalent N–Si bond (solvent—$CDCl_3$).[21,22,26,42,43]

Compound	Chemical formula	$^1J_{NSi}$, Hz	δ(^{15}N), p.p.m.	δ(^{29}Si), p.p.m.
(XX)	$Pr^iHNSiMe_3$	17.1	—	2.6
(XXI)	$Pr^iHNSiMe_3$	17.0	—	0.9
(XXII)	$Bu^tHNSiMe_3$	17.2	−323.9	−2.3
(XXIII)	$PhHNSiMe_3$	15.7	−314.9	1.7
(XXIV)	Et_2NSiMe_3	19.2	—	3.8
(XXV)	Pr_2NSiMe_3	19.7	—	3.9
(XXVI)	$(CH_2)_6NSiMe_3$	19.6	—	3.5
(XXVII)	$(CH_2)_5NSiMe_3$	17.8	—	3.9
(XXVIII)	$(CH_2)_4NSiMe_3$	16.5	—	2.5
(XXIX)	$(CH_2)_3NSiMe_3$	13.6	—	1.8
(XXX)	$(CH_2)_2NSiMe_3$	<5	—	14.1
(XXXI)	$PhHNSiHMe_2$	16.4	−320.4	—
(XXXII)	$Bu^tHNSiMe_2Ph$	18.8	−325.7	−9.6
(XXXIII)	$PhHNSiMe_2Ph$	17.3	−317.7	−5.8
(XXXIV)	$Bu^tHNSiMePh_2$	19.8	−327.3	−15.4
(XXXV)	$PhHNSiMePh_2$	18.3	−319.5	−11.8
(XXXVI)	$(PrHN)_2SiMe_2$	21.5	−351.0	−8.1
(XXXVII)	$(Bu^tHN)_2SiMe_2$	20.8	−317.4	−16.9
(XXXVIII)	$(PhHN)_2SiMe_2$	19.9	−312.7	−12.8
(XXXIX)	$PrHNSi(OEt)Me_2$	21.8	−348.9	−4.8
(XL)	$Bu^tHNSi(OEt)Me_2$	21.5	−317.6	—
(XLI)	$PhHNSi(OEt)Me_2$	19.9	−310.8	−5.1
(XLII)	$Pr_2NSi(OEt)Me_2$	23.8	—	−3.4
(XLIII)	$(PrHN)_3SiMe$	25.8	−351.6	−23.3
(XLIV)	$(PrHN)_3SiCH{=}CH_2$	27.0	−353.6	−36.4
(XLV)	$(PrHN)_3SiPh$	27.4	−353.5	−33.0
(XLVI)	$(PhHN)_3SiMe$	25.4	−313.1	−29.5
(XLVII)	$(PhHN)_3Si(OEt)Me$	27.3	−313.5	−30.1
(XLVIII)	$Bu^tHNSi(OEt)_2Me$	30.9	−321.5	—
(XLIX)	$PhHNSi(OEt)_2Me$	29.0	−314.4	−34.2
(L)	$PhSi(OCH_2CH_2CH_2)_3N$	27.7	—	−48.9
(LI)	$Si(NHPr)_4$	31.7	−354.4	−40.6
(LII)	$(Bu^tHN)_2Si(OEt)_2$	39.8	−324.9	—
(LIII)	$(PhHN)_2Si(OEt)_2$	40.1	−319.2	−63.0
(LIV)	$Bu^tHNSi(OEt)_3$	44.6	−330.4	—
(LV)	$PhHNSi(OEt)_2$	43.9	−322.3	−71.6
		43.7*1	−321.5*1	—
		43.2*2	−320.7*2	—
(LVI)	$Et_2NSi(OEt)_3$	47.6	−349.9	−69.2
(LVII)	$HC(O)NMeSiMe_3$	12.7	—	—
(LVIII)	$MeC(O)NHSiMe_3$	13.4	—	5.3
(LIX)	 R=H	12.0	−281.3	7.1
(LX)	 R=$SiMe_3$	12.8	−280.1	6.4
(LXI)	$(p\text{-}MeC_6H_4SO_2)NHSiMe_3$	*3	−283.1	9.7
(LXII)	$(Me_3SiNH)_2CO$	*3	—	1.8
(LXIII)	$Me_2SiN{=}C{=}O$	14.5	—	3.9
(LXIV)	$Me_2SiN{=}C{=}S$	12.2*4	−265.3	5.3
(LXV)	$Si(N{=}C{=}S)_4$	(32.5)*5	(−237.2)*6	—
(LXVI)	$Me_2SiN{=}N{\equiv}N$	<5	—	15.8
(LXVII)	$N(CH_2CH_2NH)_3SiMe$	25.3	−352.8	−68.3
(LXVIII)	$N(CH_2CH_2NH)_3SiCH{=}CH_2$	25.8	−354.0	−79.2
(LXIX)	$N(CH_2CH_2NH)_3SiPh$	26.5	−354.1	−77.2

*1 Solvent—C_6D_{12}.

*2 Solvent—$(CD_3)_2SO$.

*3 $^1J_{NSi}$ is not observed because of the rapid intermolecular exchange of the $SiMe_3$ groups.

*4 $^1J(^{14}N-^{29}Si)$ = 8.4 Hz.

*5 Calculated from $^1J(^{14}N-^{29}Si)$ = 23.2 Hz by multiplying it by $\gamma(^{15}N)/\gamma(^{14}N)$.

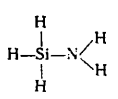
*6 The δ(^{14}N) chemical shift is quoted.

The parallel variation of the $^{15}N-^{29}Si$ and $^{29}Si-^{13}C$ (for the $Si-CH_3$ bond) SSCC has been observed in silylamines.[22] A linear correlation has been discovered for aniline derivatives:

$$^1J(^{15}N-^{29}Si) = 0.41\ ^1J(^{29}Si-^{13}C) - 7.3 \quad (r = 0.97,\ n = 7). \qquad (10)$$

Bearing in mind that $^1K_{SiC} > 0$ [35] and that this SSCC is determined by the contribution of the FC interaction,[36] it has been postulated that a similar equation is valid also for $^1K_{NSi}$.

The first calculation of the $^{15}N-^{29}Si$ SSCC for the silylamine (XIX) was carried out recently by the *ab initio* method:[37]



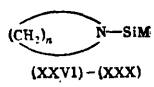
(XIX)

PC = 25.97 Hz
OD = 0.02 Hz
OP = −1.00 Hz
SD = 0.29 Hz
$^1J_{theor} = 25.26$ Hz.

The theoretical quantity (25.26 Hz) reflects correctly the sign of $^1K_{NSi}$ and has a reasonable value. An important result of these calculations has been the conclusion that the $^{15}N-^{29}Si$ SSCC is determined by the sign of the FC interaction.

Bearing in mind that the $^{15}N-^{29}Si$ SSCC for silylamines have large and positive values, it has been suggested that they can be interpreted within the framework of the ΔE approximation, i.e. in conformity with Eqns. (6) and (7). Consequently the application of the $^{15}N-^{29}Si$ SSCC in structural studies in no less promising than the application of $^1J_{NC}$. The higher value of $^1J_{NSi}$ and the possibility of measuring them for the natural isotope abundances make them actually preferable.

An example in illustrating the sensitivity of $^1J_{NSi}$ to the hybridisation of the nitrogen atom is the significant decrease of the $^{15}N-^{29}Si$ SSCC on passing to smaller rings which has been observed for the trimethylsilyl (TMS) derivatives of the cyclic amines (XXVI)–(XXX) [21] and has been explained by the enhancement of the pyramidal configuration of the nitrogen atom.



(XXVI)–(XXX)

(XXVI): $n = 6$, (XXIX): $n = 3$,
(XXVII): $n = 5$, (XXX): $n = 2$.
(XXVIII): $n = 4$,

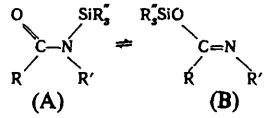
The similar phenomenon observed for silazanes is also associated with the decrease in the valence angle at the nitrogen atom in smaller rings.[31]

The anomalous decrease in $^1J_{NSi}$ on passing from the NBu^t derivatives to the NPh derivatives of silylamines has been explained by the weakening of the $d_\pi-p_\pi$ conjugation via the N–Si bond as a result of the stronger competing conjugation of the LEP of the nitrogen atom with the phenyl group.[26] It has been suggested that this leads to lengthening of the N–Si bond, as a result of which the degree of overlap of the valence *s* orbitals diminishes and $^1J_{NSi}$ also decreases.

(c) Silylamides

Fairly low $^{15}N-^{29}Si$ SSCC have been observed for trimethylsilylamides [compounds (LVII)–(LXII)]. It has been suggested that this is a consequence of the stronger competing conjugation of the LEP of the nitrogen atom with the carbonyl group.

The high polarity of the N–Si bond in trimethylsilylamide increases the rate of the intramolecular and intermolecular exchange of the Me_3Si groups. The question which of the structures (A) or (B) predominates in solution has been most frequently discussed for these compounds.[38–40]



(A) (B)

The ^{29}Si chemical shifts do not always make it possible to solve unambiguously this problem, whereas the $^{15}N-^{29}Si$ SSCC can be used as significant evidence in support of structure (A).

The ^{15}N and ^{29}Si chemical shifts also failed to permit the observation of the intermolecular exchange of the $SiMe_3$ groups. On the other hand, using the $^{15}N-^{29}Si$ SSCC it is possible, in principle, not only to observe the process but also to determine the activation parameter by means of dynamic NMR methods.[41] For a detailed investigation of this process, specimens enriched in the ^{15}N isotope are apparently essential. However, it has been demonstrated by simulating the ^{29}Si line form that the observation of the ^{15}N satellites in the ^{29}Si NMR spectrum is difficult or impossible if the free energy of activation for the intermolecular exchange of $SiMe_3$ group ($\Delta G^{\neq}$) is smaller than 80 kJ mol^{-1}.[22]

(d) Silicon isocyanates

The relatively long relaxation times of the ^{14}N nuclei in these compounds frequently make it possible to find the $^{14}N-^{29}Si$ SSCC directly. Thus a relatively well resolved triplet with a splitting of 8.4 Hz has been observed in the ^{29}Si NMR spectrum of trimethylsilyl isothiocyanate (LXIV) (Fig. 3). The low solubility and long relaxation time of the ^{29}Si nuclei of the compound (LXV) precluded the measurement of the ^{29}Si NMR spectrum of this compound. However, it has been possible to observe the ^{29}Si satellites in the ^{14}N NMR spectrum and to measure the $^{14}N-^{29}Si$ SSCC.[22]

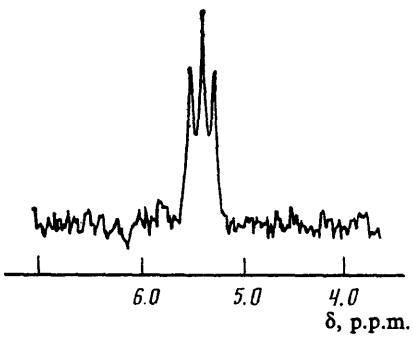


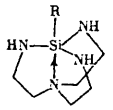
Figure 3. The splitting of the signal in the ^{29}Si NMR spectra of the compound $Me_3SiN=C=S$ as a result of the $^{14}N-^{29}Si$ spin–spin coupling. The spectrum was obtained using the INEPT pulse train for a 50% solution in $CDCl_3$ at a frequency of 71.55 MHz.[22]

The constants $^1J_{NSi}$ for the isocyanates (LXIII)–(LXV) are relatively small, which has been explained tentatively by the increase in the length of the N–Si bond in trimethylsilyl isocyanate (1.76 Å) and trimethylsilyl isothiocyanate (1.78 Å) compared with trimethylsilyl-amine (cf. the value 1.72 Å).

The $^{15}N-^{29}Si$ SSCC could not be found for trimethylsilyl azide (LXVI) with the natural isotope abundances.[22] The ^{29}Si line width (0.4 Hz) shows that $^1J_{NSi}$ is apparently not high (< 10 Hz). The difficulties in the measurement of the $^{15}N-^{29}Si$ SSCC were in this case associated with the fact that the ^{15}N satellites in the ^{29}Si spectra are apparently broadened as a result of the long-range $^{14}N-^{29}Si$ coupling; the lines in the ^{15}N spectra are also broadened as a result of the $^{14}N-^{15}N$ coupling; furthermore, there is a possibility of the intermolecular exchange of the $SiMe_3$ groups.

(e) Other compounds

The $^{15}N-^{29}Si$ SSCC can be used to investigate the influence of the transannular N → Si interaction on the properties of equatorial bonds in the triazasilatranes (LXVII)–(LXIX).[42]

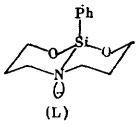


(LXVII): R=Me,
(LXVIII): R=CH=CH$_2$,
(LXIX): R=CH$_2$Cl.

(LXVII)–(LXIX)

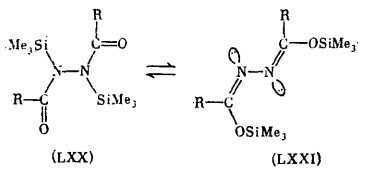
The decrease in the SSCC for these compounds relative to the corresponding aminosilanes [compounds (XLIII)–(XLV)] has been explained by the diminution of the $d_\pi-p_\pi$ interaction in the equatorial N–Si bond in compounds (LXVII)–(LXIX) with increase in the N → Si bond strength.

The $^{15}N-^{29}Si$ SSCC for compound (L) is much lower than the SSCC for compound (XLVIII) (Table 3),[43] indicating a pyramidal structure of the nitrogen atom in the given compound, which is fairly unusual, since in silylamines the nitrogen atom has a planar structure. The phenomenon is apparently caused by ring strain.



(L)

The study of compounds of type (LXX) and (LXXI) enriched in the ^{15}N isotope is an example of the use of the $^{15}N-^{29}Si$ SSCC for the investigation of tautomeric processes and for demonstrating the presence of the N–Si bond:[44]



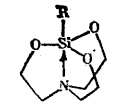
(LXX) (LXXI)

Although the quantity $^1J_{NSi}$ could not be measured accurately, since second order effects were observed in the ^{29}Si NMR spectra, nevertheless the very fact of this $^{15}N-^{29}Si$ spin–spin coupling is evidence in support of the structure (LXX).

2. Interaction across a coordinate bond

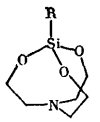
(a) Silatranes

The $^{15}N-^{29}Si$ SSCC for the silatranes (LXXII)–(LXXIX) have been measured using specimens enriched in the ^{15}N isotope (Table 4).[45–47] The structures of the silatranes (LXXII)–(LXXIX) have been studied in detail by X-ray diffraction of crystals (see the review of Voronkov et al.[49]), which made it possible to study in detail the dependence of the $^{15}N-^{29}Si$ SSCC on the N → Si bond length [l(N–Si)]. The structures of compounds (LXXII)–(LXXIX) in crystals depend significantly on the N → Si bond strength.

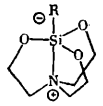


(LXXII)–(LXXIX)

(LXXII): R=Me,
(LXXIII): R=CH=CH$_2$,
(LXXIV): R=Ph,
(LXXV): R=OMe,
(LXXVI): R=H,
(LXXVII): R=CH$_2$Cl,
(LXXVIII): R=CHCl$_2$,
(LXXIX): R=Cl



(A)



(B)

If the N → Si bond is absent [structure (A)], the nitrogen atom is planar and the silicon atom is tetrahedral. With increase in the strength of the N → Si bond, the pyramidal configuration of the nitrogen atom is enhanced, whilst the configuration of the silicon atom approaches the trigonal-bipyramidal configuration [structure (B)]. The majority of silatranes have a structure intermediate between (A) and (B). In solutions, the $^{15}N-^{29}Si$ SSCC increase with decrease in the length of the N → Si bond found in crystals and also with increase in solvent polarity[45] and with decrease in temperature.[47] This indicates the corresponding increase in the mutual polarisability of the valence s orbitals of the N and Si atoms (π_{NSi}). The dependence of $^1J_{NSi}$ on l(N–Si) is non-linear and its character varies as a function of the nature of the solvent (Fig. 4). One of the causes of this behaviour of $^1J_{NSi}$ is the weakening of the N → Si bond on passing from crystals to solutions and also on passing to solvents with a lower polarity. Simultaneously with increase in $^1J_{NSi}$, the constant $^1J_{NC}$ diminishes, which clearly reflects the redistribution of the s character of the bond with increase in strength of the 1,5-transannular N → Si interaction in silatranes. A linear dependence of $^1J(^{15}N-^{13}C)$ on $^1J(^{15}N-^{29}Si)$ was then observed:

$$^1J(^{15}N-^{13}C) = 7.30-0.28\,^1J(^{15}N-^{29}Si) \quad (r = -0.96,\ n = 16). \tag{11}$$

The decrease in the $^{15}N-^{13}C$ SSCC with increase in strength of the N → Si bond was explained by the increasingly pyramidal configuration of the nitrogen atom. This shows that the relation between the structure and the N → Si bond strength, observed in crystals, persists also in solutions.

In the case of 1-hydrosilatrane, a linear correlation was observed between $^1J_{NSi}$ and the stretching vibration frequency, ν_{SiH}, of the Si–H bond in the IR spectra (for different solvents):

$$\nu_{SiH} = 2159-23.23\,^1J(^{15}N-^{29}Si) \quad (r = 0.99,\ n = 4). \tag{12}$$

Extrapolation of this relation to ν_{SiH} in nujol yielded the value of $^1J_{NSi}$ for solid 1-hydrosilatrane, which proved to be 2.97 Hz.

A similar reaction has also been observed for $^1J(^{15}N-^{29}Si)$ and $^1J(^{29}Si-^1H)$:

$$^1J(^{29}Si-^1H) = 290.0-10.63\,^1J(^{15}N-^{29}Si) \quad (r = 0.96,\ n = 4). \tag{13}$$

Relation (13) also indicates a redistribution of the s character of the bonds, i.e. the involvement of the valence s orbitals of the Si atom in the formation of the Si–H bond diminishes with increasing s character of the N → Si bond.

Since the $^{29}Si-^{1}H$ and $^{15}N-^{13}C$ SSCC reflect the *s* character of the corresponding bonds and the ΔE approximation is applicable to them [Eqns. (6) and (7)], the existence of the correlations between $^{1}J_{SiH}$ and $^{1}J_{NC}$, on the one hand, and $^{1}J_{NSi}$, on the other, indicates that the ΔE approximation is valid also for the quantitative interpretation of the constants for the $^{15}N-^{29}Si$ spin–spin coupling across a N → Si bond. Using the model of a S_N2 substitution reaction, this made it possible to obtain equations for the calculation of the length *l* and order *P* of the N → Si bond in solutions:[45]

$$l(\text{N—Si}) = 2.291 - 0.084\ ^{1}J(^{15}\text{N—}^{29}\text{Si}), \quad (14)$$

$$P(\text{N—Si}) = \sqrt{^{1}J(^{15}\text{N—}^{29}\text{Si})/25.1}. \quad (15)$$

We may note that Eqns. (14) and (15) are valid provided that the electronegativity of the substituent R at the Si atom is close to the electronegativity of the H atom. With increase in the electronegativity of the substituent (for example, in the case of R = OMe and Cl), the $^{15}N-^{29}Si$ SSCC acquire values smaller than expected. This has been explained by the tendency of ΔE to increase with increase in the electronegativity of the substituent.

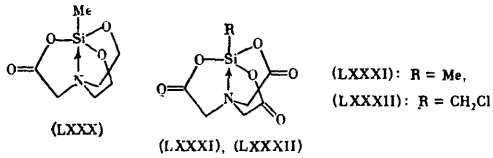
Table 4. The $^{15}N-^{29}Si$ SSCC for the silatranes (LXXII)–(LXXIX) and the silatranones (LXXX)–(LXXXII) at 303 K.[45,47,51]

Compound	Solvent	$^{1}J_{NSi}$, Hz	$\delta(^{15}N)$, p.p.m.	$\delta(^{29}Si)$, p.p.m.
(LXXII)	$CDCl_3$	<0.2	−360.0	−65.4
	DMSO-d_6	0.70	−357.0	−69.8
(LXXIII)	$CDCl_3$	0.55	−357.9	−81.1
	DMSO-d_6	1.47	−355.3	−85.3
(LXXIV)	$CDCl_3$	0.66	−357.2	−80.4
	DMSO-d_6	1.43	−355.0	−83.9
(LXXV)	$CDCl_3$	1.17	−353.1	—
	DMSO-d_6	1.65	−352.3	−95.8
(LXXVI)	$CDCl_3$	1.10	−355.9	−83.5
	acetone-d_6	1.17	−355.1	—
	acetone-d_6 (183 K)	2.20	—	−86.3
	CD_3CN	1.76	—	—
	DMSO-d_6	2.05	−353.9	−86.0
(LXXVII)	$CDCl_3$	1.54	−355.2	−80.2
	DMSO-d_6	2.57	−353.2	−83.1
	CD_3CN	2.4 [48]	—	—
(LXXVIII)	CD_3CN	3.3 [48]	—	—
(LXXIX)	$CDCl_3$	1.98	−348.8 [48]	−85.8
	DMSO-d_6	3.37	−347.8 [48]	−87.0
(LXXX)	DMSO-d_6	0.9	−344.3	−73.0
(LXXXI)	DMSO-d_6	8.2	−319.9	−135.8
(LXXXII)	DMSO-d_6	10.9	−320.6	−144.7

A non-linear dependence of the $^{15}N-^{29}Si$ SSCC on the ^{15}N chemical shift has been observed (Fig. 5). Here too low values of $^{15}N-^{29}Si$ SSCC are observed for R = OMe and Cl. The correlation between $\delta(^{15}N)$ and $^{1}J(^{15}N-^{29}Si)$ can be used to introduce a correction for the electronegativity of the substituent at the Si atom. In particular, this makes it possible to obtain a better agreement between the quantities *l*(N–Si) calculated from the chemical shifts of the ^{15}N atom[50] and $^{1}J_{NSi}$.[45]

(b) Silatronones

The $^{15}N-^{29}Si$ SSCC for the silatronones (LXXX)–(LXXXII)[45,47,51] increase with increase in the number of CO groups in the molecule (Table 4), which can be explained by the increase in strength of the N–Si bond as a consequence of the increase in the polarity of the equatorial Si–O(CO) bonds in silatronones. A pronounced temperature dependence of the $^{15}N-^{29}Si$ and $^{15}N-^{13}C$ SSCC for silatrane-3,7,10-triones has been observed.[47]



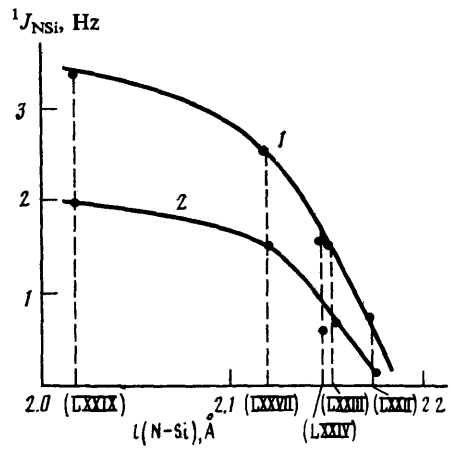


Figure 4. Dependence of the $^{15}N-^{29}Si$ SSCC on the N → Si bond length in the crystals of the silatranes (LXXII)–(LXXIV), (LXXVII), and (LXXIX) in DMSO-d_6 (*1*) and $CDCl_3$ (*2*).[45]

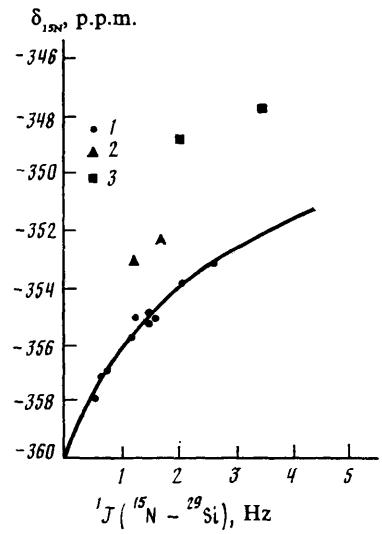


Figure 5. Relation between the ^{15}N chemical shifts and the $^{15}N-^{29}Si$ SSCC for the silatranes (LXXII)–(LXXIX): *1*, R = alkyl, Ph, or CH_2 = CH; *2*, R = OMe; *3*, R = Cl.

(c) Silocans

The $^{15}N-^{29}Si$ SSCC for the silocans (1,3-dioxa-6-aza-2-silacyclooctanes) (LXXXIII)–(XC) have been measured both for specimens enriched in the ^{15}N isotopes and for specimens with the natural abundances of the isotopes (Table 5). The range of variation of the constant $^1J_{NSi}$ for silocans is much greater than for silatranes, which can be explained by the smaller rigidity and greater variation of the substituents at the nitrogen and silicon atoms in silocans. The sign of $^1K_{NSi}$ for compound (LXXXVI) (Table 5) has been determined. Assuming that $^1J(^{29}Si-^1H) < 0$ and $^2J(^{15}N-Si-^1H) < 0$, it was noted that $^1J(^{15}N-^{29}Si)$ and $^1K_{NSi}$ are positive.

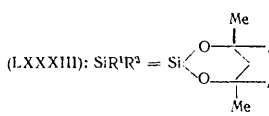
Table 5. The $^{15}N-^{29}Si$ SSCC for the silocans (LXXXIII)–(XC).

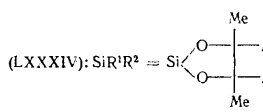
Compound	Solvent	*T*, K	$^1J_{NSi}$, Hz (Ref.45)	$\delta(^{15}N)$, p.p.m. (Ref.45)	$\delta(^{29}Si)$, p.p.m. (Ref.47)
(LXXXIII)	$CDCl_3$	238	<0.2	—	−81.1
(LXXXIV)	CCl_4÷C_6D_6	286	1.85	—	—
	$CDCl_3$	298	2.71	—	−91.5
	DMSO-d_6	314	3.18	—	−92.2
	DMSO-d_6	298	3.30	—	−92.5
(LXXXV)	DMSO-d_6	303	8.36	—	−95.1
(LXXXVI)	acetone-d_6	303	+3.5	—	−57.3
	DMSO-d_6	303	4.3	—	−61.5
(LXXXVII)	acetone-d_6	303	1.2	—	−28.0
Ph (*a*), Me (*e*)	acetone-d_6	193	3.96	—	−30.7
Me (*a*), Ph (*e*)	acetone-d_6	193	1.47	—	−30.2
(LXXXVIII)	DMSO-d_6	303	5.31	−347.0	−106.3
(LXXXIX)	DMSO-d_6	303	6.63	−348.2	−90.2
(XC)	DMSO-d_6	303	10.61	−347.2	−92.4

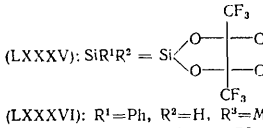
The characteristic features of the variation of the $^{15}N-^{29}Si$ SSCC for silocans and silatranes are similar. A tendency towards a decrease in $^1J_{NSi}$ with increase in the [strength?] of the N → Si bond in the crystals, with decrease in solvent polarity, and with increase in temperature has also been noted for silocans.[45]



(LXXXIII)–(XC)

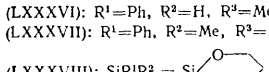
(LXXXIII): SiR^1R^2 =  , R^3=Me;

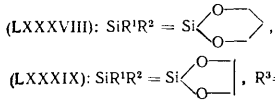
(LXXXIV): SiR^1R^2 =  , R^3=Me;

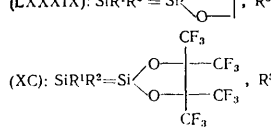
(LXXXV): SiR^1R^2 =  , R^3=Me;

(LXXXVI): R^1=Ph, R^2=H, R^3=Me;

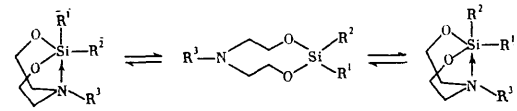
(LXXXVII): R^1=Ph, R^2=Me, R^3=Me;

(LXXXVIII): SiR^1R^2 =  , R^3=H;

(LXXXIX): SiR^1R^2 =  , R^3=H;

(XC): SiR^1R^2=  , R^3=H.

By virtue of the smaller rigidity of silocans in solutions, the dissociation of the N → Si bond, accompanied by the inversion of the eight-membered ring and the positional exchange of substituents at the Si atom, has been observed in these compounds.



Using the dynamic NMR method, this fact makes it possible to determine the free energy of dissociation of the N → Si bond.[45,52] A linear relation between $^1J_{NSi}$ and $\Delta G^{\neq}$ has been observed for compounds (LXXXIII)–(LXXXV) (Table 5):

$$\Delta G^{\neq} = 51.4 + 51.11^1J(^{15}N-^{29}Si) \quad (r = 0.999,\ n = 5). \tag{16}$$

Using Eqn. (16) and assuming that $\Delta G^{\neq} \simeq \Delta H^{\neq}$, the dissociation energy of the N → Si bond in silatranes was determined. The measurement of this characteristic for silatranes by NMR is impossible.[45] A satisfactory agreement was noted between the energies calculated by Eqn. (16) and the values obtained by other methods.

In the general case, the dependence of the $^{15}N-^{29}Si$ SSCC on the nature of the substituents at the N and Si atoms is complex. On the one hand, the strength and *s* character of the N → Si bond increase with increasing electronegativity of the substituents at the Si atom [52] and the $^{15}N-^{29}Si$ SSCC tends to increase. On the other hand, as a result of the increase under these conditions of the electron density on the Si atom and of its decrease on the nitrogen atom, the difference between the energies of the occupied and unoccupied MO rises (ΔE increases), which leads in its turn to some decrease in the $^{15}N-^{29}Si$ SSCC. Thus, one can explain, for example, the higher values of $^1J_{NSi}$ for compounds (LXXXVI) and (LXXXVII) compared with (LXXXIII) and (LXXXIV) (Table 5).

V. Germanium-73

The ^{73}Ge nucleus is exceptionally "unsuitable" for the observation of scalar spin–spin coupling. The presence of a relatively large quadrupole moment and the low frequency of the observation greatly complicate the recording of the ^{73}Ge NMR spectra. As a consequence of the effective relaxation via the quadrupolar mechanism, the direct observation of the SSCC is possible only for highly symmetrical compounds. As a result of the low value of $\delta(^{73}Ge)$ (Table 1) the observed SSCC involving the ^{73}Ge nuclei have low values.[53] The expected values of the $^{14}N-^{73}Ge$ and $^{15}N-^{73}Ge$ SSCC range from 0 to 11 and 15 Hz respectively.

VI. Tin-117 and tin-119

1. Coupling across a covalent bond

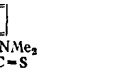
(a) Amines

The first studies on the $^{15}N-^{119}Sn$ SSCC showed[54–56] that the constants $^1K_{NSn}$ can be both positive and negative. This is associated with the relatively large atomic radius and polarisability of Sn, which leads to more negative values of π_{NSn} compared with π_{NSi}. The decrease in the degree of overlap of the valence *s* orbitals of the N and Sn atoms (β_{NSn}) compared with β_{NSi} leads to a more pronounced dependence of the sign and absolute value of $^1K_{NSn}$ on

the properties of the substituents at the N and Sn atom. For this reason, the ΔE approximation is inapplicable to the $^{15}N-^{119}Sn$ SSCC and they must be interpreted on the basis of Eqn. (4).

Subsequent systematic studies of the $^{15}N-^{119}Sn$ SSCC showed[57-60] that the quantity $^1K_{NSn}$ depends in a complex manner on the properties of the substituents at the N and Sn atoms. It has been suggested that β_{NSn} increases with the increasing electronegativity of the substituent. As a result, π_{NSn} becomes more positive and the observed values of $^1J_{NSn}$ become positive, having passed through zero. Thus Eqn. (4) makes it possible to describe at least qualitatively the trend in the variation of $^1K_{NSn}$, in particular the change in the sign of the $^1K_{NSn}$ when H or $SnMe_3$ is substituted by the more electronegative Me or PMe_2 group (Table 6).

Table 6. The $^{15}N-^{119}Sn$ SSCC for tin derivatives.[55-62,66-71]

Compound	Chemical formula	Solvent	$^1J^{*1}_{NSn}$, Hz	$\delta(^{15}N)$, p.p.m.	$\delta(^{119}Sn)$, p.p.m.
(XCI)	$(Me_3Sn)_3N$	C_6D_6	(—) 82.5	—392.2	—
			(—) 79.6	—	86.3
(XCII)	$(Me_3Sn)_3NGeMe_3$	C_6D_6	(—) 68.4	—	73.3
(XCIII)	$(Me_3Sn)_2NBu^t$	C_6D_6	(—) 38.0	—326.7	40.7
(XCIV)	$(Me_3Sn)_2NPh$	C_6D_6	—41.4	—333.9*2	61.0
(XCV)	$Me_3SnNHPh$	C_6D_6	—26.5	—327.9*2	46.4
(XCVI)	Me_3SnNEt_2	C_6D_6	<1	—	60.0
(XCVII)	$Me_3SnNMePh$	C_6D_6	+2.2	—331.1*2	73.0
(XCVIII)	$Me_2Sn(NMePh)_2$	C_6D_6	+24.0	—323.9*2	30.5
(XCIX)	$MeSn(NMePh)_3$	C_6D_6	+87.0	—321.6*2	—66.0
(C)	$Sn(NMePh)_4$	C_6D_6	+175.0	—319.9*2	—175.6
(CI)	$Me_2SnN[P(S)Me_2]Ph$	C_6D_6	—21.0	—307.8*2	66.0
(CII)	$Me_2SnN(PMe_2)Ph$	C_6D_6	+9.5	—332.8*2	63.5
(CIII)		C_6D_6	6.4	—216.2	72.9
(CIV)	$(Me_3Sn)_2N-NMe_2$	C_6D_6	46.0	—	49.0
(CV)	$(Bu^n)_3SnN=C=S$	C_6D_6	(—) 307.0	—	—
(CVI)	$(C_6H_{11})_3SnN=C=S$	C_6D_6	(—) 190*3	—264.2(^{14}N)	—3.2
(CVII)	$Sn(N=C=S)_6^{2-}$	CH_3OH	(+) 210*3	—227(^{14}N)	—842.0
(CVIII)	$Sn[N(SiMe_3)_2]_2$	C_6D_6	(—) 344*3	—239.2	776
(CIX)	$Et_3P-Pt(Cl)(SnCl_3)-NH_2C_6H_4Cl$-*n*	C_6D_6	9 ($^2J_{NSn}$)	—344.1	—243
(CX)	$Et_3P-Pt(Cl)(SnCl_3)-NH_2C_6H_4Me$-*p*	C_6D_6	10 ($^2J_{NSn}$)	344.7	—248
(CXI)	$Bu^tSn(OCH_2CH_2)_3N$	$CDCl_3$	64.9	—	—245.5
		(263K)	69.9	—365.3	—246
(CXII)	$MeSn(OCH_2CH_2)_3N$*4 (A), (B), and (C)	$CDCl_3$	75.6	—354	—537
		(263K)	110.0	—360	—353
(CXIII)	$Bu^t_2Sn(OCH_2CH_2)NH$	C_6D_6	37.1	—	—
(CXIV)	$Sn(OCH_2CH_2)_2NMe$	$CDCl_3$	109.0	—	—303
		DMSO-d_6	117.5	—	—
(CXV)	$(CO)_5CrSn(OCH_2CH_2)_2NMe$	$CDCl_3$	173.3	—340.3	—27.0
(CXVI)	$(CO)_5MoSn(OCH_2CH_2)_2NMe$	$CDCl_3$	167.8	—345.7	—88.3
(CXVII)	$(CO)_5WSn(OCH_2CH_2)_2NMe$	$CDCl_3$	161.1	—346.3	—208.2

*1 The postulated sign is indicated in brackets (if the sign is not indicated, this means that it is unkown; in other cases, the sign has been established experimentally).

*2 The literature data relative to $NMe_4^+I^-$ have been recalculated in terms of the $MeNO_2$ scale in accordance with the relation $\delta[^{15}N(MeNO_2)] = \delta[^{15}N(NMe_4^+I^-)] - 337.3$.

*3 The constants were calculated by multiplying $^1J(^{14}N-^{119}Sn)$ by $\gamma(^{15}N)/\gamma(^{14}N)$.

*4 Data for the three isomers (A), (B), and (C) are presented.

It has been suggested that, for low values of $^1K_{NSn}$, the latter may be influenced significantly by steric factors, which in the general case complicates the determination of quantitative relations. This explains the more negative value of $^1K_{NSn}$ for $Me_3SnN[P(S)Me_2]Ph$ compared with $Me_3SnN(PMe_2)Ph$,[57] although the first substituent has a higher electronegativity. However, one cannot rule out in this instance also the influence by the LEP of the P^{III} atom on the $^{15}N-^{119}Sn$ SSCC.

The $^{15}N-^{119}Sn$ and $^{31}P-^{119}Sn$ SSCC have been compared qualitatively.[57] It has been shown that, on the whole, the constants $^1K_{PSn}$ have more negative values than the constants $^1K_{NSn}$, since the LEP of the P^{III} atom has a greater amount of *s* character.

(b) Isothiocyanates

Direct observation of the $^{14}N-^{119}Sn$ SSCC is possible for the isothiocyanates (CVI) and (CVII) (Table 6)[61,62] because of the relatively slow relaxation of the ^{14}N nuclei as a result of the high symmetry of the charge distribution around the nitrogen atom.

A multiplet made up of 11 lines (13 have been predicted theoretically), with the relative intensities 6:14:36:67:90:100:90:67:36:14:6 and a splitting of 150 Hz as a result of the $^{14}N-^{119}Sn$ spin–spin coupling, has been observed[62] in the ^{119}Sn NMR spectrum of compound (CVII). The ratios of the line intensities of the multiplet, the high value of the $^{14}N-^{119}Sn$ SSCC, and the chemical shifts of the ^{14}N and ^{119}Sn nuclei confirm the hexacoordinate structure of the ion, demonstrating that the Sn atom is linked to the nitrogen and not the sulphur atom and showing that the intermolecular exchange of the NCS groups is slow (on the NMR time scale). All this demonstrates that the SSCC $^1J_{NSn}$ have a high information content.

$^{14}N-^{119}Sn$ spin–spin coupling has also been observed in the ^{119}Sn NMR spectrum of compound (CVI). In this case the ^{119}Sn signal was observed in the form of a well resolved triplet with a splitting of 136 Hz.

The $^{14}N-^{119}Sn$ SSCC cannot be observed directly for compound (CV),[62] which is extremely unexpected. It has been noted that this is associated with the rapid quadrupolar relaxation of the nitrogen atom in compound (CV) (T_{qN} = 0.15 ms) compared with compounds (CVI) and (CVII) (T_{qN} = 35 and 50 ms respectively). Only the $^{15}N-^{119}Sn$ SSCC has been measured for compound (CV).

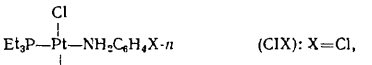
It is noteworthy that the $^1K_{NSn}$ for the isothiocyanates investigated have comparable values. Since the sign of these SSCC has not been established, in order to account for this phenomenon it is reasonable to assume that $^1K_{NSn} > 0$ for compound (CVII) and $^1K_{NSn} < 0$ for compounds (CV) and (CVI) (Table 6).

(c) Sn^{II} derivatives

Hitherto only one $^1J_{NSn}$ SSCC has been determined for Sn^{II} compounds. A signal in the form of a poorly resolved quintet as a consequence of the $^{14}N-^{119}Sn$ spin–spin coupling with $J = 245 \pm 10$ Hz has been observed[58] in the ^{119}Sn spectrum of compound (CVIII) at 80 °C. This SSCC represents at the present time the highest absolute value of $^1K_{NSn}$. It is reasonable to assume that $^1K_{NSn} < 0$ [$^1J(^{14}N-^{119}Sn) > 0$]. Such a negative value of $^1K_{NSn}$ can be accounted for by the high amount of *s* character of the LEP of the Sn(II) atom, which is indicated also by structural data.[63] In particular, the $N-Sn^{II}$ bonds are on average longer than the $N-Sn^{IV}$ bonds and the values of β_{NSn} are therefore smaller for Sn^{II}. This leads to more negative values of π_{NSn} and ultimately to negative values of $^1K_{NSn}$ for Sn^{II} derivatives. It is noteworthy that a similar phenomenon is known also for phosphorus derivatives, i.e. $^1K_{NP} > 0$ for P^V and $^1K_{NP} < 0$ for P^{III}.[64]

(d) Long range SSCC

Long range SSCC has so far been little studied. Using specimens enriched in the ^{15}N isotope, it has been observed[65] that the constants $^2J(^{15}N-^{119}Sn)$ are 9–10 Hz for the platinum complexes (CIX) and (CX).



(CIX), (CX)

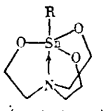
(CIX): X=Cl, (CX): X=Me.

Presumably these SSCC can be used to determine the *cis*- and *trans*-configurations of the ligands in similar complexes, by analogy with the widely known variation of the $^2J(^{31}P-^{119}Sn)$ SSCC.[66]

2. Coupling across the coordinate bond

(a) Sn^{IV} derivatives

The $^{15}N-^{117}Sn$ and $^{15}N-^{119}Sn$ SSCC have been measured for ^{15}N-enriched specimens and have been used mainly to demonstrate the existence of the N → Sn bond in solutions of the test compounds (Table 6). The first constants for the $^{15}N-^{117/119}Sn$ across a coordinate bond were measured for the stannatranes (CXI) and (CXII):

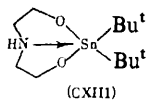


(CXI): R = Bu^t
(CXII): R = Me.

(CXI), (CXII)

Three sets of signals have been observed in the ^{15}N and ^{119}Sn NMR spectra of 1-methylstannatrane (CXII), which was explained by the formation of trimers in solution. The observed SSCC indicates the existence of the N → Sn bond in all the isomers and reflects quantitatively its strength. It has been noted that, in conformity with Bent's rules, the smallest $^{15}N-^{117/119}Sn$ SSCC are characteristic of the largest $^{119}Sn-^{13}C$ and $^{119}Sn-C-^1H$ SSCC [isomer (A)]. This indicates a redistribution of the *s* character of the bonds in the axial fragment of the molecule. A significant temperature dependence of the $^{15}N-^{117/119}Sn$ SSCC for the given compounds has not been observed.

Lower values of the $^{15}N-^{117/119}Sn$ SSCC have been noted for the stannocan (CXIII), which probably indicates a weaker N → Sn bond.[69]

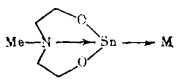


(CXIII)

It has been noted that the $^{15}N-^{117/119}Sn$ SSCC decrease as the temperature is raised. This has been explained by the dissociation of the N → Sn bond at higher temperatures.

(b) Derivatives of Sn^{II}

The $^{15}N-^{117/119}Sn$ SSCC for the Sn^{II} stannocans (CXIV)–(CXVII) greatly exceed the values observed for the analogous Sn^{IV} derivative (CXIII).



(CXIV)–(CXVII)

M = LEP(CXIV), $Cr(CO_5)$(CXV), $Mo(CO)_5$(CXVI), $W(CO)_5$(CXVII).

This is partly associated with the greater strength of the N → Sn bond in Sn^{II} derivatives.[70,71] However, one should note that compounds (CXIII) and (CXIV) have comparable N → Sn bond dissociation energies, whereas the corresponding SSCC differ significantly.

It has been noted that the $^{15}N-^{117/119}Sn$ SSCC increase on passing to more polar solvents.[70]

VII. Lead-207

The $^{15/14}N-^{207}Pb$ SSCC have been investigated in less detail than the constants involving ^{29}Si and $^{117/119}Sn$. It is of interest to note that almost all compounds with the exception of compound (CXX) (Table 7) have been investigated for the natural abundances of the isotopes, which was facilitated by the high natural abundance of the ^{207}Pb isotope (22.6%). In certain cases the $^{14}N-^{207}Pb$ SSCC were measured directly in the ^{207}Pb spectra.[57,58]

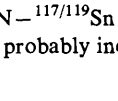
Table 7. The $^{14}N-^{207}Pb$ and $^{15}N-^{207}Pb$ SSCC.[57–59,72–75]

Compound	Chemical formula	Solvent	$^1J(^{14}N-^{207}Pb)/$ $^1J(^{15}N-^{207}Pb)$, Hz	δ(^{15}N), p.p.m.	δ(^{207}Pb) p.p.m.
(CXVIII)	$Me_3PbN(SnMe_3)_2$	C_6D_6	(—) 170/238*1	—	242.0
(CXIX)	$(Me_3Pb)_2NSnMe_3$	C_6D_6	(—) 170/238*1	—	268.0
(CXX)	$Me_3PbNMePh$	C_6D_6	—/+261 (5)	—321.8*2	226.5
(CXXI)	Me_3PbN 	C_6D_6	—/(+) 290	—206.7	204.0
(CXXII)	$Pb[N(SiMe_3)_2]_2$	C_6D_6	(—) 300/(421) *1	—209.1	4916
(CXXIII)	Pb(Cydta)]$^{2-}$ *3	H_2O/D_2O	—/187.5	—312.3	—
		H_2O/D_2O	—/188.3	—	—
(CXXIV)	$[Pb(L)][NO_3]_2$ *4	DMSO-d_6	—/207.5	—318.8	—
		DMSO-d_6	—/19.8	—325.5	—

*1 Calculated by multiplying $^1J(^{14}N-^{207}Pb)$ by $\gamma(^{15}N)/\gamma(^{14}N)$.

*2 The literature data relative to $NMe_4^+I^-$ have been recalculated in terms of the $MeNO_2$ scale in accordance with the relation $\delta[^{15}N(MeNO_2)] = \delta[^{15}N(NMe_4^+I^-)] - 337.3$.[7]

*3 Cydta = *trans*-1,2-diaminocyclohexane-*NNNN'*-tetraacetate.

*4 L = 

It has been established[72] that the SSCC $^1K_{NPb}$ have high negative values. This is associated with the high polarisability of the Pb atom and the weak overlap of the valence *s* orbitals of the N and Pb atoms. The values of $^1K_{NPb}$ for Pb^{IV} derivatives are comparable in magnitude despite the significant variation of the nature of the substituents at the nitrogen atom. This has been explained by the fact that the high and negative values of π_{NPB} are less sensitive to the variation of the character of the chemical bond than the quantity π_{NSn}.

The highest absolute value of $^1K_{NPb}$, which is probably negative, has been observed for a Pb^{II} derivative [compound (CXXII) in Table 7]. As for the Sn analogue, this can be explained by the low value of β_{NPb} and the large amount of *s* character of the LEP of the Pb^{II} atom.

The $^{15}N-^{207}Pb$ SSCC have been measured for two Pb coordination compounds, namely (CXXIII) and (CXXIV). The marked difference between the $^{15}N-^{207}Pb$ SSCC for the equatorial and axial bonds in compound (CXXIV) led to some misunderstanding,[73-75] since in crystals the lengths of these bonds differ little (2.43 and 2.47 Å for the equatorial bonds and 2.47 and 2.48 Å for the axial bonds[73,74]). It has been suggested that the frequency 207.5 Hz corresponds to the normal equatorial bonds and 19.8 Hz corresponds to bonds in the highly distorted axial fragment.

In our view, the SSCC data reflect the real bonding situation in the given compound in solution, i.e. the nature of the equatorial and axial bonds (length and strength) in solutions is significantly different in contrast to their apparent equivalence in crystals. In particular, this is indicated by the valence isomerisation process observed in solutions of compound (CXXIV),[73-75] which has an extremely high activation energy ($\Delta H^{\neq} = 100 \pm 10$ kJ mol^{-1}, $\Delta S^{\neq} = 105 \pm 20$ J mol^{-1} K^{-1}) at 298 K, probably leading to the averaging of the ^{15}N chemical shifts and SSCC. Some increase in the $^{15}N-^{207}Pb$ SSCC in the case of equatorial bonds in compound (CXXIV) compared with the analogous SSCC observed for the complex (CXXIII) agrees well with the shorter $Pb-N_e$ distance in the crystals of compound (CXXIV) compared with (CXXIII) (Table 7).

VIII. Conclusion

The $^{15}N-X$ (X = ^{29}Si, $^{117/119}Sn$, ^{207}Pb) SSCC make it possible to obtain information about the electronic and steric structures of nitrogen-containing Group IV organoelement compounds. A dependence of the $^{15}N-X$ SSCC on the hybridisation of the N and X atoms, their geometry, the *s* character of the N–X bond, its polarity and length, and the degree of $d_\pi-p_\pi$ conjugation between the N and X atoms has been observed for compounds with a covalent N–X bond. At the same time, these constants must be interpreted taking into account the position of the element X in the Periodic System. With increase in the atomic number of X, the constant $^1K_{NX}$ becomes more negative, which is associated with the increasing polarisability of the X atom. Thus all the $^1K(^{15}N-^{29}Si)$ SSCC known hitherto are positive, the constants $^1K(^{15}N-^{117/119}Sn)$ have both positive and negative values, while the constants $^1K(^{15}N-^{207}Pb)$ have only negative values. The highest absolute values of $^1J(^{15}N-X)$ increase in the same sequence: 47.6 Hz (X = ^{29}Si, 344 Hz for ^{119}Sn, and 421 Hz for ^{207}Pb. The constants $^1K(^{15}N-X)$ for the X(II) derivatives are as a rule more negative than the constant ^1K for X(IV). This is associated with the fact that the valence *s* shells in X(II) are less accessible compared with the *s* shells in X(IV), i.e. are less involved in the formation of chemical bonds with the nitrogen atom. With increase in the number of electro-negative substituents at the X atom, the constants $^1K(^{15}N-X)$ become more positive, since the polarisability of the X atom then diminishes and the amount of *s* character of the N–X bond increases. Hitherto the long-range $^{15}N-X$ SSCC have been hardly investigated.

The $^{15}N-X$ SSCC for the coordinate N → X bond make it possible to obtain very valuable information about the nature of the bond in solutions. In many instances, these SSCC have been used as direct evidence for the existence of the N → X bond in solutions. Quantitative relations have been obtained between the $^{15}N-^{29}Si$ SSCC and the length, dissociation energy, and the order of the N → Si bond. However these relations are valid only for related compounds. A correspondence between the change in $^1J(^{15}N-X)$ and the properties of the N → X bond have been observed also for X = $^{117/119}Sn$ and ^{207}Pb. The $^{15}N-X$ SSCC then as a rule increase with increase in the strength of the N → X bond. This is one of the reasons why we have suggested in the present review that all the constants $^1K(^{15}N-X)$ for spin–spin coupling across a N → X coordinate bond are positive. However, in order to justify this hypothesis, it is essential to carry out additional studies (in the first place theoretical studies), since the mechanism of the spin–spin coupling across a coordinate bond remains obscure.

At the present time the measurement of the $^1J(^{15}N-X)$ SSCC for the natural abundances of isotopes presents no difficulties in most cases. The recently developed ultrahigh resolution NMR method[76-78] has led to the possibility of measuring the long-range $^{15}N-X$ SSCC for the natural abundances of the isotopes.[79,80] Hence one may expect that the study of these constants and their employment in structural research will expand.

References

1. J Kowalewski *Annu. Rep. NMR Spectrosc.*, 1982, **12** 81
2. A Laaksonen *Spec. Period. Rep.: Nucl. Magn. Reson.*, 1985, **14** 621; 1984, **13** 64
3. I Ando, G A Webb *Theory of NMR Parameters*, Acad. Press., London, 1983, 218 pp
4. W Q McFarlane *Rev. Chem. Soc.*, 1969, **2b** 187
5. G C Levi, R L Lichter *Nitrogen-15 NMR Spectroscopy*, Wiley, New York, 1979, p. 108
6. W Freyer *Z. Chem.*, 1981, **21** 47
7. G J Martin, M L Martin, J P Gouesnard *NMR Basic Principles and Progress. B.*, Springer-Verlag, Berlin, 1981, Vol. 18, p. 382
8. G Binsch, J B Lambert, B W Roberts, J D Roberts, *J. Am. Chem. Soc.*, 1964, **86** 5564
9. R E Wasylishen *Can. J. Chem.*, 1976, **54** 833
10. N F Ramsey *Phys. Rev.*, 1953, **91** 303
11. C J Jameson, H S Gutowsky *J. Chem. Phys.*, 1969, **51** 2790
12. J A Pople, D P Santry *Mol. Phys.*, 1964, **8** 1
13. E N Gur'yanova, I P Gol'dshtein, I P Romm *Donorno–Aktsceptornaya Svyaz'* (The Donor–Acceptor Bond), Izd. Khimiya, Moscow, 1973, 342 pp
14. J A Pople, W G Schneider, H J Bernstein *High-resolution Nuclear Magnetic Resonance* McGraw-Hill, New York, 1959, 381 pp
15. M Witanowski, G A Webb *Nitrogen NMR*, Plenum Press, 1973, 403 pp
16. C Brevard, P Granger *Handbook of High Resolution Multinuclear NMR*, Wiley, New York, 1981, 229 pp
17. J Mason *Chem. Rev.*, 1981, **81** 205
18. W Philipsborn, R Müller *Angew. Chem., Int. Ed. Engl.*, 1986, **25** 383
19. R Benn, H Günther *Angew. Chem., Ind. Ed. Engl.*, 1983, **22** 350
20. G A Morris *Magn. Reson. Chem.*, 1986, **24** 371
21. E L Kupče, E Liepiņš, E Lukevics *Angew. Chem., Int. Ed. Engl.*, 1985, **24** 568
22. E L Kupče, E Lukevics *J. Magn. Reson.*, 1988, **76** 63
23. B Wrackmeyer, S Kerschl, C Stader, K Horchler *Spectrochim. Acta, Part A*, 1986, **42** 1113
24. S J Blunden, A Frangou, D G Gillies *Org. Magn. Reson.*, 1982, **20** 170

25. G R Hays, D G Gillies, L P Blaauw, A D H Claque *J. Magn. Reson.*, 1981, **45** 102
26. E Kupče, E Liepiņš, O Pudova, E Lukevics *J. Chem. Soc., Chem. Commun.*, 1984, 581
27. C Stader, B Wrackmeyer *J. Magn. Reson.*, 1987, **72** 544
28. D W W Anderson, J E Bentham, D W H Rankin *J. Chem. Soc., Dalton Trans.*, 1973, 1215
29. E A V Ebsworth, J M Edward, D W H Rankin *J. Chem. Soc., Dalton Trans.*, 1976, 1673
30. E Kupče, E Liepiņš, O A Pudova, E Lukevics *Spektroskopiya YaMR Tyazhelykh Yader Elementoorganicheskikh Soedinenii: Tezisy Dokladov* (NMR Spectroscopy of the Heavy Nuclei of Organoelement Compounds. Abstract of Reports), Irkutsk, 1983, p. 15
31. E Kupče, E Liepiņš, E Lukevics, B Astapov *J. Chem. Soc., Dalton Trans.*, 1987, 1593
32. H A Bent *Chem. Rev.*, 1961, **61** 275
33. G Fritz, H Schäfer *Z. Anorg. Allg. Chem.*, 1974, **409** 137
34. H Marsmann *NMR Basic Principles and Progress*, Springer-Verlag, Berlin, 1981, Vol. 17, p. 235
35. H Dreeskamp, K Hildenbrand *Liebigs Ann. Chem.*, 1975, **5** 712
36. K Kovacevic, Z B Maksic *J. Mol. Struct.*, 1973, **17** 203
37. G Fronzoni, V Galasso *Chem. Phys.*, 1986, **103** 29
38. J Iley, A R Bassindale, P Patel *J. Chem. Soc., Perkin Trans. 2*, 1984, 77
39. A R Bassindale, T B Posner *J. Organomet. Chem.*, 1979, **175** 273
40. H Jancke, G Engelhardt, S Wagner, et al. *J. Organomet. Chem.*, 1977, **134** 21
41. J Sandström *Dynamic NMR Spectroscopy*, Acad. Press, London, 1982, 235 pp
42. E Kupče, E Liepiņš, A Lapsina, et al. *J. Organomet. Chem.*, 1987, **333** 1
43. I Urtane, G Zelcans, E Liepiņš, et al. *Zh. Obshch. Khim.*, 1987, **57** 1110
44. B N Khasanov, A V Kalinin, A Ya Shteinshneider, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 1296
45. E Kupče, E Liepiņš, A Lapsina, et al. *J. Organomet. Chem.*, 1985, **279** 343
46. E Liepiņš, I Birgele, G Zelcans, E Lukevics *Zh. Obshch. Khim.*, 1979, **49** 1537
47. E Kupče, Candidate's Thesis in Chemical Sciences, Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga, 1984
48. V A Pestunovich, B Z Shterenberg, M G Voronkov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 1435
49. M G Voronkov, V M Daykov, S V Kirpichenko *J. Organomet. Chem.*, 1982, **233** 1
50. V A Pestunovich, B Z Shterenberg, E Lippmaa et al. *Dokl. Akad. Nauk SSSR*, 1981, **258** 1410
51. E Kupče, E Liepiņš, A Lapsina, et al. *J. Organomet. Chem.*, 1983, **251** 15
52. E Kupče, E Liepiņš, E Lukevics *J. Organomet. Chem.*, 1983, **248** 131
53. R K Harris, J D Kennedy, W McFarlane *NMR and Periodic Table*, Acad. Press, London, 1978, 432 pp
54. G J Jenks *Aust. Dept. Supply. Def. Stand. Lab.: Tech. Note*, 1966, No. 87
55. J D Kennedy, W McFarlane, G S Pyne, B Wrackmeyer *J. Chem. Soc., Dalton Trans.*, 1975, 386
56. W McFarlane, B Wrackmeyer *J. Chem. Soc., Dalton Trans.*, 1976, 2351
57. J D Kennedy, W McFarlane, G S Pyne, B Wrackmeyer *J. Organomet. Chem.*, 1980, **195** 285
58. B Wrackmeyer *J. Magn. Reson.*, 1985, **61** 536
59. B Wrackmeyer *J. Organomet. Chem.*, 1985, **297** 265
60. B Wrackmeyer *Annu. Rep. N. M. R Spectrosc.*, 1985, **16** 73
61. K C Molloy, K Quill, S J Blunden, R Hill *J. Chem. Soc., Dalton Trans.*, 1986, 875
62. S J Blunden, D A Cusack, D G Gillies *J. Magn. Reson.*, 1984, **60** 114
63. T Fjeldberg, H Hope, M F Lappert, et al. *J. Chem. Soc., Chem. Commun.*, 1983, 639
64. W McFarlane, B Wrackmeyer *Inorg. Nucl. Chem. Lett.*, 1975, **11** 719
65. A Albinati, H Moriyama, H Rüegger, et al. *Inorg. Chem.*, 1985, **24** 4430
66. P S Pregosin, R W Kunz *NMR Basic Principles and Progress*, Springer-Verlag, Berlin, 1979, Vol. 16, p. 153
67. K Jurkschat, C Mügge, A Tzschach, et al. *J. Organomet. Chem.*, 1979, **171** 301
68. K Jurkschat, C Mügge, A Tzschach, et al. *Z. Anorg. Allg. Chem.*, 1980, **463** 123
69. A Tzschach, H Weichmann, K Jurkschat *J. Organomet. Chem., Library*, 1981, **12** 293
70. A Zscunke, C Mügge, M Scheer, et al. *J. Cryst. Spectrosc. Res.*, 1983, **13** 201
71. A Zschunke, M Scheer, M Völtzke, et al. *J. Organomet. Chem.*, 1986, **308** 325
72. J D Kennedy, W McFarlane, B Wrackmeyer *Inorg. Chem.*, 1976, **15** 1299
73. N W Alcock, N Herron, P Moore *J. Chem. Soc., Dalton Trans.*, 1979, 1497
74. N W Alcock, N Herron, P Moore *Inorg. Chim. Acta*, 1979, **32** L25
75. H H Curzon, N Herron, P Moore *J. Chem. Soc., Dalton Trans.*, 1980, 721
76. A Allerhand, R E Addleman, D Osman *J. Am. Chem. Soc.*, 1985, **107** 5809
77. A Allerhand, C H Bradley *J. Magn. Reson.*, 1986, **67** 173
78. E Kupče, E Lukevics *J. Magn. Reson.*, 1988, **80** 359
79. S R Maple, A Allerhand *J. Am. Chem. Soc.*, 1987, **109** 56
80. E Kupče, E Lukevics, Yu M Varezhkin *Organometallics*, 1988, **7** 1649

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Adiabatic compression in studies on the kinetics and mechanism of reactions involving fluorine-containing carbenes

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ABSTRACT. The physicochemical principles of adiabatic compression and its characteristics and potentialities in studies on the kinetics and mechanism of thermal gas-phase reactions are examined. The results of studying reactions involving fluorine-containing carbenes are presented. Information is given on the high-temperature tautomerism of tetrafluoroethylene–trifluoromethylfluorocarbene, which has been detected and studied using kinetic spectroscopy during adiabatic compression. The set of experimental data on the pyrolysis and gas-phase isomerisation of perfluoroolefins has been interpreted using the concept of tautomeric changes involving the 1,2-shift of a fluorine atom in olefins.

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I. Introduction

The method of adiabatic compression is not very widely known to chemists. Therefore, we considered one of the aims of the present review to be a demonstration of the characteristics and potentialities of this method for studying the kinetics and mechanism of thermal gas-phase reactions. All the examples that we will use to illustrate the potentialities of adiabatic compression relate to reactions of organofluorine compounds and primarily to reactions involving the formation and conversion of fluoroolefins.

This choice can be substantiated from different viewpoints. Firstly, reactions involving carbenes are highly characteristic for this region of chemistry; secondly, it was in this direction that a number of basic results were obtained using adiabatic compression; and thirdly, we took into account the considerable significance of thermal (pyrolytic) processes in the present-day technology for obtaining monomers for fluorinated rubbers and fluoroplastics. The latter circumstance makes the task of establishing a detailed mechanism of pyrolysis that is directed at the preparation of fluorinated monomers an urgent one for the development of scientific principles in optimising their production.

II. Adiabatic compression in physicochemical studies

The term "adiabatic" in thermodynamics relates to processes for which $dQ = 0$ in the equation of the First Law of Thermodynamics. For this condition to be maintained, the compression of gas must be sufficiently rapid that heat exchange between the gas and the wall of the vessel can be neglected. There are two possible ways of bringing about such a compression: one—with specific times less than the characteristic time for transmitting a sound distances of the order of the linear dimensions of the compressed volume of gas; the second is a slower compression, when the ratio of these times is given by a number greater than unity. In the first of these cases, shock waves develop in the gas and the process is represented by the Hugoniot adiabatic equation, in the second case shock waves do not develop and the process is given by Poisson's adiabatic equation. In units for the adiabatic compression of gases using a piston, its rate of movement is several times less than the speed of sound and, in accordance with Poisson's adiabatic equation, the pressure and temperature of an ideal gas on compression change according to the principle $p = p_0\varepsilon^\gamma$ and $T = T_0\varepsilon^{\gamma-1}$, where $\gamma = C_p/C_V$, the adiabatic factor; C_p and C_V are the specific heats at constant pressure and constant volume respectively; ε is the geometric compression ratio ($\varepsilon = V_0/V$, where V_0 and V are the initial and current values of the volume of gas). With such a compression the entropy of the system does not change and therefore it is sometimes called isentropic compression, taking into account the adiabatic process represented by Poisson's adiabatic equation. In order that the reader can form some idea about the values of the parameters reached in isentropic compression, we shall give one example that illustrates the potentialities of this method. If a monoatomic inert gas is at a temperature $T = 500$ K and pressure $p_0 = 2$ atm. before compression, with a compression ratio $\varepsilon = 50$ the parameters $T_{max} = 6700$ K and $p_{max} = 1320$ atm will be reached in it (the index "max" indicates that the value of the parameter relates to the moment of attaining the maximum compression ratio). No single apparatus could withstand such a combination of pressure and temperature if their duration was not about 10^{-4} s. Heat losses to the wall can hardly take place during this time, and so the compression proves to be adiabatic, the walls of the reactor are not heated up, and the apparatus is not destroyed. Thus, a new region of combinations of high values of p and T parameters is opened up for chemical studies. There are virtually no kinetic data (and sometimes also no thermodynamic data) for this region, and it is extremely important from both a purely scientific and a practical viewpoint to obtain these data.

When chemical reactions are studied using this method, attempts are made in all cases to maintain conditions in which

heat exchange between the gas and the wall can be neglected. However, in far from every case is it possible to ignore the evolution (or absorption) of heat produced by the chemical reaction itself. This does not result in a change in fundamental approach of the method but it must be taken into account in calculations. This will be discussed below.

Two principal features of the method should be apparent from what has been stated: the possibility of studying a gas-phase reaction with a previously known elimination of the effect from the vessel walls and the fact that all of the gas parameters vary with time. Since the temperature is included in these parameters, the adiabatic compression method can be classed as anisothermal. We shall consider these questions in more detail.

In studying the kinetics and mechanism of homogeneous gaseous reactions, problems relating to the effect of the surface of the reaction vessel and in particular its quantitative determination are among the most complex.[1] We consider this point because at the present time the role of the surface has been established in a whole range of processes when they are carried out both under steady-state conditions and in flow reactors of different types.[2-11]

Adiabatic compression can essentially reduce the effect of heterogeneous factors to a negligible level. The lack of isothermal conditions in adiabatic compression led, particularly at the beginning, to difficulties in processing the results. Therefore, in the first stage of studies on reaction kinetics using this method, so-called overall single-stage reactions were mainly studied and approximation methods were used to determine kinetic parameters.[12-17] At the present time reliable computer methods have been developed to calculate kinetic parameters from the experimental data obtained from adiabatic compression. We should note that, in principle, anisothermal methods are more informative than isothermal ones and their advantage can be effectively realised using computers.

We shall consider below approaches to the calculations of kinetic parameters from experimental data obtained on adiabatic compression units. First of all we can demonstrate that adiabatic compression actually ensures that gas reactions take place homogeneously. An obvious condition for homogeneity in the diffusion transfer of a substance[19-21] is that the marked inequality $L_{dif} \ll L_{reac}$, where L_{dif} is the diffusion length and L_{reac} is the characteristic dimension of the reaction volume, should be fulfilled. Let us choose Xe as the gas diluent, a temperature of 1600 K, and an adiabatic factor for the mixture of $\gamma = 1.6$. Such parameters are attained in a gas with standard properties when the compression ratio is 17, which corresponds to a density of the medium 17 times higher and a coefficient of diffusion 17 times lower than at atmospheric pressure. Taking into account the fact that the coefficient of self-diffusion of xenon at a pressure p_{atm} and 1600 K is 1 $cm^2\ s^{-1}$,[18] and the characteristic duration of these parameters during adiabatic compression is about 10^{-3} s, we deduce that the diffusion length will be of the order of 10^{-2} cm, whereas the characteristic dimension of the reaction volume for a compression ratio of 17 in units for studying the kinetics of chemical reactions by this method is usually of the order of 1 cm. Thus, the marked inequality referred to above is fulfilled.[19-21]

Figure 1 depicts the basic diagram of a unit for studying chemical reactions by means of adiabatic compression. The details of the experimental procedure and techniques are reported in detail in a book.[22]

We should say a few words about the treatment of experimental results. All experiments can provisionally be divided into two large groups. In one of them "normal" data—the composition of the products before and after the compression pulse—will occur; in the other group are data from experiments in which (optical) measurements are taken directly during the compression–expansion cycle. We shall only refer here to experiments of the first group. For greater clarity the simplest example can be considered without losing a common approach.

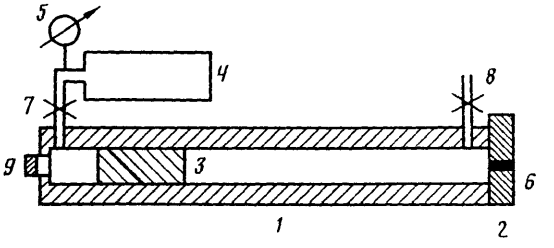


Figure 1. Basic diagram of the adiabatic compression unit:[22] *1*, cylinder; *2*, flange; *3*, piston; *4*, driving gas receiver; *5*, manometer; *6*, pressure gauge; *7*, valve for driving gas; *8*, valve for admission of operating mixture and withdrawal of samples for analysis; *9*, inertial valve.

Let the reaction under study be written in the form:

$$A + Xe \rightarrow \sum_{i=1}^{n} b_i B_i + Xe,$$
$$i = 1, 2 \ldots n,$$

where b_i are stoichiometric coefficients; n is the number of products, including unreacted substance A; B_i are reaction products. The kinetic equation may be written in the form:

$$\dot{N}_A = -kN_A (N_{Xe}/Sx),$$

where N_A and N_{Xe} are the numbers of moles of A and Xe respectively, k is the rate constant, S is the square of the cross section of the (cylinder) piston, x is the piston coordinate. It is assumed that the Arrhenius equation is satisfied, namely:

$$k = k_0 \exp(-E/RT).$$

Thus, in the kinetic equation, not only N_A proves to be a function of time as is usually the case but also the rate constant (since $T = T(t)$, where t is the time) and in addition the volume of the system $V = Sx$, since x also depends on time. Therefore, it is necessary to introduce equations which determine the dependences on time of both the piston coordinate and the temperature.

The piston coordinate can be found by interpreting the equation of its movement:

$$m\ddot{x} = S(p - p_d),$$

where m is the mass of the piston, p is the pressure of compressible gas, p_d is the pressure of driving gas. In this equation the frictional forces acting on the piston when it is moving in the cylinder are not taken into account since the experimental data show that the movement of the piston is wholly determined

by the pressure, and the frictional forces have virtually no effect on the movement of the piston. As is well-known, the relationship between pressure and temperature of a gas is given by the equation of state. In relatively simple cases (up to a compression ratio of about 17 for xenon) the equation of state of an ideal gas can be used. When a high compression is used in kinetic experiments, a virial equation of state must be used. Since the details of the calculation are naturally not covered here, we shall turn our attention to the dependence of temperature on time—the third value necessary to calculate the kinetic parameters. The calculation of temperature can be made in accordance with the equation of the conservation of energy:

$$N_\Sigma C_V^{mx}\dot{T} = q_V\dot{N}_A - Sp\dot{x},$$

where C_V^{mx} is the specific heat of the mixture at constant volume, q_V is the heat effect of the reaction at constant volume, and N_Σ is the total number of moles of the components of the gas mixture.

Thus we obtained a system of three differential equations for all three quantities that are dependent on time: the number of moles of reacting substance, the volume, and the temperature of the working mixture.

Such a simple situation is naturally exceptional. In practice it is necessary to deal with complex reactions, when there are more kinetic equations (according to the number of components) and the dependence of the specific heat of the mixture and the heat effect of the reaction on temperature must be taken into account. With high compression it is also necessary to include the dependences of the virial coefficients on temperature. However, an experiment to resolve these systems of differential equations in a study of the kinetics and mechanism of chemical reactions by means of adiabatic compression showed that the majority of the difficulties in this case were of a technical nature, the operating time expended was comparatively short, and the results were completely reliable. It is difficult now to point to another method used to study homogeneous gas reactions at high temperatures and pressures which is as effective as adiabatic compression.

Studies on high adiabatic compression of gases using a piston were started in the USSR Academy of Sciences on the initiative and under the direction of Khariton in the 1930's in Leningrad. Reinov and Klyazer participated in the studies. After the Second World War research was resumed by Ryabinin, Markevich, and their co-workers at the Institute of Chemical Physics of the USSR Academy of Sciences. Further details about this and references to the literature of those years are given by Kolbanovskii and Markevich.[23]

III. High-temperature carbene reactions involving fluorine-containing molecules

1. Early ideas about the mechanism of formation of lower perfluoroolefins during pyrolysis

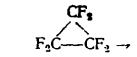
Attempts to construct a consistent scheme for the mechanism of formation of C_2F_4, C_3F_6, and C_4F_8 during pyrolysis were undertaken right from the beginning when this area of chemistry was being developed.

The question concerning the formation of tetrafluoroethylene (TFE) by pyrolysis of CHF_2Cl (Cl-22) was perhaps one of the first to be elucidated. It was shown that the decomposition of Cl-22 leads to the formation of difluorocarbene (DFC), and the subsequent recombination of two molecules of the latter gives tetrafluoroethylene:

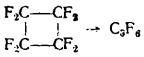
$$CHF_2Cl \rightarrow CF_2 + HCl, \quad (1)$$

$$2\,CF_2 \rightarrow C_2F_4. \quad (2)$$

However, even for the next member of the perfluoroolefin series—hexafluoropropylene (HFP)—elucidation of the kinetics and mechanism of formation proved to be a complex task. The usual method for obtaining HFP is the pyrolysis of TFE. In the opinion of different authors[24,25] two reactions were responsible for the formation of HFP by pyrolysis of TFE:

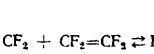


$$\rightarrow C_3F_6, \quad (3)$$

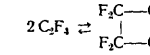


$$\rightarrow C_3F_6 + CF_2. \quad (4)$$

In this case both of the small rings are actually formed during pyrolysis according to the reactions:[26–36]

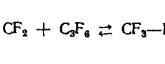


$$, \quad (5)$$

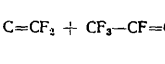


$$. \quad (6)$$

Traditional ideas concerning the formation of the different isomers of C_4F_8 are also based on a similar approach:



$$, \quad (7)$$



$$\rightarrow (CF_3)_2C{=}CF_2 + CF_3{-}CF{=}CF{-}CF_3 + CF_2{=}CF{-}CF_2{-}CF_3. \quad (8)$$

Let us analyse the basis of these conclusions. Cycloaddition reactions (5) and (7) are well-known for dihalocarbenes as is the cyclodimerisation of TFE. But these reactions do not give fluoroolefins directly, and therefore the conclusion about the mechanism of formation of perfluoroolefins was based on the results of the pyrolysis of perfluorocyclopropane and perfluorocyclobutane—in both the first and second cases HFP was found in the products. However, no real kinetic analysis of these experiments was carried out at that time. As regards reaction (8), there were no reliable data on the pyrolysis of perfluoromethylcyclopropane in the literature.

Let us now consider how the problem of determining the kinetics and mechanism of formation and the reactions of fluoroolefins at high temperatures was resolved.

2. Evidence for the incorrect nature of the early ideas about the mechanism of formation of perfluoroolefins by pyrolysis

We obtained the first evidence of this type without any special experiments at all. It was sufficient to analyse the results of one study[37] by means of comparative selectivities; it transpired that HFP is not a primary product of the pyrolysis of perfluorocyclopropane and hence reaction (3) does not take place. It follows from the same analysis that the only reaction in which this three-membered ring participates is reaction (5) in reverse. Only in this case TFE will be the sole primary stable product of the pyrolysis of perfluorocyclopropane.

Following this, doubts arose as to the possibility of the analogous reaction (8), about which there were no reliable experimental data, taking place. Therefore, an experimental study of the pyrolysis of perfluoromethylcyclopropane was undertaken using adiabatic compression. We shall only report here the qualitative results of this study carried out by Grigor'ev, German, Chepik, and the present author;† only TFE and HFP are found amongst the primary stable decomposition products and there are no compounds with the formula C_4F_8. This means that only reaction (7) in reverse takes place while reaction (8) does not occur at all.

Thus, only reaction (4) remained from the originally proposed mechanism for the formation of perfluoroolefins with composition C_3 and C_4. In order to determine the possible role of reaction (4) in the formation of HFP by pyrolysis of TFE, we undertook a study of the kinetics of the decomposition of octafluorocyclobutane by means of adiabatic compression. We shall report here only the principal results of this study.[38] It was established that the decomposition of perfluorocyclobutane is a first-order kinetic reaction with a rate constant of $10^{15.9\pm1.0}\exp(-322 \pm 19 \text{ kJ mol}^{-1}/RT)$. It was shown by the method of comparative selectivities that the sole primary stable product is TFE. It was found that the order of reaction for formation of HFP with respect to the initial compound was equal to 3/2, which is also not consistent with a scheme involving reaction (4)‡—formation of HFP is evidently first order with respect to the initial compound for this reaction.

Thus, it was shown during the initial studies that not a single one of the previously proposed reactions for formation of HFP and C_4F_8 occurs during pyrolysis and the mechanism of pyrolytic reactions involving lower perfluoroolefins had to be completely re-examined. It was established in this case in particular that perfluorocyclopropane and its derivatives do not undergo isomerisation reactions with ring-opening and decomposition to an olefin and CF_2 is the only route of their thermal reactions.

Thus, it was necessary not only to develop new, more thorough methods for the experimental study of the mechanism of high-temperature reactions involving carbenes but also to formulate a new hypothesis about such processes, since it was clear that a model for the mechanism which was based on any combination of previously proposed stages was not consistent with experiment.

3. Experimental detection of the high-temperature tautomerism $C_2F_4 \rightleftarrows CF_3 \simeq CF$:

We should mention initially that only for the convenience of presentation we will not start this section with an analysis of the literature data relating to the present subject and also with data on the "traditional" study of the kinetics of the pyrolysis of perfluoroolefins using adiabatic compression. These findings will be presented below.

Since it had transpired that not all of the data from studying the mechanism of pyrolysis that were solely based on an analysis of the final stable products could be successfully used, a spectroscopic method of studying the mechanism of pyrolysis was incorporated within the adiabatic compression technique. This method and the main results obtained from it are reported in a study[40] which we will mainly rely on in our review.

The following elements were incorporated into the adiabatic compression unit described in Section II. Windows made of optical quartz for spectroscopic probing of the compressed gas directly during a pulse were positioned at a distance of 9 mm from the closed end (see Fig. 1). The unit was provided with all the necessary equipment for evacuation of the working volume. The whole unit was rigidly fixed in a horizontal position on a main wall. Parallel to a line joining the centres of the quartz windows was positioned an optical bench. A light source (DRSh-500 lamp) and the necessary quartz optical equipment were fixed on it. A wide-aperture SDL-1 spectrometer with an FEU-39 and a double-beam storage S1-13 oscilloscope with a screen on which was recorded the optical signal and the signal from a piezoelectric pressure gauge were used. The data given below were obtained using a mixture of 5 vol. % C_2F_4 + 95 vol. % Ar.

It was necessary first of all to obtain spectroscopic purity in the adiabatic compression unit. There were certain misgivings about the possibility of aerosols being formed when the piston moved in the cylinder. It was therefore necessary to ensure that absorption of light by scattering on aerosol particles was excluded. This was tested in different regions of the ultraviolet and visible spectrum. It can be seen in Fig. 2 that the compression of specially purified argon does not alter the amplitude of the optical signal.

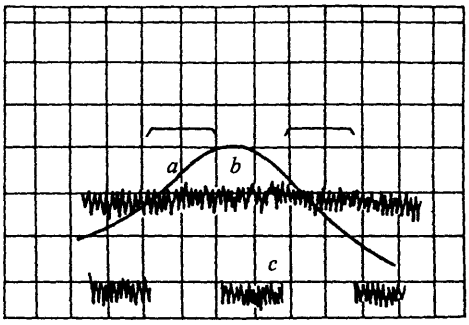


Figure 2. Oscillogram of the compression–expansion cycle of specially purified argon:[40] *a*, signal from piezoelectric pressure gauge; *b*, optical signal at λ = 248.3 nm.

After this it was necessary to ensure that the traces of triethylamine added to TFE in order to prevent it polymerising spontaneously did not contribute to the absorption of light. In order to do this, a comparison of the optical signal was made in two parallel experiments, in one of which TFE was not specially purified and in the other triethylamine was removed by careful freezing out at −60 °C. Within the limits of experimental error no difference was found between the oscillograms of these two experiments.

At high temperatures TFE is known to undergo reversible dissociation to two difluorocarbenes:

$$C_2F_4 \rightleftarrows 2CF_2. \quad (9)$$

†Presented at the anniversary session of the Scientific Council of the Institute of Petrochemical Synthesis, USSR Academy of Sciences, in November 1987.

‡A similar conclusion was reached by Preses et al.,[39] who studied the laser-initiated decomposition of cyclo-C_4F_8.

Amongst the studies investigating reaction (9) we should mention that of Schug and Wagner,[41] in which the values of the equilibrium constant and rate constant of the forward and reverse reaction of (9) were verified again using kinetic spectroscopy in shock waves at 1200–1600 K. The values of the kinetic constants found in this study[41] were used in our study.[40] However, when the first set of data from adiabatic compression was obtained it was found that with the values of the extinction coefficient of CF_2 given in the literature, the optical absorption at the maximum (Fig. 3), being attributed to CF_2, corresponded to concentrations of it that were much higher than that at equilibrium. Since there could be no notions of an excess equilibrium at the moment of maximum absorption during these experiments (on the contrary, it could be shown that the concentration of CF_2 at this point must be the equilibrium concentration) the conviction grew that during compression another component in addition to CF_2 appeared in the system, absorbing light in this region of wavelength. It could also be proved that this component was unstable and that its appearance was the result of a reversible process, since at the end of the compression–expansion pulse the absorption of light disappeared and the original transmission was restored. The result of resolving a direct kinetic problem was used as an addition argument. In this case a calculated curve of optical absorption during a pulse was obtained on the basis of literature data on the kinetics of reaction (9) with known values of the extinction coefficient. This curve was considerably different from the experimental one not only in amplitude, which has already been discussed, but also the characteristic time of the process: 1.8–1.9 ms instead of ~ 3 ms.

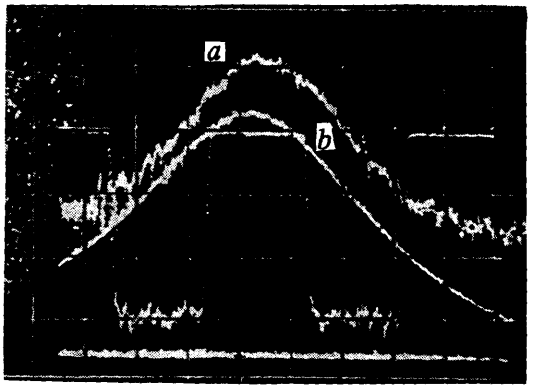


Figure 3. Oscillogram of the adiabatic compression–expansion cycle of a mixture of 5 vol. % C_2F_4 + 95 vol. % specially purified argon:[40] *a*, signal from piezoelectric pressure gauge; *b*, optical signal at λ = 248.3 nm; timescale: 1 square = 5×10^{-4} s.

Two experiments[40] provided definite clarification of the situation. Firstly, absorption of light was detected at a wavelength of 250 nm, where CF_2 does not absorb (taking into account the possible broadening of the lines and slit width). This experiment was based on the data of another study,[42] in which the electronic absorption spectrum of CF_2 was given. Secondly, there is an absorption at a wavelength of 271 nm, where it transpired that only CF_2 absorbs (Fig. 4). It can be clearly seen in Fig. 4 that the characteristic time of the signal actually constitutes about 2 ms, in exact agreement with the kinetic calculations for CF_2.

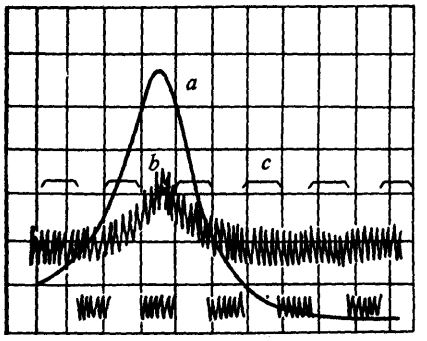


Figure 4. Oscillogram of the compression–expansion cycle of the same mixture (see Fig. 3); λ = 271.37 nm, 1 square = 10^{-3} s.

We should also mention that in all our experiments[40] absorption occurred starting at a temperature of about 820–850 K, although the absorption due to CF_2 at that point was far beyond the sensitivity limits of the spectrometer. Thus, the absorption of light by the carbene $CF_3–CF$:, not recorded previously by any direct methods, was detected in a region of light absorption typical for carbenes at a wavelength of 240–270 nm during the pulsed heating of C_2F_4 in argon. We should emphasise that the process is completely reversible and that the chemical conversion of C_2F_4 to other stable products under the conditions of our study[40] is at a level of about 2% (octafluorocyclobutane, which does not absorb at all in this region of the spectrum, is mainly formed).

It was not difficult to establish from the kinetic absorption curve that the process studied is kinetically first order. This means that trifluoromethylfluorocarbene is formed through a unimolecular reaction involving the 1,2-shift of a fluorine atom. In our opinion, this phenomenon is of basic significance for this area of chemistry and we are attempting to show here not only what conclusions folllow from it for an understanding of a whole series of experimental data but also the predictive power of the concept of olefin–carbene tautomerism in fluoroolefins.

Before going to the next section, it should be mentioned that Kushina et al.[43] had previously interpreted the formation of benzotrifluoride together with fluorobenzene in the combined pyrolysis of tetrafluoroethylene and cyclopentadiene as the result of the formation of $CF_3–CF$: from C_2F_4 and had proposed that this carbene must play an important role in the formation of HFP in the pyrolysis of TFE. Lipkind et al.,[44] by examining the data on the combined pyrolysis of C_2F_4 and C_3F_6 with cyclopentadiene and indene, also suggested that the carbenes CF_3CF and $(CF_3)_2C$ might possibly participate in these processes.

4. Kinetics and mechanism of the pyrolysis of TFE and HFP

In Sections III.1 and III.2 it was shown that the previously held ideas about the mechanism of the high-temperature reactions of TFE and HFP could not be consistent with experiment and it was

necessary to develop a new theory concerning the mechanism of these processes. In this connection let us consider the experimental data obtained using adiabatic compression and a kinetic analysis of the mechanism for pyrolysis of TFE and HFP. In interpreting the experimental results it is assumed that all changes in the number of carbon atoms in perfluoroolefins result from carbene reactions, with the carbenes formed either by decomposition of the olefin at the double bond or by tautomeric changes, namely, through a 1,2-shift of a fluorine atom.

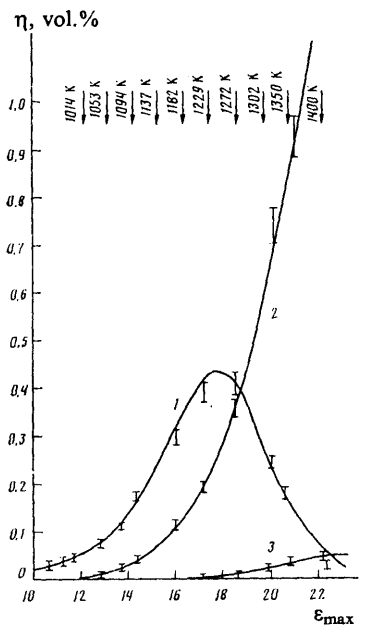


Figure 5. Pyrolysis of 5 vol. % C_2F_4 in specially purified argon by adiabatic compression;[22] T (deg K)—maximum temperature in one compression–expansion cycle; ε_{max}—maximum compression ratio; η—content in mixture after experiment in vol. % of: *1*, cyclo-C_4F_8; *2*, C_3F_6; *3*, C_4 fraction; points—experiment; lines—calculation.

The experimental data of Buravtsev et al.[45] on the pyrolysis of TFE and HFP using adiabatic compression are displayed in Figures 5 and 6. The experimental conditions are indicated in the captions. In Table 1, which is derived from the data collected and obtained by Grigor'ev,[46] are represented the fundamental stages which constitute in totality the mechanism for formation of HFP by pyrolysis of TFE. The values of the rate constants, some of which it was possible to determine for the first time using adiabatic compression, are also given.

An interesting detail was discovered in a computer calculation of the current concentration values of all components of the mixture during a single compression–expansion cycle. It transpired that the concentration of perfluorocyclopropane during pyrolysis was several orders less than the concentration of carbenes in all the systems of practical interest.

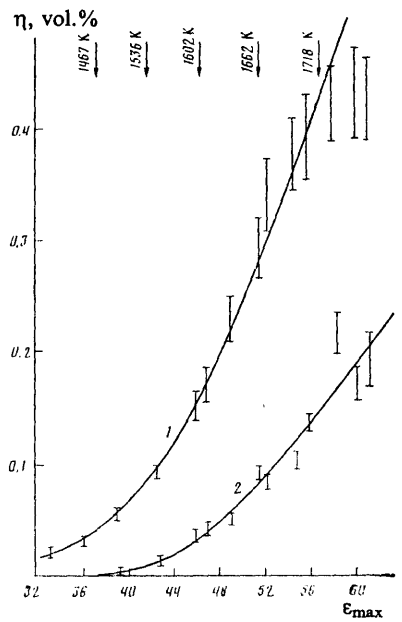


Figure 6. Pyrolysis of 4.65 vol. % C_3F_6 in specially purified argon by adiabatic compression[46] (see Fig. 5 for notation); *1*, C_2F_4; *2*, C_4 fraction.

Table 1. Arrhenius parameters of the fundamental reactions in the initial stages of the pyrolysis of $k = AT^n \exp(-E/RT)$ of TFE.[46]

Sample No.	Reaction	log A	E, kcal mol^{-1}	n
1	$2C_2F_4 \rightarrow$ cyclo-C_4F_8	12.1	30.3	0
2	cyclo-$C_4F_8 \rightarrow 2C_2F_4$	16.1	75.6	0
3	$C_2F_4 \rightarrow 2CF_2$	15.5	68.1	0
4	$2CF_2 \rightarrow C_2F_4$	8.7	1.2	1
5	$C_2F_4+CF_2 \rightarrow$ cyclo-C_3F_6	9.8	7.5	0
6	cyclo-$C_3F_6 \rightarrow CF_2+C_2F_4$	13.3	38.6	0
7	$C_2F_4 \rightarrow CF_3CF$	6.0*	18.0	0
8	$CF_3CF \rightarrow C_2F_4$	4.5*	0.6	0
9	$CF_3CF+CF_2 \rightarrow C_3F_6$	6.7*	1.2	0
10	$C_3F_6 \rightarrow CF_2+CF_3CF$	16.6	90.3	1

*Provisional value.

It is clear that only the stages of initial pyrolysis are given in Table 1, where secondary products, in particular perfluorobutenes of different structures, have not yet been formed. The processes relating to the formation and decomposition of C_4 perfluoroolefins require a separate treatment. As regards the pyrolysis of HFP, it is clear from the data given in Fig. 6 that the only stable primary product in this case is TFE. The reaction in which TFE is formed

by the pyrolysis of HFP is also given in Table 1 [reaction (9)] together with the calculated values of the pre-exponential factor and the energy of activation of the rate constant. The comment made above regarding the kinetics and mechanism of the formation and decomposition of C_4 perfluoroolefins is also valid with respect to the pyrolysis of HFP.

5. Pyrolysis and isomerisation of perfluorobutenes in the gas phase

In all of the data discussed in this review there is specific information on the formation of C_4F_8 compounds, but with two exceptions we will refrain from interpreting it. Let us recall these two cases. Firstly, from the data on the pyrolysis of perfluoromethylcyclopropane, amongst whose primary products there were no C_4 compounds, we could not regard it as an unstable intermediate during the formation of perfluoroolefins $C_2 \rightarrow C_3 \rightarrow C_4$. Secondly, there could be no doubt that the cyclic compound C_4F_8 — octafluorocyclobutane — is readily formed by cyclodimerisation of TFE but does not undergo isomerisation with ring-opening. Thus, it remained unclear how the principal minor products — C_4 perfluorocarbons with an open ring — are formed and how they behave during high-temperature pyrolysis. It should be mentioned that before studies using adiabatic compression were started, there was no information on this question in the literature familiar to us.

Let us consider first the data of German et al.[47] on the pyrolysis and isomerisation of perfluorobutenes of normal structure, obtained by means of adiabatic compression. In the pyrolysis of a mixture of 1.3 vol. % perfluorobut-2-ene (PFB-2) and argon the following was established. Even before the start of other reactions at a maximum temperature during the pulse of about 1100 K *cis-trans*-isomerisation becomes appreciable. When the temperature is increased further to 1200 K the *cis*/*trans* ratio remains almost constant at 0.35. Only TFE and HFP in the molar ratio 1 : 2 are recorded as stable primary products for low degrees of conversion of PFB-2. It must be admitted that for German et al.[47] this result was unexpected. In fact, after studying the pyrolysis of TFE and HFP, where it was found that their decomposition occurs by a carbene mechanism, it was natural to expect similar behaviour for the next members of the homologous series of perfluoroolefins, especially for PFB-2. In such a case only TFE should be amongst the stable primary pyrolysis products. In order for TFE and HFP to be in the stable primary pyrolysis product in the ratio 1 : 2, it was necessary in some way to eliminate from PBF-2 one CF_2 group, which does not exist in this molecule. The experimental data would readily demonstrate if decomposition were preceded by the isomerisation of PFB-2 to PFB-1. The decomposition of PFB-1 at its double bond must result in the formation of two carbenes:

$$CF_2=CF-CF_2-CF_3 \rightarrow CF_2 + CF-CF_2-CF_3.$$

The subsequent recombination of difluorocarbene and 1,2-shift of a fluorine atom in perfluoroethylfluorocarbene would give TFE and HFP in the observed ratio. However, PFB-1 was not found amongst the pyrolysis products of PFB-2. It was therefore necessary to make a second assumption: the isomerisation of PFB-2 to PFB-1 occurs more slowly than the decomposition of PFB-1. In other words, PFB-1 is considerably less stable at high temperatures than its isomer.

The data on the pyrolysis of PFB-1 that were obtained in the same study[47] confirmed both of these assumptions. In fact, when PFB-1 is pyrolysed, the stable primary products are TFE and HFP in the ratio 1 : 2 and the thermal stability of PFB-1 is markedly lower than for PFB-2. At 1174 K, when PFB-2 is completely stable, the degree of conversion of PFB-1 reaches 6%. It is important to mention that small quantities of PFB-2 are also found in this instance. This suggests that there is isomerisation on the double bond under the strictly homogeneous conditions of adiabatic compression. Previously there had been no information about this reaction. In addition, we should mention one further interesting feature of the pyrolysis of PFB-2. At high temperatures (about 1500 K) decomposition on the double bond proceeds more rapidly than isomerisation — TFE starts to predominate in the reaction products. In the pyrolysis of PFB-2 formation of its structural isomer — perfluoroisobutylene (PFI) — was only recorded at very high degrees of conversion and only in trace amounts, while in the pyrolysis of PFB-1 it was not detected at all. It must be concluded that the structural isomerisation of butenes does not occur during homogeneous pyrolysis.

Let us now consider the mechanism for the isomerisation of perfluorobutenes on the double bond. We shall also take into account here the strictly homogeneous reaction conditions and its kinetic first order. Using the concept of tautomeric changes in perfluoroolefins through the 1,2-shift of a fluorine atom, the following scheme can be proposed:

$$CF_3=CF-CF_2-CF_3 \rightleftarrows CF_3-C-CF_2-CF_3 \rightleftarrows CF_3-CF=CF-CF_3.$$

However, it is necessary here to make a reservation which in our opinion is very important. According to quantum-chemical calculations,[48] bis(trifluoromethyl)carbene $(CF_3)_2C$: has a triplet ground state which is separated from an excited singlet by 17.8 kcal mol^{-1}. It may be assumed that other carbenes which do not have fluorine atoms on the carbene carbon atom will also have a triplet ground state. But in that case the type of isomerisation depicted above is spin-forbidden unless we are dealing with the formation of a carbene in an electronically excited (singlet) state by a 1,2-shift. An alternative approach is isomerisation via a 1,3-shift. At the present time it appears to us premature to make a definite choice. For simple molecules, for example triatomic ones, spin-forbidden reactions are in fact known to occur via the formation of species in electronically excited states, as takes place, in particular, in the decomposition of nitrous oxide. There are up to now no data on reactions involving complex molecules of this type.

Let us now turn to the question of the mechanism for formation of PFI in the pyrolysis of perfluoroolefins. We recall (this has already been mentioned above) that in the decomposition of perfluoromethylcyclopropane no compounds with the formula C_4F_8 are formed. The simplest assumption of all is that PFI is formed by recombination of two carbenes:

$$CF_2 + (CF_3)_2C: \rightarrow CF_2=C(CF_3)_2.$$

However, the formation of bis(trifluoromethyl)carbene in the ground state by a 1,2-shift of a fluorine atom in HFP is spin-forbidden, according to Dixon.[48] Moreover, recombination of triplet $(CF_3)_2C$ with difluorocarbene, which has a singlet ground state, is also forbidden. Consequently, only a singlet electronically excited carbene must be obtained for the formation of PFI by this means through a 1,2-shift. In our opinion, this problem merits an additional special study. At the same time there is no prohibition for the formation of PFB-1, for example, in a recombination reaction

$$CF_2 + CF-CF_2-CF_3 \rightarrow CF_2=CF-CF_2-CF_3$$

since the carbene $CF-CF_2-CF_3$ which is formed by another 1,2-shift of a fluorine atom in HFP has a singlet ground state and such a shift is not spin-forbidden. It cannot be excluded that the formation of large quantities of PFI, which often occurs on pyrolysis in tubular reactors, is due to reactions on the wall of the tube, especially if there are deposits of carbon on it. Coking of the walls in metal tubes during pyrolysis is a familiar phenomenon and even in an earlier study[49] it was noted that reactions for the formation of bis(trifluoromethyl)carbene from HFP occur on activated carbon. Formation of the corresponding thioketone was accounted for exactly in this way:

$$CF_3-CF=CF_2 \rightarrow (CF_3)_2C:$$
$$S + (CF_3)_2C: \rightarrow (CF_3)_2C=S.$$

IV. Conclusion

It is evident from what has been stated above that high-temperature reactions of perfluoroolefins, having extensive practical application, have also proved interesting from the point of view of theoretical organic chemistry. We attempt here to arrive at some results. Since this article is both about "carbenes" and "method", our conclusion will touch upon both topics.

Let us start with method. The concentration of the tautomeric form of TFE in the temperature range 800–1000 K as found by Kolbanovskii et al.[40] reaches an equilibrium value after about 10^{-3} s. In adiabatic expansion such temperatures are reached at a compression ratio of 10, and hence the concentration of TFE increases relative to its initial value (under normal conditions) by a factor of 10. The equilibrium concentration of trifluoromethylfluorocarbene correspondingly increases by a factor of 10. With normal procedures for conducting the reaction, heating the gas to 1000 K leads a reduction in its density by approximately a factor of 3. Thus, the concentration of the tautomeric form of TFE using adiabatic compression when other conditions are the same is as a result one and a half decimal orders higher than it would be in conventional experiments at atmospheric pressure§ (in which it could hardly be detected and in fact has not been). It should be noted that in this respect the shock tube method is also considerably inferior to adiabatic compression. As regards the other advantages of adiabatic compression, they are described in sufficient detail in Section II.

Let us now turn to the "carbene" aspect of this review. We shall start with one important qualitative rule. The known processes for pyrolysis of hydrocarbons are usually aimed at obtaining products with a lower molecular weight than the initial starting material. A classic example of this type of process is the pyrolysis of gasoline to obtain ethylene. With perfluoroolefins everything is reversed; in the pyrolysis of C_1 (Cl-22), C_2F_4 is obtained, and in the pyrolysis of the latter, C_3F_6 is obtained. The mechanism of the pyrolysis of hydrocarbons consists of a set of radical chain reactions, as was established earlier by Rice. At the same time the synthetic processes for perfluoroolefins have a non-chain carbene mechanism. It is interesting to note that when it is necessary to account for certain high-temperature processes involving an increase in carbon chain in the chemistry of hydrocarbons, ideas about a carbene reaction mechanism also have to be included. Judging by recent studies, the formation of carbon black from acetylene occurs in precisely this manner.[50] It cannot be stated that high-temperature radical processes are untypical for perfluoroolefins. At high temperatures (usually above 1500 K) even after short pulses ($\sim 10^{-3}$ s), products such as C_2F_6 or C_4F_6 which result from radical reactions are formed from perfluoroolefins. However, even under these conditions, when free-radical reactions take place, chains do not develop.

Some comments should now be made regarding the tautomeric changes of perfluoroolefins. As was mentioned above, if the conversion of C_2F_4 to its tautomeric form is postulated, it is on the basis of indirect data (the final stable reaction products). As regards the reverse conversion of carbene to olefin, we cannot ignore two other studies,[51,52] in which not only was the IR spectrum of $(CF_3)_2C$: obtained for the first time (the carbene was obtained by photolysis of bis(trifluoromethyl)diazirine in an argon matrix at 12 K) but also some of its chemical reactions were studied. We only want to mention here the fact that at a temperature above 40 K this carbene disappeared and C_3F_6 appeared. This was the first direct observation of a reverse (carbene–olefin) change involving the 1,2-shift of a fluorine atom. The occurrence of this reaction at 40 K indicates that the reverse fluorine shift is a reaction which has virtually no energy barrier. There is no reason to suppose that for the other perfluorocarbene—CF_3CF:—there would be a different situation (or, at least, substantially different). At the same time, according to quantum-chemical calculations,[53] for fluoroethylene $CFH=CH_2$ the 1,2-shift of a fluorine atom requires an energy of activation both in the olefin and in the carbene.

In concluding our review of the reactions involving a 1,2-shift of a fluorine atom, we should like to draw the attention of the reader to a study that has been familiar for quite some time.[53] In this study the pyrolysis of trifluoroethylene gave the butene $CF_3-CH=CH-CF_3$ as the main product. When the concept of a 1,2-shift of a fluorine atom is applied, this result has a natural and perhaps the only reasonable explanation, if the following scheme is assumed:

$$CF_2=CHF \rightleftarrows CF_3-CH:,$$
$$2CF_3-CH: \rightarrow CF_3-CH=CH-CF_3.$$

There is no doubt that at the present time by no means everything has yet been clarified with regard to carbene reactions in the high-temperature conversions of organofluorine compounds. It is possible to identify such problems as the reasons for the low values of the recombination coefficients of C_2 and C_3 perfluorocarbenes (it is unclear whether they reduce solely to steric factors or whether there are other more fundamental causes), the possibility of forming electronically excited carbenes when the transition reactions to the ground state are spin-forbidden (this question is closely related to the mechanism for formation of PFI), and certain others. However, on the whole, it can be stated that by using adiabatic compression in studying high-temperature carbene reactions it was possible to obtain a series of new experimental results which did not simply supply facts but also served as a basis for developing the concept of tautomeric changes in fluorinated olefins.

§Dilution of C_2F_4 with an inert gas is necessary in any method for studying its tautomeric changes— otherwise the concentration of TFE will decrease sharply because of its cyclodimerisation.

References

1. M E Bogoyavlenskaya, A A Koval'skii *Zh. Fiz. Khim.*, 1946, **20** 1325 [English translation in *Russ. J. Phys. Chem.*, 1946(6)]
2. A B Nalbandyan, A A Mantashyan *Elementarnye Protsessy v Medlennykh Gazofaznykh Reaktsiyakh* (Simple Processes in Slow Gas-Phase Reactions), Izd. Akad. Nauk ArmSSR, Erevan, 1975, p. 160
3. V V Azatyan, N N Semenov *Kinet. Katal.*, 1972, **13** 17
4. V V Azatyan, E N Aleksandrov, M S Khachatryan *Fiz. Goreniya i Vzryva*, 1973, **9** 456
5. V V Azatyan, N N Semenov *Problemy Khimicheskoi Kinetiki* (Problems in Chemical Kinetics), Izd. Nauka, Moscow, 1979, p. 5
6. A M Chaikin *Zh. Fiz. Khim.*, 1962, **36** 1306 [English translation in *Russ. J. Phys. Chem.*, 1962(6)]
7. G V Sukhanov, S I Molchanova, A F Revzin, et al. *Kinet. Katal.*, 1971, **12** 854
8. M A A Clyne, D H Stedman *Trans. Faraday Soc.*, 1968, **64** 1816
9. A A Westenberg, N Haas *J. Chem. Phys.*, 1968, **48** 4405
10. P F Ambidge, I N Bradley, D A Whytock *J. Chem. Soc., Faraday Trans. I*, 1976, **68** 2143
11. V V Azatyan, E N Dinaburg, M A Namoradze *Fiz. Goreniya i Vzryva*, 1973, **9** 716
12. A M Markevich, V V Azatyan, N A Sokolova *Kinet. Katal.*, 1962, **3** 431
13. I E Volokhonovich, A M Markevich, I F Masterovoi, V V Azatyan *Dokl. Akad. Nauk SSSR*, 1962, **146** 387
14. V N Kondrat'ev *Khimicheskaya Kinetika i Tsepnye Reaktsii* (Chemical Kinetics and Chain Reactions), Izd. Nauka, Moscow, 1966, 165
15. V K Sarkisyan, Candidate's Thesis in Chemical Sciences, Institute of Chemical Materials, Academy of Sciences, Armenian SSR, Erevan, 1979, p. 107
16. F B Vurzel', L S Polak, V S Shchipachev *Kinet. Katal.*, 1966, **7** 1068
17. D B Glebov, M E Polyakova, V S Shchipachev *Issledovanie Khimicheskikh Reaktsii pri Adiabaticheskom Szhatii Gazov* (A Study of Chemical Reactions during Adiabatic Compression of Gases), Izd. Nauka, Moscow, 1978, p.74
18. I K Kikoin (editor) *Tablitsy Fizicheskikh Velichin. Spravochnik* (Tables of Physical Quantities: Handbook), Atomizdat, Moscow, 1976
19. O V Pavlenishvili, Candidate's Thesis in Chemical Sciences, Institute of Petrochemical Synthesis, USSR Academy of Sciences, 1980, p. 153
20. Yu A Kolbanovskii, O V Pavlenishvili, R V Tsagareli, V S Shchipachev *Kinet. Katal.*, 1979, **20** 24
21. Yu A Kolbanovskii, O V Pavlenishvili, R V Tsagareli, et al. *Kinet. Katal.*, 1980, **21** 1397
22. Yu A Kolbanovskii, V S Shchipachev, N Ya Chernyak, et al. *Ipul'snoe Szhatie Gazov v Khimii i Tekhnologii* (Pulsed Compression of Gases in Chemistry and Technology), Izd. Nauka, Moscow, 1982, Ch. 2
23. Yu A Kolbanovskii, A M Markevich *Voprosy Sovremennoi Eksperimental'noi i Teoreticheskoi Fiziki* (Problems in Contemporary Experimental and Theoretical Physics), Izd. Nauka, Leningrad, 1984, p. 37
24. S F Politanskii *Kinet. Katal.*, 1969, **10** 500
25. J R Dasey, J Litter *Can. J. Chem.*, 1969, 3871
26. M Lenzi, A Mele *J. Chem. Phys.*, 1965, **43** 1974
27. N Cohen, J Heicklen *J. Chem. Phys.*, 1965, **43** 871
28. B Atkinson, D McKeagan *Chem. Commun.*, 1966, (7) 189
29. H E O'Neal, S W Benson *J. Phys. Chem.*, 1968, **72** 1866
30. R Fields, R N Haszeldine *J. Chem. Soc.*, 1964, 1881
31. J R Lacher, G W Tompkin, J D Park *J. Am. Chem. Soc.*, 1952, **74** 1693
32. B Atkinson, A B Trenwith *J. Chem. Soc.*, 1953, 2082
33. B Atkinson, V A Atkinson *J. Chem. Soc.*, 1957, 2086
34. J N Butler *J. Am. Chem. Soc.*, 1962, **84** 1393
35. G A Drennan, R A Matula *J. Phys. Chem.*, 1968, **72** 3462
36. N N Buravtsev, A S Grigor'ev, Yu A Kolbanovskii *Kinet. Katal.*, 1985, **26** 7
37. S H Bauer, K C Hou, E L Resler *The Physics of Fluids. Suppl. I*, 1969, Vol. 12, Pt. II, No. 5, 125
38. I E Volokhonovich, A S Grigor'ev, A M Markevich, et al. *Issledovanie Khimicheskikh Reaktsii pri Adiabaticheskom Szhatii Gazov* (A Study of Chemical Reactions during Adiabatic Compression of Gases), Izd. Nauka, Moscow, 1978, p. 123
39. Y M Preses, R E Weston, G W Flynn *Chem. Phys. Lett.*, 1977, **46** 69
40. Yu A Kolbanovskii, E R Mamikonyan, L N Matveeva, V S Shchipachev *Khim. Fiz.*, 1988, **7**(4) 539
41. K P Schug, H G Wagner *Ber. Bunsenges. Phys. Chem.*, 1978, **82** 719
42. D S King, P K Schenck, J C Stephenson *J. Mol. Spectrosc.*, 1978, **78** 1
43. I D Kushina, N U Fedurtsa, V G Barabanov *V Vsesoyuznaya Konferentsiya po Khimii Ftororganicheskikh Soedinenii. Tezisy Dokladov* (Abstracts of Reports at the Vth All-Union Conference on the Chemistry of Organofluorine Compounds), Izd. Nauka, Moscow, 1986, p. 146
44. M B Lipkind, S F Polivanskii, N V Volchkov, O M Nefedov *V Vsesoyuznaya Konferentsiya po Khimii Ftororganicheskikh Soedinenii. Tezisy Dokladov* (Abstracts of Reports at the Vth All-Union Conference on the Chemistry of Organofluorine Compounds), Izd. Nauka, Moscow, 1986, p. 105
45. N N Buravtsev, A S Grigor'ev, Yu A Kolbanovskii *IV Vsesoyuznaya Konferentsiya po Khimii Karbenov. Tezisy Dokladov* (Abstracts of Reports at the IVth All-Union Conference on the Chemistry of Carbenes), Izd. Nauka, Moscow, 1987, p. 118
46. A S Grigor'ev, Candidate's Thesis in Chemical Sciences, Institute of Petrochemical Synthesis, USSR Academy of Sciences, 1989, p. 146
47. L S German, A S Grigor'ev, Yu A Kolbanovskii, S D Chepik *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 2143
48. D A Dixon *J. Phys. Chem.*, 1986, **90** 54
49. K V Martin *J. Chem. Soc.*, 1964, 2944
50. V T Popov, A A Merkulov, L S Polak *Zh. Fiz. Khim.*, 1986, **60** 2692 [English translation in *Russ. J. Phys. Chem.*, 1986(11)]
51. A K Mal'tsev, P S Zuev, O M Nefedov *V Vsesoyuznaya Konferentsiya po Khimii Ftororganicheskikh Soedinenii. Tezisy Dokladov* (Abstracts of Reports at the Vth All-Union Conference on the Chemistry of Organofluorine Compounds), Izd. Nauka, Moscow, 1986, p. 139
52. A K Mal'tsev, P S Zuev, O M Nefedov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, p. 146
53. G Frenking, J Schmidt, *Tetrahedron*, 1984, **40** 2123
54. I L Knunyants, L S German, I N Rozhkov *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1962, (9) 16

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Azaadamantanes with nitrogen atoms in the bridgehead positions

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ABSTRACT. The methods of synthesis and properties of 1-aza-, 1,3-diaza-, and 1,3,5-triaza-adamantanes and their derivatives are discussed and treated systematically. The prospects for the employment of azaadamantanes in the solution of certain theoretical problems in the chemistry of nitrogen-containing compounds and for practical purposes—in catalysis, polymer technology and pharmacology—are demonstrated.

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V. Conclusion 1044

I. Introduction

Skeletal heterocyclic compounds with the adamantane structure (heteroadamantanes) constitute a large but so far only slightly investigated class of saturated heterocyclic compounds. They merit the continuous attention of chemists not only because of their structural relation to the unique hydrocarbon adamantane (I) but also because they have a set of specific properties resulting from the presence of heteroatoms in the adamantane nucleus. The published data on heteroadamantanes have been surveyed in a number of reviews[1–6] and in a separate chapter of a monograph on adamantanes.[7]

Azaadamantanes with nitrogen atoms in the bridgehead positions constitute a special branch of the chemistry of heteroadamantanes.



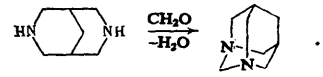
(I) (II) (III) (IV) (V)

They include 1-azaadamantane (II), 1,3-diazaadamantane (III), and 1,3,5-triazaadamantane (IV). Hexamethylenetetramine or 1,3,5,7-tetraazaadamantane (V) is also an azaadamantane. Together with this compound, azaadamantanes constitute an unusual series of compounds with identical molecular skeletons and common properties determined by the specific structure of their molecules (high melting point, volatility, thermodynamic stability, etc.) and by the presence of nitrogen atoms (basicity, high solubility in water, capacity for complex formation, etc.).[8]

Azaadamantane	(I)	(II)	(III)	(IV)	(V)
M.p., °C	269—272	250—252	260—264	260—262	287—288
p*K* (in DMSO)		9.70	8.80	7.60	6.40
p*K* (in water)		10.92	8.80	6.63	4.86

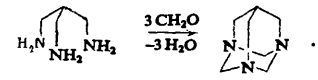
[8]

Together with common properties, there are also significant chemical differences between azaadamantanes. Whereas azaadamantanes (II) is a typical tertiary amine with a skeletal structure, in diazaadamantane (III) one of the methylene groups, located between the two nitrogen atoms, is an animal methylene group and the compound is the product of the condensation of 3,7-diazabicyclo[3.3.1]nonane (bispidine) (VI) with formaldehyde.



(VI) (III)

In triazaadamantane (IV), there are three aminal methylene groups and it is the product of the condensation of 2-aminomethyl-1,3-diaminopropane [tris(aminomethyl)methane] (VII) with formaldehyde.



(VII) (IV)

Azaadamantanes were first synthesised at the beginning of the 1950s and immediately aroused interest among investigators in different fields because of the possibility of using them in the solution of important theoretical problems in the chemistry of nitrogen-containing compounds and because of the prospect for their practical application in the synthesis of new biologically active preparations, rocket fuel components, and additives to fuel-lubricating materials, in photography, and in other fields.

The growth of the number of publications in the development of new novel methods of synthesis and the study of the properties of azaadamantanes and also the fields of their practical application which have arisen have given rise to the necessity for a survey and a separate examination of data which have accumulated on this new aspect of synthetic organic chemistry.

The review discusses literature data published up to 1987 inclusive.

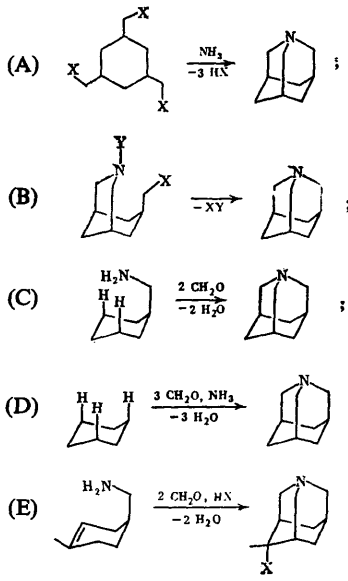
II. Methods of synthesis

Despite the existing general approaches to the synthesis of azaadamantanes, the ways leading to the formation of the structures of different azaadamantanes are extremely specific and require separate consideration. Whereas in the initial period of the development of the chemistry of azaadamantanes they were synthesised mainly by the gradual construction of rings, methods based on the condensation of acyclic or monocyclic compounds with the single-stage closure of all three rings of the adamantane nucleus

at once have been developed in recent years. Nevertheless, the multistage methods developed previously remain of practical value for the synthesis of individual representatives.

1. Synthesis of 1-azaadamantane and its derivatives

The methods of synthesis of azaadamantanes (II) and its derivatives are extremely varied but most of them can be reduced to the following several formal schemes:[4]

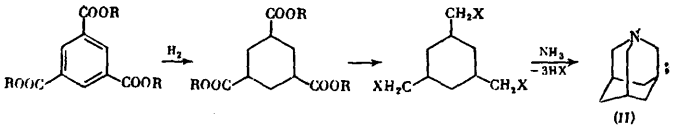


Pathway (A) represents the alkylation of ammonia, while pathway (B) represents the intramolecular alkylation of 3-azabicyclo-[3.3.1]nonane systems frequently with the simultaneous, preliminary, or subsequent elimination of the substituent at the nitrogen atom. Pathways (C) and (D) are based on the aminomethylation reaction of the type of the Mannich reaction and presuppose the presence of activating groups next to the designated hydrogen atoms. Pathway (E) is based on the condensation of alkenes with formaldehyde and amines.

The formal schemes present only the final stages of the formation of the azaadamantanes structure from the intermediates, whose synthesis is frequently a multistage process and requires special consideration.

(a) The synthesis of 1-azaadamantane from trimesic acid

Azaadamantane (II) was first obtained in several stages from trimesic acid.[9−11] Subsequently individual stages of this synthesis were improved.[8,12] In the first stage, the methyl or ethyl ester of trimesic acid is hydrogenated in the presence of a platinum catalyst to esters of cyclohexanetricarboxylic acid and the latter are reduced with lithium tetrahydroaluminate to 1,3,5-tri(hydroxymethyl)cyclo-hexane.

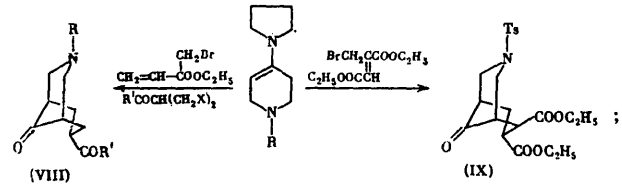


R=CH3, C2H5; X=OH, Br.

The latter is converted into azaadamantane (II) via 1,3,5-tribromo-methylcyclohexane or directly by interaction with ammonia over alumina at 375 °C.[12] Despite the low (not exceeding 10%) overall yield, this method still remains virtually the only one available for the synthesis of the unsubstituted azaadamantane (II).[8]

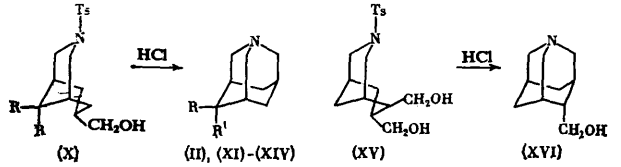
(b) Intramolecular alkylation of 3-azabicyclo[3.3.1]nonane derivatives

The intramolecular alkylation method is based on the αα′-annelation of enamines derived from 4-piperidinones with esters of β-bromomethacrylic,[13,14] ββ′-dibromoisobutyric,[13−16] and bromomethylfumaric[17] acids or with 2-benzoyl-1,3-dichloropropane,[18] which leads to the formation of 3-azabicyclo[3.3.1]nonanes (VIII) and (IX). The initial piperidinones were obtained in several stages from available initial compounds.



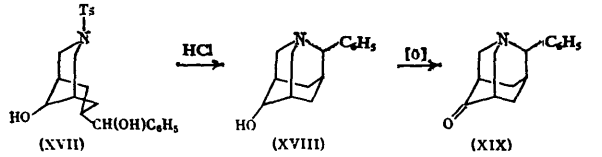
R=Ts, C6H5CO, C6H5CH2OCO; R′=C2H5O, C6H5;
X=Cl, Br.

After the modification of the keto-group in compounds (VIII) and (IX), the ester groups are reduced with lithium tetrahydroaluminate to the hydroxymethyl group. It has been observed that, when 7-hydroxymethyl-*N*-tosyl-3-azabicyclo[3.3.1]nonanes (X) and (XV), formed as a result of the reactions described above, are heated in acetic acid saturated with dry hydrogen chloride, simultaneous dissociation of the bond between the nitrogen atom and the tosyl group and intramolecular alkylation with formation of azaadamantane (II) and its derivatives (XI)−(XIV) and (XVI) take place.[14,15,17,18]



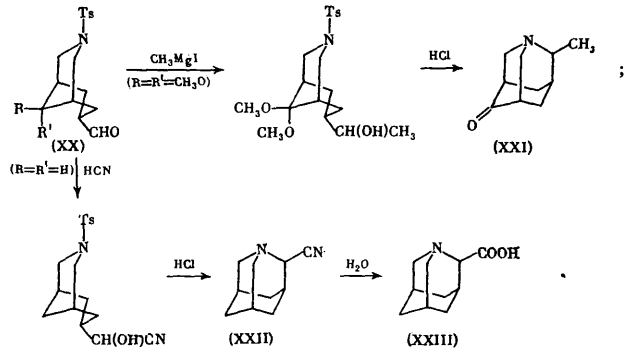
RR′ = O (XI); R = H, R′ = OH (XII);
R = OH, R′ = H (XIII); R = H, R′ = NH2 (XIV).

The diol (XVII)—the product of the reduction of the diketone (VIII, R = Ts, R′ = C6H5) (Ts = tosyl) with lithium tetrahydro-aluminate, cyclises in exactly the same way. Oxidation of 2-phenyl-1-azaadamantan-6-ol (XVIII), formed as a result of the cyclisation, with silver carbonate yields 2-phenyl-1-azaadamantan-6-one (XIX):[18]

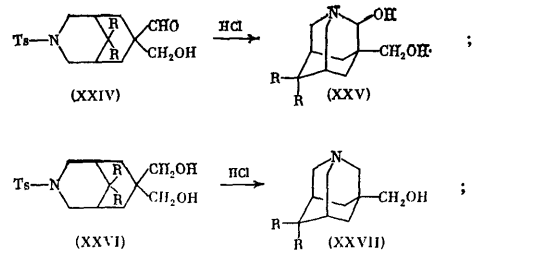


Oxidation of the 7-hydroxymethyl group in compounds (X) with R = R′ = H or CH_3O or with RR′ = SCH_2CH_2S affords the corresponding azabicyclononane derivatives (XX), from which azaadamantane derivatives with substituents at the C(2) atom can be obtained.[14,19] Thus treatment of the dimethoxy-derivative (XX, R = CH_3O) with a Grignard reagent or of the derivative (XX, R′ = H) with hydrocyanic acid, followed by treatment of the

resulting hydroxy-derivatives with hydrogen chloride in acetic acid, yielded respectively 2-methyl-1-azaadamantan-6-one (XXI) and 2-cyano-1-azaadamantane (XXII). 1-Azaadamantane-2-carboxylic acid (XXIII) was obtained from the latter by hydrolysis:[20]



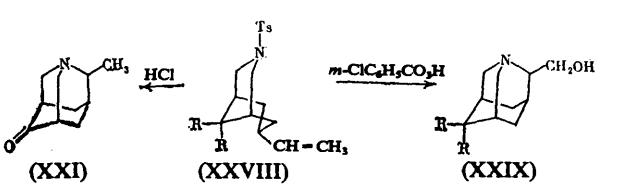
Condensation of formylazabicyclononanes (XX) with formaldehyde afforded the hydroxymethylformyl derivatives (XXIV), which cyclise on treatment with hydrogen chloride in acetic acid to 3-hydroxymethyl-1-azaadamantan-2-ol derivatives (XXV).[19] 2-Hydroxy-3-hydroxymethyl-1-azaadamantan-6-one (XXV, RR = O) obtained in this way is a rare example of a stable hemiaminal, whose stability can be explained by the incorporation of the hemiaminal nitrogen atom in the adamantane nucleus.



R=H, CH_3O; RR=O, SCH_2CH_2S.

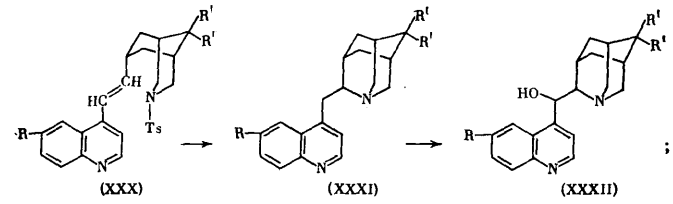
The 7,7-dihydroxymethyl derivatives of azabicyclononane (XXVI), obtained by reducing the aldols (XXIV), cyclise on treatment with hydrogen chloride in acetic acid to derivatives of 3-hydroxymethyl-1-azaadamantane (XXVII), but 3-hydroxymethyl-1-azaadamantane (XXVII, R = H) itself is not formed in this case. It is obtained[19] by eliminating sulphur from the thiolan derivative (XXVII, RR = SCH_2CH_2S) with Raney nickel.

The vinylazabicyclononanes (XXVIII) have been obtained from the corresponding formyl derivatives of azabicyclononane (XX) by the Wittig reaction. They are converted into azaadamantane derivatives (XXI) and (XXIX) by heating in acetic acid saturated with hydrogen chloride or by treatment with *m*-chloroperbenzoic acid.[19]



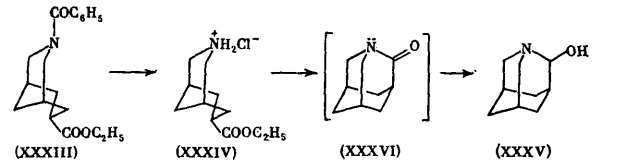
(XXVIII): R=H, CH_3O; (XXIX): R=H, RR=O.

Condensation of the aldehydes (XX) with the lithium derivatives of quinolinylmethylphosphonic acid esters afforded quinolinylvinylazabicyclononane derivatives (XXX), which cyclise on treatment with hydrogen chloride to azaadamantane derivatives (XXXI). These were later used to obtain analogues of the quinuclidine alkaloids (XXXII) which contain the 1-azaadamantane nucleus instead of the quinuclidine nucleus.[21]



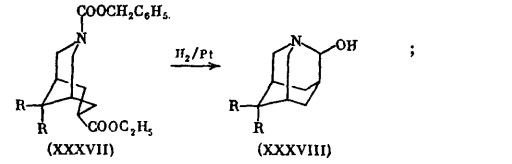
R=H, CH_3O; R′=H, CH_3O; R′R′=O, CH_2.

When an attempt was made to synthesise 1-azaadamantane (II) from *N*-benzoyl-7-ethoxycarbonyl-3-azabicyclo[3.3.1]nonane (XXXIII) the product of the annelation of compound (VIII, R = C_6H_5CO, R′ = C_2H_5O), i.e.



via the ester (XXXIV) (which was hydrogenated over a platinum catalyst in the form of the hydrochloride), 1-azaadamantan-2-ol (XXXV) was obtained unexpectedly instead of 1-azaadamantane (II).[16] It has been suggested that the readily reducible 2-oxo-1-azaadamantane (XXXVI) is formed as an intermediate. It is an unusual lactam, since the lone electron pair at its nitrogen atom is not conjugated with a carbonyl group but is disposed at a right angle to the C=O π-system.[16]

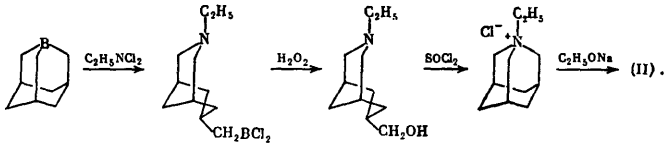
The *N*-benzyloxycarbonyl derivatives of azabicyclononane (XXXVII), obtained from the annelation product (VIII, R = $COOCH_2C_6H_5$, R′ = C_2H_5O), do in fact afford the corresponding derivatives of 2-hydroxy-1-adamantane (XXXVIII) on hydrogenation over a palladium catalyst.[16]



R=H; RR=OCH_2CH_2O.

Yet another method of synthesis of azaadamantane (II) via azabicyclononane derivatives has been developed by Soviet workers.[22] By treating 1-boraadamantane with ethyldichloroamine and subsequent oxidation of the resulting 7-dichloroboryl-methyl-*N*-ethyl-3-azabicyclo[3.3.1]nonane by hydrogen peroxide, they obtained *N*-ethyl-7-hydroxymethyl-3-azabicyclo[3.3.1]nonane (XXXIX). Its treatment with thionyl chloride in moist benzene leads

to 1-azaadamantane ethochloride. The ethyl group bound to the nitrogen atom is then removed by treatment with sodium ethoxide in alcohol.



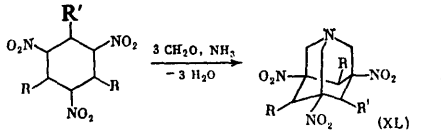
(XXXIX)

Improvement of the last two stages of the synthesis of azaadamantane (II) makes it possible to replan the synthesis of azaadamantane derivatives via azabicyclononanes.

(c) Aminomethylation of cyclohexane derivatives

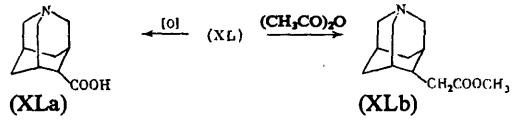
The possibility of synthesising the azaadamantane structure by condensing cyclohexane derivatives with formaldehyde and ammonia was first demonstrated in the synthesis of 3,5,7-trinitro-1-azaadamantane (XL, R = R′ = H) from trinitrocyclohexane, obtained by reducing trinitrobenzene [23] or picric acid [23–25] with sodium tetrahydroborate. Methyl- and dimethyl-trinitrocyclohexanes are obtained similarly from trinitrotoluene and trinitroxylene.[26] Trialkyltrinitrocyclohexanes are obtained by treating trinitrobenzene with Grignard reagents.[27] Hydroxymethyltrinitrocyclohexane has been obtained by reducing trinitrobenzaldehyde.[28] Treatment of trinitrobenzene with ketones in an alkaline medium followed by reduction with sodium tetrahydroborate afforded trinitrocyclohexane derivatives with a hydroxy-group in the side chain.[29,30]

The aminomethylation of trinitrocyclohexane and its derivatives is carried out in an aqueous medium using formaldehyde and ammonia or ammonium nitrate.[26,31,32] The yield of trinitroazaadamantane and its derivatives is between 10 and 50%. Instead of trinitrocyclohexanes, one can also use the hydroborate complexes, formed in the reduction of trinitroarenes, without isolating them in a pure form.[31–34] There are also other modifications of this reaction.[26,32]



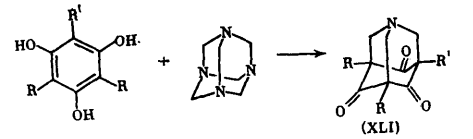
R = H, CH_3, C_2H_5, C_3H_7; R′ = H, CH_3, C_2H_5, C_3H_7, CHO, CH_2OH, $CH_3CH(OH)CH_2$, $(CH_2)_3CH(OH)CH$, $(CH_2)_4CH(OH)CH$.

Oxidation of hydroxymethyltrinitroazaadamantane (XL, R = H, R′ = CH_2OH) afforded the acid (XLa) and its acylation gave rise to the acetate (XLb).[28]



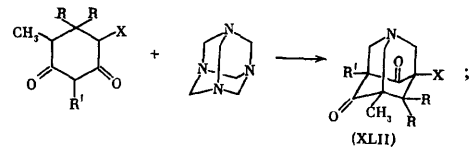
(XLa) (XLb)

Active hydrogen atoms, which are essential for aminomethylation, are also present in phloroglucinols, but phloroglucinol itself gives rise to only tarry products of the type of phenolformaldehyde resins in its reaction with formaldehyde and ammonia. On the other hand, it has been observed [35–37] that trialkylphloroglucinols are capable of condensing with hexamethylenetetramine to form 3,5,7-trialkyl-1-azaadamantane-4,6,10-triones (XLI) in high yields.



R = CH_3, C_2H_5, iso-C_3H_7; R′ = CH_3, C_2H_5.

1-Azaadamantane-4,6-dione derivatives (XLII) are obtained by condensing cyclohexane-1,3-diones with hexamethylenetetramine.[38–40]

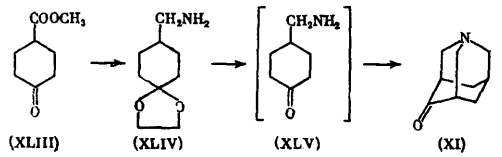


R = H, CH_3; R′ = CH_3, C_2H_5, n-C_8H_{17}, $C_6H_5CH_2$; X = $COOCH_3$, CN.

The initial cyclohexanediols are obtained by condensing α-vinylketones with malonic or cyanoacetic ester.

(d) Condensation of 4-(aminomethyl)cyclohexanone with formaldehyde

The possibility, in principle, of synthesising azaadamantane derivatives from 4-(aminomethyl)cyclohexanone derivatives has been demonstrated in relation to the synthesis of 1-azaadamantan-4-one (XI).[41]

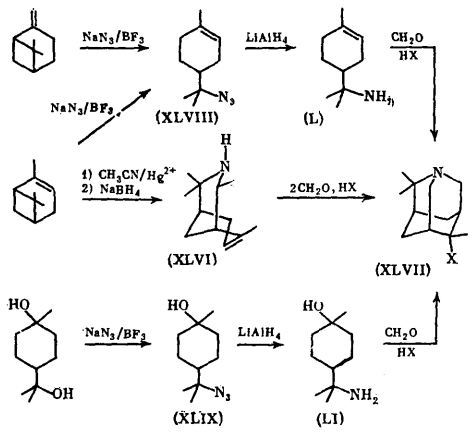


4-Methoxycarbonylcyclohexanone (XLIII), obtained from malonic and acrylic acid esters[41–43] or from 4-hydroxybenzoic acid,[44] was used as the starting material in this synthesis. After protecting the keto-group, the ketoester (XLIII) is converted into the amine (XLIV) (via the amide). When the latter is condensed with paraformaldehyde or trioxane in dilute sulphuric acid, the ketone protecting group is removed and the aminoketone (XLV) condenses with formaldehyde to azaadamantan-4-one (XI).[41] The value of the method is reduced by the low yield of the product (XI) in the condensation of the aminoketone (XLV) with formaldehyde.

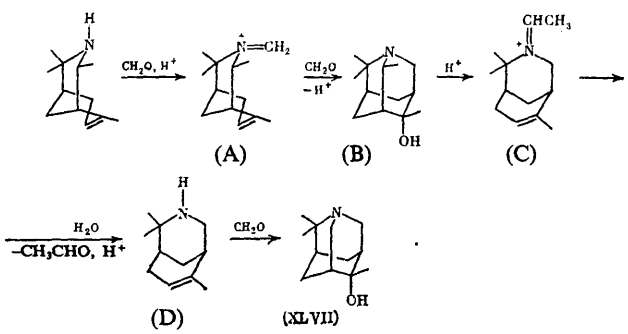
(e) Synthesis of 1-azaadamantane derivatives from terpenes

An unusual approach to the building of the azaadamantane structure has been developed by French investigators.[44–48] They observed that, when α-pinene is treated with acetonitrile in the presence of mercury nitrate and the resulting adduct is reduced with sodium tetrahydroborate, 2,2,4,6-tetramethyl-3-azabicyclo[3.3.1]non-6-ene (XLVI) is obtained; the latter reacts in an acid medium with formaldehyde, whereupon the process involves formally the elimination of the methyl substituents from the C(6) atom and the formation of 4,8,8-trimethyl-1-azaadamantan-4-ol (XLVII, X = OH). By carrying out the reaction in the presence of azide or acetate ions, it is possible to obtain 4-azido- and 4-acetoxy-4,8,8-trimethyl-1-azaadamantanes (XLVII, X = N_3, CH_3COO). 4-Amino-4,8,8-trimethyl-1-azaadamantane (XLVII, X = NH_2) has

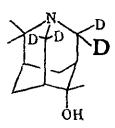
been obtained by reducing the azide with lithium tetrahydroaluminate.



The unusual elimination of the methyl group in the condensation of compound (XLVI) with formaldehyde is explained by the fact that, in the cyclisation of the methyleneimmonium cation (A) to the azaadamantane derivative (B), the methyl group at the C(4) and C(9) atoms are subjected to strong diaxial repulsion, which induces the dissociation of the C(2)–C(3)σ-bond of the type of Grob fragmentation. In the hydrolysis of the ethylideneimmonium cation (C), formed as a result of such fragmentation, a molecule of acetaldehyde is split off and the bicyclic product (D) condenses subsequently with formaldehyde, affording azaadamantanol (XLVII, X = OH).



In order to confirm the mechanism described, the deuteriated analogue of formaldehyde was employed instead of the usual formaldehyde, as a result of which deuteriated azaadamantanol was obtained.



The use of the toxic mercury nitrate in the synthesis described above creates disadvantages which can be avoided by employing a somewhat different scheme for the synthesis of azaadamantane derivatives (XLVII). Thus treatment of α-pinene with sodium azide in ether in the presence of boron trifluoride leads to the opening of the four-membered ring and the formation of the azide (XLVIII). The same product is formed under analogous conditions also from β-pinene. The azidoalcohol (XLIX) is formed from terpyne hydrate under the same conditions. Both azides, (XLVIII) and (XLIX), were reduced with lithium tetrahydroaluminate to the amines (L) and (LI), which were then condensed with formaldehyde in an acid medium to azaadamantanol (XLVII, X = OH).

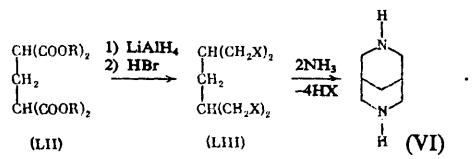
The development of methods of synthesis of azaadamantane derivatives from terpenes leads to their availability, which permits their practical employment.

2. Synthesis of 1,3-diazaadamantane and its derivatives

The methods of synthesis of 1,3-diazaadamantane (III) and its derivatives frequently reduce to the synthesis of bispidine (VI) and its derivatives followed by their condensation with aldehydes, in some cases without isolating the bispidines.

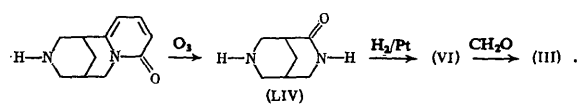
(a) Synthesis of 1,3-diazaadamantane and its derivatives via bispidine and its derivatives

The methods of synthesis of 3,7-diazabicyclo[3.3.1]nonane (bispidine) (VI) and its derivatives have been examined in detail in other reviews.[49,50] They included data published up to 1972. The synthesis of bispidine (VI) and diazaadamantane (III) from the products of the condensation of malonic ester with formaldehyde (LII), which is subsequently reduced with lithium tetrahydroaluminate to 2,4-di(hydroxymethyl)pentane-1,5-diol (LIII, X = OH), was reported later.[51] Treatment of the last compound with hydrogen bromide in acetic acid yields 1,5-dibromo-2,4-di(bromomethyl)-pentane (LIII, X = Br). When this tetrabromo-derivative is heated in a methanol solution of ammonia, bispidine (VI) is formed.

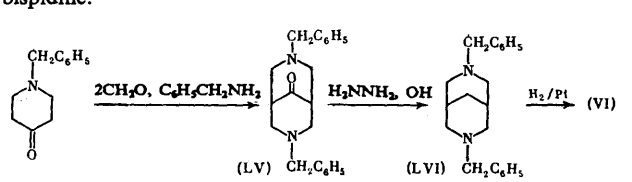


The method requires further improvement, especially in the stage involving reduction and the conversion of the tetrabromo-derivative (LIII, X = Br) into bispidine (VI), since in these stages the products are formed in a low yield, which reduces the overall yield (<7%).

The synthesis of diazaadamantane from the alkaloid cytisine has been reported.[52] In the first stage, 2-oxobispidine (LIV) is obtained by the ozonolysis of cytisine. Its hydrogenation in the presence of a platinum catalyst leads to bispidine (VI) from which diazaadamantane (III) is synthesised in its turn.

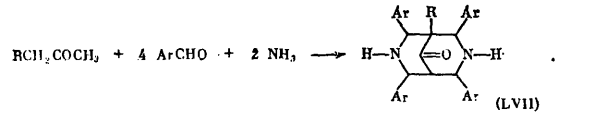


Perhaps the most effective method of synthesis of bispidine (VI) is based on the condensation of the readily available *N*-benzyl-4-piperidinone with paraformaldehyde and benzylamine, which leads to the formation of the unstable *NN'*-dibenzylbispidinol (LV). It is reduced, without isolation, by the Huang-Minlon method to *NN'*-dibenzylbispidine (LVI). Hydrogenation of the latter in acetic acid under pressure in the presence of a palladium catalyst leads to bispidine.[53]

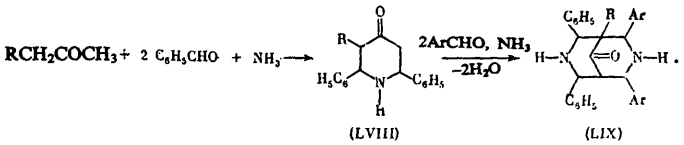


The overall yield of bispidine (VI) recalculated in terms of *N*-benzylpiperidinone is about 60%.

Condensation of acetone or ethyl methyl ketone (but not other ketones) with various aromatic aldehydes and ammonia or their reaction products affords exceptionally readily tetraarylbispidinones (LVII, R = H, CH_3) with aryl substituents at the bridging carbon atoms. In order to obtain bispidinones with various aryl substituents, the reaction is carried out in two stages: the first stage yields diphenylpiperidinones (LVIII, R = H, CH_3), while the second stage gives rise to the bispidinones (LIX):[54-58]

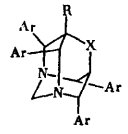


(LVII)



(LVIII) (LIX)

The keto-group in tetraarylbispidinones (LVII) and (LIX) is then reduced to the methylene or hydroxy-group. The condensation of tetraarylbispidines with paraformaldehyde in carbon tetrachloride, dichloroethane, dimethylformamide, or dioxane gives rise to the corresponding tetraaryldiazaadamantanes (LX).



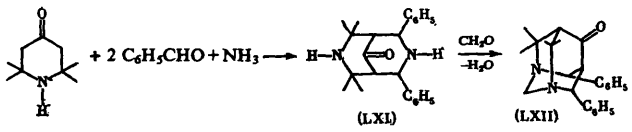
(LX)

R = H, CH_3; X = CH_2, CHOH, CO; Ar = C_6H_5, 4-$CH_3OC_6H_4$, 4-ClC_6H_4, 2-ClC_6H_4, 3,4-$(CH_3O)_2C_6H_3$, 4-$CH_3C_6H_4$, α-C_5H_4N.

Tetraaryldiazaadamantanols (LX, X = CHOH) and tetraaryldiazaadamantanes (LX, X = CH_2) are also obtained by reducing diazaadamantanones (LX, X = CO) with lithium tetrahydroaluminate or by the Wolff–Kishner method.

It has long been assumed,[59,60] that only formaldehyde can condense with diarylbispidine, but it has been found that aromatic aldehydes also react similarly;[56,58] however, the reaction is very slow (45 days) and the yield does not exceed 10%.

By a procedure similar to that used for tetraaryldiazaadamantanes (LX), tetramethyldiphenyldiazaadamantanone (LXII) can be obtained from triacetoneamine via a substituted bispidinone (LXI).[61,62]



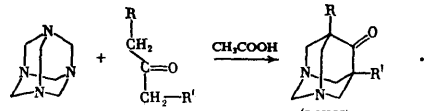
(LXI) (LXII)

Despite the ease of their synthesis, tetraaryldiazaadamantanes (LX) are apparently not very promising because of the cumbersome nature of their molecules, only a small proportion of which corresponds to the diazaadamantane nucleus.

(b) Synthesis of 1,3-diazaadamantan-6-ones

The most convenient and readily available intermediates for the synthesis of various diazaadamantane derivatives are at present 1,3-diazaadamantan-6-ones (LXIII). Until recently, they were obtained by condensing the corresponding ketones with formaldehyde and ammonia. Mainly ketones with activated α- and α′-hydrogen atoms were used in the reaction. 5,7-Diphenyl-,[63-65] 5,7-dimethoxy- and 5,7-diethoxy-,[65,66] 5,7-di(phenylthio)-,[63] 5-phenyl-7-phenylthio- and 5-phenyl-7-*p*-tolylthio-,[67,68] 7-ethoxycarbonyl-5-phenyl-,[69] and 7-methoxycarbonyl-5-phenylthio-1,3-diazaadamantan-6-ones[70] have been obtained in this way. It was shown later that 5,7-dimethyl-1,3-diazaadamantan-6-one can also be obtained by the same method but in a low yield.[71]

A more effective and a more general method of synthesis of diazaadamantanones (LXIII) is based on the condensation of ketones with hexamethylenetetramine.[72-74]



(LXIII)

The replacement of formaldehyde and ammonia by hexamethylenetetramine makes it possible to increase the yield of dimethyldiazaadamantanone (LXIII, R = R′ = CH_3) from 20 to 74% and that of diphenyldiazaadamantanone (LXIII, R = R′ = C_6H_5) from 59 to 90%; however, the most significant feature is that the new method makes it possible to obtain diazaadamantanones not only with two hydrocarbon substituents virtually of any kind but also with one substituent.

The increase in the yield of diazaadamantanones (LXIII) when hexamethylenetetramine is used can be explained by a change in the chemistry of the process. When ketones are condensed with formaldehyde and ammonia, the diazaadamantane structure is formed as a result of a large number of intermolecular reactions,[75] each of which may be accompanied by the formation of side products. On the other hand, in the condensation with hexamethylenetetramine, diazaadamantanones can be formed as a result of a single intermolecular interaction of the protonated form of hexamethylenetetramine with a ketone and subsequent intramolecular rearrangements with elimination of the methylenediamine fragment in one of the concluding stages and the formation of diazaadamantone.

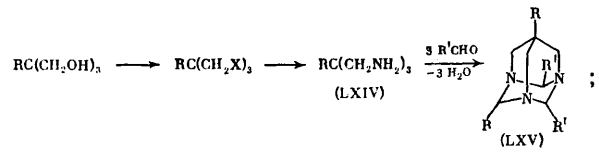
3. Synthesis of 1,3,5-triazaadamantane and its derivatives

1,3,5-Triazaadamantane (IV), which represents, as already mentioned, the products of the condensation of tris(aminomethyl)-methane (VII) with formaldehyde, was first obtained by this reaction in 1952.[76] The initial tris(aminomethyl)methane (VII) is difficult to obtain; it is synthesised by a complex multistage method from malonic and acetonedicarboxylic acid esters via methanetriacetic acid and its amide:[76]

$$HC(CH_2COOH)_3 \rightarrow HC(CH_2CONH_2)_3 \rightarrow HC(CH_2NH_2)_3.$$
(VII)

The homologues of tris(aminomethyl)methane (LXIV) can be obtained much more readily. They are obtained from the available

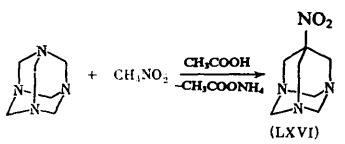
tris(hydroxymethyl)ethane and its homologues via the tribromo-derivatives by the phthalimide method[71] or via the tritosylate and the triazide:[78]



$R = CH_3$, $C_{12}H_{25}$; X = Br, N_3; $R' = H$, C_6H_5, α-C_5H_4N.

Condensation of the triamines (LXIV) with formaldehyde affords triazaadamantane (LXV, R′ = H) derivatives with substituents at the bridgehead carbon atom,[77,79] while condensation with benzaldehyde and 2-formylpyridine gives rise to tribenzyl- and tri-α-pyridyl-triazaadamantanes (LXV, R = CH_3, R′ = H, C_6H_5, α-C_5H_4N) containing substituents also at the aminal carbon atoms.[80,81]

Triazaadamantane derivatives with functional groups at the bridgehead carbon atom are obtained from 7-nitro-1,3,5-triazaadamantane (LXVI), which was first synthesised[82] by condensing nitromethane with formaldehyde and ammonia. A number of modifications of this process were proposed later.[83–92] The best method involves the condensation of hexamethylenetetramine with nitromethane in the presence of acetic acid[83,88,90] first proposed by Kuznetsov et al.[83]



By optimising the process, it was found[93] that the highest yield of the target product (LXVI) is obtained for the molar ratios hexamethylenetetramine : nitromethane : acetic acid = 1 : 1.1 : 2.3. The proposed mechanism of the formation of nitrotriazaadamantane (LXVI) has been described.[94]

The simple and convenient methods of synthesis of azaadamantane derivatives developed in recent years, especially those based on the condensation of hexamethylenetetramine with nitro-compounds and carbonyl compounds, make them extremely readily available for study and for use in the synthesis of other azaadamantane derivatives.

III. Chemical properties

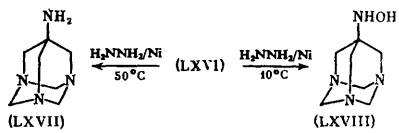
The chemical properties of azaadamantanes are determined primarily by the presence and mutual influence of the nitrogen atoms in the bridgehead positions in the adamantane nucleus. The presence of aminal methylene groups in di- and tri-azaadamantanes is responsible for the tendency of these compounds to react with certain electrophiles. The similarity to adamantane (I), which increases as the number of nitrogen atoms is reduced, suggests that such derivatives, especially azaadamantane (II), have properties characteristic of adamantane, in particular those associated with the increased reactivity of hydrogen atoms at the bridgehead positions.

The mutual influence of nitrogen atoms affects primarily the basicity of azaadamantanes, which decreases with increase in the number of nitrogen atoms in the molecule.[8] Protonation of one of the nitrogen atoms leads to the distribution of the charge between the remaining nitrogen atoms of the molecule. Polyazaadamantanes usually behave as monoacidic bases in their reactions with acids. The aminal character of the methylene groups linking the nitrogen atoms in di- and tri-azaadamantanes is manifested to a much lesser extent than for the usual aminals or hexamethylenetetramine. Thus, whereas the latter readily breaks down on heating with inorganic acids, di- and tri-azaadamantanes do not decompose even on prolonged heating with concentrated hydrochloric acid.

1. Reactions of functional groups

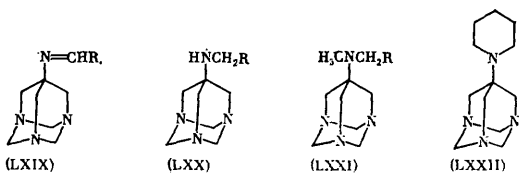
The method of synthesis of azaadamantane described in the previous Section lead as a rule to the formation of derivatives with functional groups which serve as intermediates in the synthesis of other azaadamantane derivatives.

One of such available intermediates is nitrotriazaadamantane (LXVI). It is reduced to 7-amino-1,3,5-triazaadamantane (LXVII) with lithium tetrahydroaluminate,[82] with hydrogen in the presence of nickel,[82,84,85,91] cobalt,[91] rhodium[86,92] or platinum[89,92] catalysts, with zinc in an alkaline medium,[87,92] and with iron or tin in an acid medium.[87,92] The most convenient method involves reduction with hydrazine hydrate at atmospheric pressure in the presence of a nickel catalyst at 50 °C.[94]



At a lower temperature (+10 °C), 7-hydroxyamino-1,3,5-triazaadamantane (LXVIII) is obtained in 67% yield.[94]

Aminotriazaadamantane (LXVII) has also been used as an intermediate in the synthesis of a large number of derivatives. Its reactions with aromatic and aliphatic aldehydes afford the azomethines (LXIX).[95–97] Their hydrogenation in the presence of a platinum catalyst yielded alkyl- and aryl-methylaminotriazaadamantanes (LXX). The reductive methylation of the latter leads to methylalkylaminotriazaadamantanes (LXXI).[86,92]

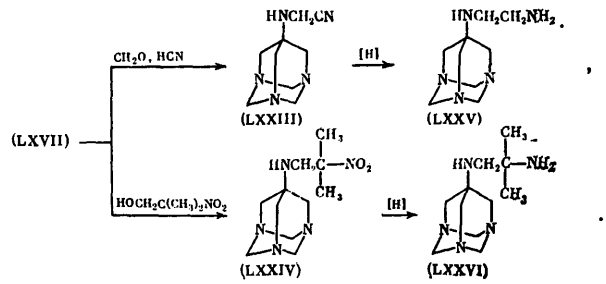


R = C_6H_5, 4-$CH_3C_6H_4$, 4-ClC_6H_4, 2-HOC_6H_4, 4-$CH_3OC_6H_4$, 4-$(CH_3)_2NC_6H_4$, α-C_5H_4N, α-C_4H_3O, CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, iso-C_4H_9, n-C_5H_{11}, H.

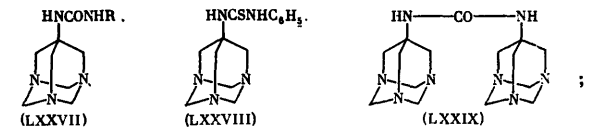
Methylaminotriazaadamantane (LXX, R = H) cannot be obtained by the reductive methylation of aminotriazaadamantane (LXVII), since dimethylaminotriazaadamantane (LXXI, R = H) is formed immediately.[84,86] Treatment of the amine (LXVII) with glutaraldehyde under reductive conditions yields 7-(1-piperidinyl)-1,3,5-triazaadamantane (LXXII).[86]

When aminotriazaadamantane (LXVII) is used as the amine component in aminomethylation reactions, only one hydrogen atom of the amino-group in compound (LXVII) participates in the reaction. The products of the condensation of compound (LXXVII) with formaldehyde and hydrocyanic acid [compound (LXXIII)] or

with 2-nitropropane [compound (LXXIV)] were reduced to the corresponding aminoethyl derivatives (LXXV) and (LXXVI).[84,89,98]



Triazaadamantanylureas (LXXVII) have been obtained by the reaction of the amine (LXVII) with isocyanates,[84,87,99,100] while the reaction with phenyl isothiocyanate afforded thiourea (LXXVIII). Heating of aminotriazaadamantane (LXVII) with urea gives rise to 1,3-bis(triazaadamantyl)urea (LXXIX).[99,101]



R = C_6H_5, 3-ClC_6H_4, 4-ClC_6H_4, C_6H_{11}.

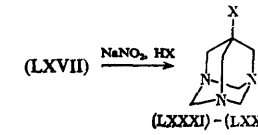
The synthesis of the amides (LXXX) from aminotriazaadamantane (LXVII) involves certain difficulties because acylating agents such as carboxylic acid anhydrides and chlorides can decompose the triazaadamantane skeleton. Therefore, in order to obtain 7-acetamido-1,3,5-triazaadamantane (LXXX, R = CH_3), the amine (LXVII) was heated with isopropyl acetate,[86] while the benzamido-derivative (LXXX, R = C_6H_5) and the nitrobenzamido-derivatives (LXXX, R = 3-$O_2NC_6H_4$, 4-$O_2NC_6H_4$) were obtained by heating the methyl benzoate and nitrobenzoate.[99] The nitrobenzamido-derivatives were reduced to the aminobenzamido-derivatives (LXXX, R = 3-$H_2NC_6H_4$, 4-$H_2NC_6H_4$).[99]



R = CH_3, C_6H_5, 3-$O_2NC_6H_4$, 4-$O_2NC_6H_4$, 3-$H_2NC_6H_4$, 4-$H_2NC_6H_4$, $C_6H_5CONHCH_2$, $C_2H_5OCONHCH_2$, $CH_3OCONHCH_2$, H_2NCH_2.

The benzamido-derivative (LXXX, R = C_6H_5) has also been synthesised by the carbodiimide method and the mixed anhydride method.[102] The acylglycinamido-derivatives (LXXX, R = $C_6H_5CONHCH_2$, $C_2H_5OCONHCH_2$, $CH_3OCONHCH_2$) have been obtained by the mixed anhydride method.[102] Their hydrolysis led to the glycinamido-derivative (LXXX, R = H_2NCH_2).[102]

In order to convert the readily available aminotriazaadamantane (LXVII) into other triazaadamantane derivatives, its diazotisation with sodium nitrite was investigated in different acids.[83,87,94] Triazaadamantanol could not be synthesised by this procedure, but, when the reaction was carried out in concentrated hydrochloric and hydrobromic acids, 7-chloro- and 7-bromo-1,3,5-triazaadamantanes (LXXXI) and (LXXXII) were obtained in preparative yields.

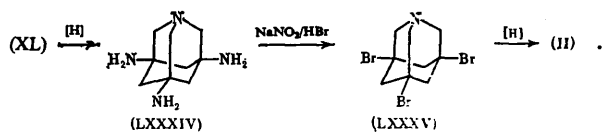


X=Cl (LXXXI), Br (LXXXII), SCN (LXXXIII).

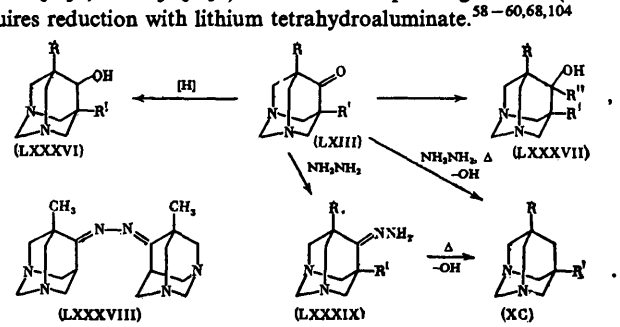
The diazotisation of compound (LXVII) in sulphuric acid in the presence of potassium thiocyanate leads to 7-thiocyanato-1,3,5-triazaadamantane (LXXXIII).[94] Heating of the latter with Raney nickel affords the unsubstituted triazaadamantane (IV).

Triazaadamantane (IV) has been synthesised in a virtually quantitative yield by reducing bromotriazaadamantane (LXXXII) with hydrazine hydrate in the presence of a nickel catalyst.[94] This is the last stage in what is nowadays the most convenient three-stage scheme for the synthesis of 1,3,5-triazaadamantane (IV) from the available nitrotriazaadamantane (LXVI).[94]

The unsubstituted 1-azaadamantane (II) can be obtained via a similar scheme from 3,5,7-trinitro-1-azaadamantane (XL), since it has been shown[103] that the diazotisation of 3,5,7-triamino-1-azaadamantane (LXXXIV), obtained by reducing compound (XL) [27] with sodium nitrite in concentrated hydrobromic acid, results in the substitution of the amino-group by a bromine atom, as in the diazotisation of aminotriazaadamantane (LXVII), and in the formation of 3,5,7-tribromo-1-azaadamantane (LXXXV). Thus deamination accompanied by substitution of aminoazaadamantane with preferential formation of halogenoazaadamantanes is a common reaction for compounds of this class; however, it does not extend to 1-aminoadamantane, which is converted into adamantan-1-ol under similar conditions.



The diazaadamantanones (LXIII) are intermediates for the synthesis of various derivatives of diazaadamantane, particularly those with functional groups at the C(6) atom. The reactivity of the carbonyl group in these compounds is determined to a large extent by the number and character of the substituents at the bridgehead positions.[104] In the presence of only one substituent or two substituents such as the methyl group, diazaadamantanones (LXIII) are reduced to 1,3-diazaadamantan-6-ols (LXXXVI, R = H, R′ = CH_3 or R = R′ = CH_3) even on treatment with sodium tetrahydroborate,[104] whereas the synthesis of the diazaadamantanols (LXXXVI, R = R′ = C_6H_5, $C_6H_5CH_2$, C_6H_5S or R = C_6H_5, R′ = C_6H_5S, 4-$CH_3C_6H_5S$) from the corresponding ketones (LXIII) requires reduction with lithium tetrahydroaluminate.[58-60,68,104]

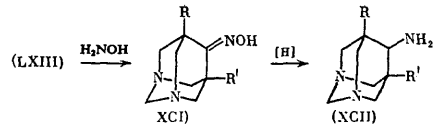


Various arylthiodiazaadamantanones (LXIII, R and/or R′ = C_6H_5S) have been obtained with the aim of their subsequent conversion into diazaadamantane derivatives without substituents at the bridgehead positions by eliminating sulphur, but the study of this reaction demonstrated their interesting and important feature: on heating with Raney nickel in alcohol, monoarylthioadamantanones (LXIII, R = C_6H_5S, R′ = C_6H_5, $COOCH_3$) smoothly eliminate sulphur with simultaneous reduction of the keto-group to an alcoholic group and are converted into monosubstituted diazaadamantanols (LXXXVI, R = H, R′ = C_6H_5, $COOCH_3$), whereas di(phenylthio)diazaadamantanone (LXIII, R = R′ = C_6H_5S) does not eliminate sulphur under these conditions and is merely reduced to di(phenylthio-diazaadamantanol (LXXXVI, R = R′ = C_6H_5S).[63]

Diazaadamantanones (LXIII) react with methylmagnesium iodide and organolithium compounds affording the corresponding tertiary alcohols (LXXXVII).[104,105]

Depending on the structure of the substituents R and R′, diazaadamantanones (LXIII) react in different ways with hydrazine: on heating with hydrazine hydrate, methyldiazaadamantanone (LXIII, R = CH_3, R′ = H) affords only the azine (LXXXVIII) as the stable product, while phenyl- and dimethyl-diazaadamantanones (LXIII, R = H, R′ = C_6H_5, CH_3 or R = R′ = CH_3) readily form the corresponding hydrazones (LXXXIX) whose fusion with alkali gives rise to the diazaadamantanes (XC).[104] Diazaadamantanones with two substituents such as the phenyl, phenylthio-, or *p*-tolylthio-group are reduced to the diazaadamantanes (XC, R = R′ = C_6H_5, C_6H_5S or R = C_6H_5, R′ = C_6H_5S, $CH_3C_6H_4S$) by the Huang-Minlon method.[59,60,63,68,104]

Monosubstituted diazaadamantanones and dimethyldiazaadamantanone react with hydroxylamine to form the oximes (XCI, R = H, R′ = CH_3, C_6H_5 or R = R′ = CH_3) in an aqueous medium,[104] whereas the oxime of diphenyldiazaadamantanone (XCI, R = R′ = C_6H_5) is formed only after prolonged heating with hydroxylamine in a pyridine-ethanol mixture in a yield of only 48%.[106]

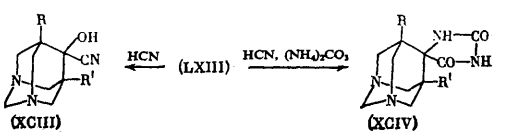


XCI) (XCII)

R=H, R′=CH_3, C_6H_5; R=R′=CH_3, C_6H_5.

The oximes (XCI) are reduced to 6-amino-1,3-diazaadamantanes (XCII) by a nickel-aluminium alloy in an aqueous alkaline medium.[104]

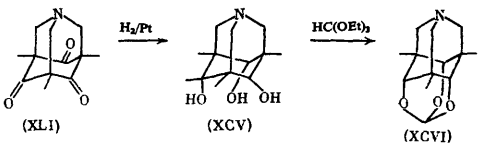
The diazaadamantanones (LXIII) with two bulky substituents, such as the phenyl and phenylthio-groups, do not form cyanohydrins, whereas methyl- and dimethyl-diazaadamantanones are readily converted into the corresponding cyanohydrins (XCIII) on heating with acetone cyanohydrin. 1,3-Diazaadamantane-6-spiro-5′-hydantoins (XCIV) were obtained from the cyanohydrins by the Bucherer method.[107]



(XCIII) (XCIV)

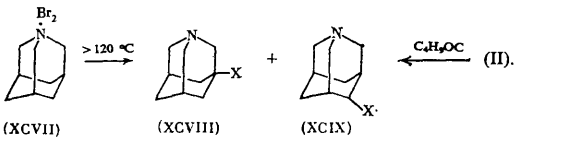
R=H, R′=CH_3; R=R′=CH_3.

The reactivity of the monoazaadamantanones (XLI) and (XLII) is still to be investigated, but so far it has been shown that the hydrogenation of trimethylazaadamantanetrione (XLI, R = R′ = CH_3) in the presence of a platinum catalyst results in the formation of trimethylazaadamantanetriol (XCV) with the axial disposition of all three hydroxy-groups relative to the cyclohexane ring, which has been confirmed by its conversion into the heterodiamantane (XCVI).[36]



(XLI) (XCV) (XCVI)

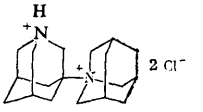
The most important intermediates in the synthesis of derivatives of adamantane (I) itself are halogenoadamantanes obtained by its halogenation.[7] The halogenation of 1-azaadamantane (II) has been investigated.[108,109] When bromine is added to a solution of azaadamantane (II) in carbon tetrachloride, complex (XCVII) is formed. When an attempt is made to obtain from it 3-bromo-1-azaadamantane (XCVIII, X = Br) via an ionic mechanism by adding aluminium chloride or bromide and bromine, it is possible to isolate only the complexes of azaadamantane with these salts. On the other hand, on heating complex (XCVII) to 120 °C, a mixture of 3- and 4-bromo-1-azaadamantanes (XCVIII, X = Br) and (XCIX, X = Br) is formed.



(XCVII) (XCVIII) (XCIX)

The absence of 2-bromo-1-azaadamantane from the radical bromination products probably indicates its instability.[108] 3-Chloro- and 4-chloro-1-azaadamantanes (XCVIII) and (XCIX) with X = Cl have been obtained by irradiating with UV light a mixture of azaadamantane and t-butyl hypochlorite.[108] Comparison of the ratios of the products of the radical halogenation of adamantane (I) and 1-azaadamantane (II) shows that the introduction of a nitrogen atom into the adamantane nucleus does not have a significant influence on the radical halogenation reaction.

When a solution of azaadamantane (II) in carbon tetrachloride is irradiated with UV light or when it is treated with hydrogen peroxide, the salt (C) is formed and can be regarded formally as the product of the alkylation of azaadamantane with 3-chloro-1-azaadamantane.

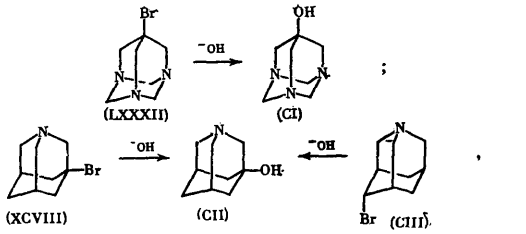


(C)

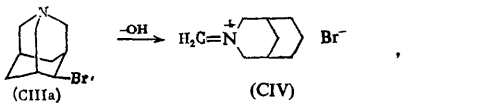
The same product is also formed in the photochemical chlorination of azaadamantane with trichloromethanesulphonyl chloride.[108] Here it was shown that 3-chloro-1-azaadamantane (XCVIII, X = Cl) does not participate in the formation of the salt (C), since irradiation of a mixture of compound (XCVIII, X = Cl) and azaadamantane (II) does not lead to the formation of the salt (C). On this basis, it has been suggested that the alkylating agent in the formation of compound (C) is the 1-azaadamantane radical-cation.[109]

The halogen atoms in 1-halogenoadamantanes, which are key intermediates in the chemistry of adamantane (I), are comparatively

readily substituted by nucleophiles. Kinetic studies have shown that the rate of hydrolysis of 3-bromo-1-aza- and 7-bromo-1,3,5-triaza-adamantanes (XCVIII, X = Br) and (LXXXII) is lower by several orders of magnitude than the rate of hydrolysis of their analogue—1-bromoadamantane.[108,110] The passivating influence of nitrogen atoms can be explained by their electron-accepting inductive effect and the impossibility, for geometrical reasons, of their anchimeric involvement, as in other β-halogenoamines. Hydrolysis of the halogenoazaadamantanes indicated leads to 1,3,5-adamantan-7-ol (CI) and 1-azaadamantan-3-ol (CII), which could not be obtained by other methods hitherto.[110]



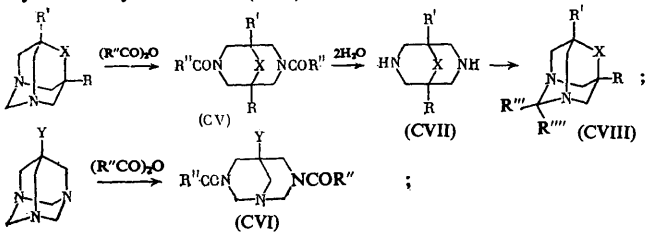
Hydrolysis of the isomeric 4-bromo-1-azaadamantanes (CIII) proceeds in different ways: the isomer (CIIIa) with the bromine atom in the axial position relative to the piperidine ring is unstable under hydrolysis conditions and is converted into the methylene-immonium cation (CIV), i.e.



where the isomer (CIIIb) with the equatorial orientation, obtained by treating 1-azaadamantan-4-ol (XII) with phosphorus pentabromide, hydrolyses to 3-hydroxy-1-azaadamantan (CII) and not to the 4-hydroxy-derivative.[16]

2. Reactions with elimination of aminal methylene groups

The di- and tri-azaadamantanes containing aminal methylene group split them off on treatment with various reagents. Diazaadamantanes react with carboxylic acid anhydrides and chlorides to form diacylbispidines (CV), while triazaadamantanes afford diacyltriazabicyclononanes (CVI).[63,64,67,68,71,112–116]



X = CO, CHOH, CH_2; Y = NO_2, NHOH, NH_2, NHCOR;
R, R′ = H, C_6H_5S, 4-$CH_3C_6H_4S$;
R″ = H, CH_3, C_6H_5, C_2H_5O, $ClCH_2$;
R‴ = H, R′′′′ = CH_3, C_2H_5, C_3H_7, C_6H_5, 4-$O_2NC_6H_4$, 4-$CH_3OC_6H_4$, α-C_4H_3O, 4-($ClCH_2CH_2$), NC_6H_4, $H(CHOH)_4$, $H(CHOH)_5$ or R‴R′′′′ = $(CH_2)_4$, $CH_2)_5$.

NN-Diformylbispidines (CV, R″ = H) can be obtained by the reaction of diazaadamantanes with chloroform in an alkaline medium.[65,114]

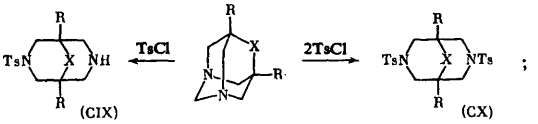
Arylthio- and diarylthio-diacetylbispidines (CV, R and/or R′ = C_6H_5S, 4-$CH_3C_6H_4S$) readily eliminate sulphur on treatment with Raney nickel, being converted into diacetylbispidines (CV, R and/or R′ = H) with one or two bridgehead positions free from substituents.[12,63,67,68]

The bispidines (CVII) without substituents at the nitrogen atoms can be obtained by the hydrolysis of diacetylbispidines (CV). They condense with various aldehydes and ketones to diazaadamantane derivatives (CVIII) with substituents at the aminal carbon atom.[63,64,68,71,115]

Under hydrolysis conditions, the bispidinones (CVII, X = CO) can be converted into the corresponding diazaadamantanones (LXIII).[63]

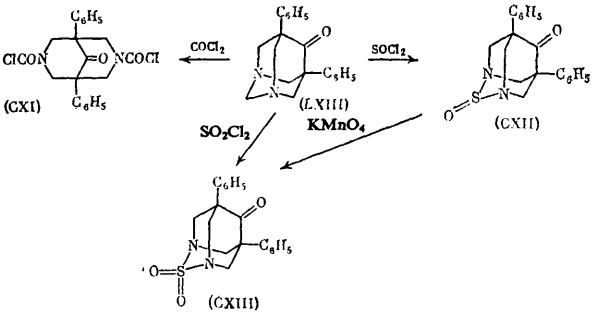
The hydroxyamino- and amino-derivatives (CVI, Y = NHOH, NH_2) can be obtained by hydrogenating nitrodiacetyltriazabicyclononane (CVI, Y = NO_2).[84,85]

Treatment of diazaadamantanes with toluene-*p*-sulphonyl chloride can yield *N*-tosylbispidines (CIX) or *NN*′-ditosylbispidines (CX).[63,109]

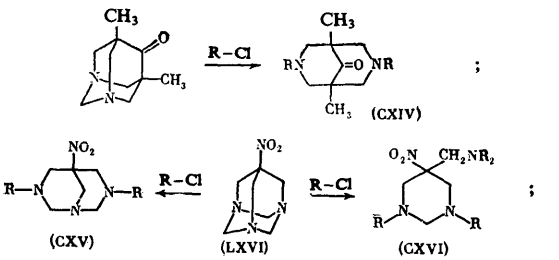


X = CO, CH_2; R = H, C_6H_5.

The attempt to replace the aminal methylene group in diphenyldiazaadamantane (LXIII, R = R′ = C_6H_5) by treating it with phosgene led to the formation of only the bispidine derivative (CXI), whereas treatment with thionyl or sulphuryl chloride in pyridine affords the 2-oxide (CXII) of the 2,2-dioxide (CXIII) of 5,7-diphenyl-1,3-diaza-2-thiaadamantan-6-one; the former can be oxidised to the latter with potassium permanganate.

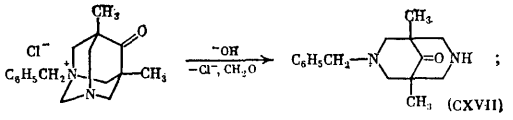


The interaction of di- and tri-azaadamantanes with benzyl, allyl, and propargyl chlorides, α-chloroketones, and chloroacetic acid esters can also be accompanied by the elimination of the aminal methylene groups; triazaadamantanes can then split off both one and two methylene groups, affording the corresponding derivatives of bispidine (CXIV), triazabicyclononane (CXV), and hexahydropyrimidine (CXVI).[118,119]

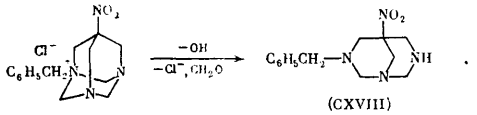


R = $C_6H_5CH_2$, CH_2=$CHCH_2$, HC≡CCH_2, $C_6H_5COCH_2$, $C_2H_5OOCCH_2$.

These reactions can be explained by the fact that, in the quaternary salts formed from di- and tri-azaadamantanes, the bond between the aminal methylene group and the quaternary nitrogen atom is weakened, which has been demonstrated by the X-ray diffraction analysis of the methiodide of diphenyldiazaadamantanone (LXIII, R = R′ = C_6H_5).[120] On treatment with bases, the aminal methylene group therefore splits off, affording the bispidine and triazabicyclononane derivatives (CXVII) and (CXVIII).[118,119]

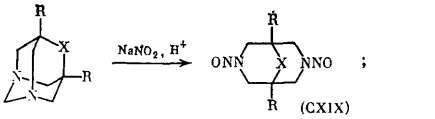


(CXVII)



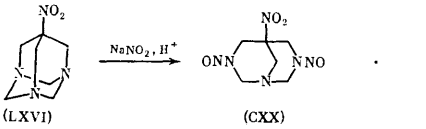
(CXVIII)

Treatment of di- and tri-azaadamantanes with nitrous acid leads to the formation of the dinitroso-derivatives of bispidine (CXIX) and triazabicyclononane (CXX).[63,121,122]



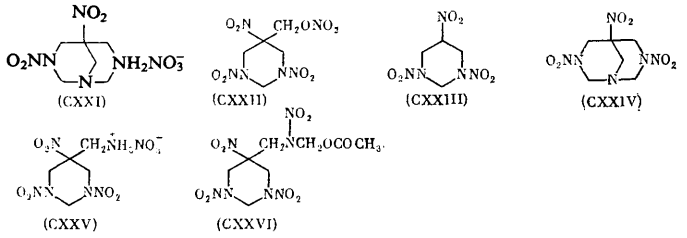
(CXIX)

R=H, C_6H_5; X=CO, CH_2.



(LXVI) (CXX)

Nitration of nitrotriazaadamantane (LXVI) [123] resembles the nitration of hexamethylenetetramine[124,125] and leads to the following products (depending on the conditions):

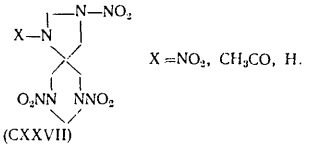


(CXXI) (CXXII) (CXXIII) (CXXIV)

(CXXV) (CXXVI)

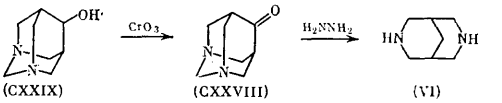
The bicyclic product (CXXI) is formed in the nitration of compound (LXVI) with fuming nitric acid at −40 °C, whereas on raising the temperature to −10 °C more far-reaching decomposition of the triazaadamantane skeleton takes place with formation of the monocyclic product (CXXII). This product is stable on heating in alcohols, but, on boiling in water, it is converted into 1,3,5-trinitrohexahydropyrimidine (CXXIII). Nitration with a mixture of concentrated nitric and sulphuric acids results in the formation of 3,5,7-trinitro-1,3,7-triazabicyclo[3.3.1]nonane (CXXIV). Nitration of compound (LXVI) with a mixture of concentrated nitric acid and ammonium nitrate gives rise to the product (CXXV), while nitration with a mixture of fuming nitric acid, acetic anhydride, and acetic acid at the usual temperature affords the product (CXXVI).

When aminotriazaadamantane (LXVII) is nitrated with fuming nitric acid, the tetraazabicyclic products (CXXVII) are formed.



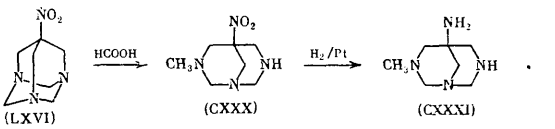
(CXXVII)

Under severe conditions, the aminal methylene groups can be split off also on treatment with hydrazine. Thus when an attempt was made to reduce 1,3-diazaadamantan-6-one (CXXVIII), [obtained by oxidising diazaadamantanol (CXXIX) with chromium trioxide[126]] by the Huang–Minlon method, bispidine (VI) was synthesised instead of diazaadamantane (III).[127]



(CXXIX) (CXXVIII) (VI)

The opening of one of the rings of nitrotriazaadamantane (LXVI) with the simultaneous reduction of the methylene group to the methyl group occurs when it is heated with formic acid under the conditions of the Leuckart reaction. The 3-methyl-5-nitro-1,3,7-triazabicyclo[3.3.1]nonane (CXXX) was hydrogenated to the amine (CXXXI) in the presence of a platinum catalyst.[23]

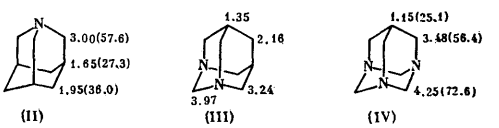


(LXVI) (CXXX) (CXXXI)

IV. Physical and spectroscopic properties

The nitrogen atoms hardly affect the spherical shape (sphere diameter 6.71 Å) [7] of the adamantane nucleus, which represents the unit cell of the crystal lattice of diamond. Such molecular geometry determines many physical and spectroscopic characteristics of azaadamantanes.

By virtue of the high molecular symmetry, the NMR spectra of azaadamantanes are exceptionally simple and characteristic. The chemical shifts δ (in p.p.m.) of the protons measured in CCl_4 are listed below[8] (the ^{13}C chemical shifts are indicated in brackets[128]):



(II) (III) (IV)

The spectra of various azaadamantane derivatives have been published in a number of communications including Refs. 73, 74, 80, 112, and 129–131.

The protons at the bridgehead positions are manifested in all cases by broadened singlets in a higher field the greater the number of nitrogen atoms in the molecule.

The spectra of mono- and tri-azaadamantanes (II) and (IV) having the same molecular symmetry are similar and consist of singlets, due to the protons of the NCH_2C groups, and of the AB-systems due to the remaining protons. On the basis of the splitting into doublets of the AB-systems, induced by the interaction

with the protons of the NCH_2C groups, a definite orientation relative to the symmetry axes of the molecules can be assigned to the corresponding protons.

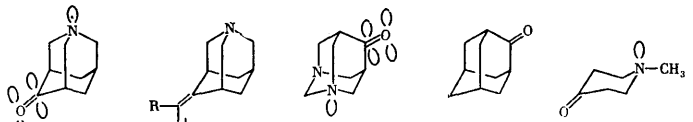
In the spectrum of diazaadamantane (III) the protons at the C(6) atoms and of the aminal methylene group are manifested by singlets, while the protons of the NCH_2C groups are manifested by an AB-system.

It is noteworthy that, whereas the nitrogen atoms shield the protons at the bridgehead positions [δ = 1.87 p.p.m. for the methylidyne proton of adamantane (I)], the protons of the methylene groups in the β-positions are strongly deshielded [δ = 1.74 p.p.m. for the methylene protons of adamantane (I)].

The mass spectra of triazaadamantane (IV) and its derivatives contain intense peaks due to molecular ions, which decompose subsequently via two independent pathways depending on the character of the substituents. If the substituents of the C(7) atom are H, Cl, Br, and NO_2, then they are readily abstracted and the spectra of different derivatives differ little from one another. On the other hand, if the substituents are electron-donating groups such as the amino-group, they are not split off and persist in all the main ions of the mass spectrum. The molecular ions of halogenotriazaadamantanes can split off, apart from halogen atoms, also hydrogen halide molecules, although with a lower probability. The most intense ion in the mass spectra of triazaadamantanes is, as for hexamethylenetetramine, the $[C_2H_4N^+]$ ion.[132]

The mass spectra of diazaadamantanones (LXII) have been considered.[74] The decomposition of the molecular ions is accompanied by the breakdown of the adamantane nucleus with formation of the ions $[C_2H_4N]^+$, $[M-C_2H_4N]^+$, $[C_3H_2RCO]^+$, and $[M-C_2H_5N]^+$, the last one being as a rule the most intense.

The UV spectra of azaadamantanone (XI), diazaadamantanone (CXXVIII),[80,127,129] and substituted 6-methyleneazaadamantanes (CXXXII, R = R′ = H, CN; R = $COOC_2H_5$, R′ = H, CN) are of special interest.[131] The last compounds were obtained from the ketone (XI) via Wittig, Horner, or Knoevenagel reactions.[17]



(XI) (CXXXII) (CXXVIII) (CXXXIII) (CXXXIV)

The point is that conditions under which the *n* electrons of the nitrogen atom can interact with the π-systems of the multiple bonds are largely maintained in these compounds: the orbitals of these electrons are almost parallel to one another and to the central bond along the σ-bonds separating them.[133–138] Such interaction, which has been called "σ-bonding interaction" or "σ-conjugation",[133] leads to the appearance in the near UV absorption spectrum of these compounds of intense bands which are not characteristic of the corresponding chromophores considered separately. Thus, whereas the spectrum of the adamantanone (CXXXIII) shows only a weak absorption with λ_{max} = 290 nm ($\varepsilon \simeq 19$), due to the $n \rightarrow \pi^*$ transition in the keto-group, in the case of azaadamantanones (XI) and (CXXVIII), a strong absorption is observed with λ_{max} = 243 nm (ε = 1366) (in hexane) and 255 nm ($\varepsilon \simeq 1700$) (in dioxane) respectively. *N*-Methylpiperidinone (CXXXIV), which is related to compound (CXXXIII) as regards the distribution of the chromophores and whose lone electron pair occupies an axial position, does not absorb at all in the near UV.

The basicity of the azaadamantanes (II)–(IV) in water (see above) and in dimethyl sulphoxide has been determined by potentiometric titration.[8] The p*K* values in water at 22 °C for 1-azaadamantane (IV) (2.96) 4-methylene-1-azaadamantane (CXXXII, R = R′ = H) (4.16), and 1-azaadamantan-4-one (XI) (5.43) have been published.[13] On the other hand, the basicity of azaadamantane derivatives in the gas phase has been determined[135] by cyclotron magnetic resonance.

The lower basicity of methyleneazaadamantane and azaadamantanone compared with azaadamantane is not caused solely by the "σ-bonding interaction", since 1-methyl-4-piperidinone (CXXXIV) (p*K* = 6.01), in which σ-conjugation is impossible, is also less basic than *N*-methylpiperidine (p*K* = 3.92).[131]

V. Conclusion

The development, especially in recent years, of simple and convenient methods of synthesis of azaadamantanes has made them entirely available for wide-scale research and practical applications.

There are as yet only a few published data concerning the practically useful properties and the possible applications of azaadamantanes. There are patent data[139] showing that the alkylaminotriazaadamantanes (LXX) and (LXXI) can be used as a solid rocket fuel, while their solutions in hydrocarbons can be used as a liquid rocket fuel. It has been suggested that the aminotriazaadamantane (LXVII) as well as the azomethines (LXIX) and ureas (LXXVII) obtained from it be used as stabilisers of various polymers against thermal light-induced ageing.[91,95,98,100,140] Diacetyltriazabicyclononanes (CVI) catalyse the formation of polyurethane resins and prevent the phase separation of liquid epoxy-resins in alcohol.[115] It has been suggested that certain triazaadamantane derivatives be used as modifying agents for rubbers.[141–145]

The thermal stability of azaadamantanes and their capacity for complex formation with various metal salts permit their application as additives to fuel-lubricating materials, as corrosion inhibitors, as high-temperature oil thickening agents, and as emulsifying agents and also for the regeneration of ion-exchange resins.[82]

Azaadamantanes can be used as catalysts in various processes,[8] for example, in the additional purification of a gas to remove sulphur.[146,147]

The use of azaadamantanes for the preparation of therapeutic drugs in medicine and veterinary science is particularly promising. It has been reported that diphenyldiazaadamantanol (LXXXVI, R = R′ = C_6H_5) and other diazaadamantanols exhibit a strychnine-like activity,[148] while diphenyldiazaadamantane (XC, R = R′ = C_6H_5) and some of its derivatives have a convulsant activity (Ref. 8, pp 348, 349). Derivatives of the trimethylazaadamantane (XLVII, X = COR) (R = alkyl, aryl, pyridyl, naphthyl, coumaryl, etc.) possess cardiovascular and antiarrhythmic activities.[149,150]

Experiments on mice have shown that the antiviral activity of 7-amino-1,3,5-triazaadamantane (LXVII) is close to that of the familiar preparation midantane.[151,152]

The available data concerning the practically useful properties of azaadamantanes and the specific chemical and physicochemical properties discovered in them lead to their differentiation as a separate new class of organic compounds of interest not only to chemists but also to representatives of other branches of science and engineering.

References

1. H Stetter *Angew. Chem.*, 1962, **74** 361
2. G Gelbard *Ann. Chim.*, 1969, **4** 331
3. T Sasaki *Kagaky no Ryoiki*, 1971, **25** 27
4. A V Averina, N S Zefirov *Usp. Khim.*, 1976, **45**(6) 1077 [English translation in *Russ. Chem. Rev.*, 1976(6)]
5. Z Kafka, V Galik *Sbornik Vysoke Skoly Chem.-Technol. v Praze. Technologie Paliv.*, 1981, Vol. 34, p. 349
6. T Sasaki *Adv. Heterocycl. Chem.*, 1982, **30** 79
7. R S Fort *Adamantane. The Chemistry of Diamond Molecules*, Decker, New York–Basel, 1976, 354 pp
8. L Meurling *Chem. Scr.*, 1975, (7) 23
9. R Lukes, V Galik *Collect. Czech. Chem. Commun.*, 1954, **19** 712
10. M S Newman, H S Lowrie *J. Am. Chem. Soc.*, 1954, **76** 4598
11. R Fusco, G Bianchetti *Gazz. Chim. Ital.*, 1956, **86** 500
12. V Galik, Z Kafka, M Safar, S Landa *Collect. Czech. Chem. Commun.*, 1974, **39** 895
13. W N Speckamp, J Dijkink, H O Huisman *J. Chem. Soc., Chem. Commun.*, 1970, 196
14. W N Speckamp, J Dijkink, A W Dekkers, H O Huisman *Tetrahedron*, 1971, **27** 3143
15. W N Speckamp, J Dijkink, H O Huisman *J. Chem. Soc., Chem. Commun.*, 1970, 197
16. W N Speckamp, J D Dijkink *Heterocycles*, 1974, **2** 291
17. A W Dekkers, W N Speckamp, H O Huisman *Tetrahedron Lett.*, 1971, 489
18. B Th Reints, W N Speckamp *Tetrahedron*, 1979, **35** 267
19. W N Speckamp, H van Oosterhout *Heterocycles*, 1977, 7 165
20. G H Wahl, S Zemyan *Tetrahedron Lett.*, 1982, **23** 4545
21. W N Speckamp, J D Dijkink *Heterocycles*, 1974, **2** 291
22. B M Mikhailov, E A Shagova *J. Organomet. Chem.*, 1983, **258** 131
23. T Severin, R Schmitz *Chem. Ber.*, 1962, **95** 1417
24. L A Kaplan *J. Am. Chem. Soc.*, 1964, **86** 740
25. L I Bagal, M D Boldyrev, G D Georgievskaya *Zh. Org. Khim.*, 1970, **6** 1342
26. V A Sokolova, M D Boldyrev, B V Gisparov, T N Timofeeva *Zh. Org. Khim.*, 1972, **8** 1243
27. T Severin, R Schmitz *Chem. Ber.*, 1963, **96** 3081
28. V A Sokolova, M D Boldyrev, B V Gisparov *Zh. Org. Khim.*, 1976, **12** 1525
29. T Severin, R Schmitz, H-L Temme *Chem. Ber.*, 1964, **97** 467
30. M J Foreman, R Foster, M J Strause *J. Chem. Soc., B*, 1970, 147
31. T Severin, D Batz, H Kramer *Chem. Ber.*, 1971, **104** 950
32. G D Georgievskaya, M D Boldyrev, L I Bagal *Zh. Org. Khim.*, 1971, 7 1618
33. L I Bagal, M D Boldyrev, G D Georgievskaya, V P Boiko *Zh. Org. Khim.*, 1969, **5** 28
34. L I Bagal, M D Boldyrev, G D Georgievskaya *Zh. Org. Khim.*, 1970, **6** 731
35. N Risch *J. Chem. Soc., Chem. Commun.*, 1983, 532
36. N Risch *Chem. Ber.*, 1985, **118** 4849
37. N Risch, W Saak *Angew. Chem.*, 1982, **94** 926
38. N Risch *Chem. Ber.*, 1985, **118** 4073
39. N Risch *Z. Naturforsch., B*, 1986, **41** 787
40. R M Black *Synthesis*, 1981, **10** 829
41. A P Krapcho *Synthesis*, 1982, **11** 893
42. P Rosenmund, W H Haase, J Bauer, R Frishe *Chem. Ber.*, 1975, **108** 1871
43. H Musso, K Naumann, K Crychtol *Chem. Ber.*, 1967, **100** 3614
44. French P. 2 358 404; *Chem. Abs.*, 1978, **89** 197 343
45. B Delpech, Q Khuong *J. Org. Chem.*, 1978, **43** 4808
46. A Pancrazi, I Kabore, B Delpech, Q Khuong-Huu *Tetrahedron Lett.*, 1979, 3729
47. B Delpech, Q Khuong-Huu *J. Org. Chem.*, 1978, **43** 4899
48. A Pancrazi, I Kabore, Q Khuong-Huu *Bull. Soc. Chim. Fr.*, 1977, 162
49. N S Zefirov, S V Rogozina *Usp. Khim.*, 1973, **42**(3) 423 [English translation in *Russ. Chem. Rev.*, 1973(3)]
50. S Chiavarelli, F Toffler, D Misiti *Ann. Inst. Super Sanita*, 1968, (4) 157
51. V Galik, S Landa *Collect. Czech. Chem. Commun.*, 1973, **38** 1101
52. K O Orazil'dyev, Kh A Aslanov, A S Sadykov *Sbornik Nauchnykh Trudov Turkmen NII Selektsii I Semenovodstva Tonkovoloknistogo Khopchatnika* (Selection and Seed-growing of the Fine Fibre Cotton Plant), 1976, No. 14, p. 156
53. P C Ruenitz, E E Smissman *J. Heterocycl. Chem.*, 1976, **13** 1111
54. S Chiavarelli, G Settimj, F M Rabagliati Canessa *Gazz. Chim. Ital.*, 1960, **90** 311
55. Z Kafka, V Galik, M Safar *Collect. Czech. Chem. Commun.*, 1975, **40** 174
56. V Baliah, R Usha *Indian J. Chem.*, 1977, **158** 684
57. H Quast, B Muller *Chem. Ber.*, 1980, **113** 2959
58. H Quast, B Muller, E-M Peters, et al. *Chem. Ber.*, 1982, **115** 3631
59. I N Azerbaev, T T Omarov, S A Baisalbaeva, V S Bazalitskaya *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.*, 1976, (4) 55
60. I N Azerbaev, T T Omarov, K Al'mukhanova, S A Baisalbaeva *Zh. Org. Khim.*, 1976, **12** 1207
61. V Baliah, R Usha *Indian J. Chem.*, 1972, **10** 319
62. I N Azerbaev, T T Omarov, S A Baisalbaeva *Zh. Org. Khim.*, 1975, **45** 1404
63. H Stetter, J Schafer, K Dieminger *Chem. Ber.*, 1958, **91** 598
64. S Chiavarelli, G Settimj *Gazz. Chim. Ital.*, 1958, **88** 1234
65. T Sasaki, S Eguchi, T Kirigama, Y Sakito *J. Org. Chem.*, 1973, **38** 1548
66. J Kuthan, J Paleck *Collect. Czech. Chem. Commun.*, 1963, **28** 2260
67. A I Kuznetsov, P F Yakushev, B V Unkovskii *Zh. Org. Khim.*, 1974, **10** 341
68. A I Kuznetsov, P F Yakushev, B V Unkovskii *Khimiya i Perspektivy Primeneniya Uglevodorodov Ryada Adamantana i Rodstvennykh Soedinenii: Tezisy Dokladov* (The Chemistry and Likely Applications of Adamantane Hydrocarbons and Related Compounds: Abstracts of Reports), Kiev, 1974, p. 74
69. P F Yakushev, A I Kuznetsov, V V Tolstikov, B V Unkovskii *Zh. Org. Khim.*, 1977, **19** 2452
70. A I Kuznetsov, I P Boiko, T D Sokolova, et al. *Khim. Geterotsikl. Soedin.*, 1985, 661
71. Ts E Agadzhahyan, G L Arutyunyan *Arm. Khim. Zh.*, 1981, **34** 963
72. A I Kuznetsov, E B Basargin, B V Unkovskii, USSR P. 1 225 843; *Byull. Izobret.*, 1986, (15)
73. A I Kuznetsov, E B Basargin, M Kh Ba, et al. *Zhur. Org. Khim.*, 1985, **21** 2607

74. A I Kuznetsov, E B Basargin, A S Moskovkin, et al. *Khim. Geterotsikl. Soedin.*, 1985, 1679
75. S Chiavarelli, F Toffler, P Mazzeo, L Gramicciomi *Farmaco, Ed. Sci.*, 1968, **23** 360
76. R Lukes, K Syhora *Chem. Listy*, 1952, **46** 731
77. E B Fleischer, A E Gebala, A Levy, P A Tasker *J. Org. Chem.*, 1971, **36** 3042
78. H Stetter, W Bochmann *Chem. Ber.*, 1951, **84** 834
79. D A Durham, F A Hart, D Shaw *J. Inorg. Nucl. Chem.*, 1967, **29** 509
80. H Edwards, G A Webb *Org. Magn. Res.*, 1984, **22** 352
81. J Skarzewsli, E Daniluk *Monatsh. Chem.*, 1983, **114** 1071
82. US P. 3 301 854; *Chem. Abs.*, 1967, **67** 21 936
83. A I Kuznetsov, O T Burdelev, B V Unkovskii *Trudy Yubileinoi Konferentsii, Posvyashchennoi 70-letiyu MITKhT im. M V Lomonosova* (Proceedings of the Jubilee Conference Commemorating the 70th Anniversary of the Lomonosov Moscow Institute of Fine Chemical Engineering), Moscow, 1970, p. 163
84. E B Hodge *J. Org. Chem.*, 1972, **37** 320
85. US P. 35 759 474; *Chem. Abs.*, 1970, **73** 66 630
86. A T Nielsen *J. Heterocycl. Chem.*, 1975, **12** 161
87. V Galik, M Safar, Z Kafka, S Landa *Collect. Czech. Chem. Commun.*, 1975, **40** 442
88. Czech P. 163 520; *Chem. Abs.*, 1977, **86** 55 494
89. M Safar, V Galik, Z Kafka, S Landa *Collect. Czech. Chem. Commun.*, 1975, **40** 2179
90. H Wiezer BRD P. 2 831 632; *Chem. Abs.*, 1980, **93** 8219
91. H Wiezer BRD P. 2 834 476; *Chem. Abs.*, 1980, **93** 8215
92. Z Kafka, V Galik, M Safar *Sbornik Vysoke Scoly Chem.-Technol.*, Praze, 1976, Vol. 32, p. 127
93. A I Kuznetsov, V A Kosmakov, A Yu Zakgeim, et al. *Izv. Vyssh. Uchebn., Khim. Khim. Tekhnol.*, 1985, **28** 111
94. A I Kuznetsov, V A Kosmakov, B V Unkovskii *Khim. Geterotsikl. Soedin.*, 1985, 837
95. BRD P. 2 637 193; *Chem. Abs.*, 1978, **88** 171 138
96. Z Kafka, V Galik, L Vodicka *Collect. Czech. Chem. Commun.*, 1978, **43** 151
97. I K Moiseev, A I Kuznetsov, L P Molevich *Nauchnaya Konferentsiya po Khimii Organicheskikh Poliedranov: Tezisy Dokladov, Volgograd* (Scientific Conference on the Chemistry of Organic Polyhedranes: Abstracts of Reports, Volgograd), 1981, p. 28
98. BRD P. 2 616 799; *Chem. Abs.*, 1978, **88** 153 558
99. V I Votyakov, O T Andreeva, M C Kitsara, et al. *Fiziologicheski Aktivnye Veshchestva*, 1978, **10** 88
100. BRD P. 2 702 205; *Chem. Abs.*, 1978, **89** 147 668
101. V Galik, Z Kafka, L Vodicka *Sbornik Vycoke Scoly Chem.-Technol.*, Praze, 1977, Vol. 36, p. 109
102. Ts E Agadzhanyan, R A Movsesyan *Arm. Khim. Zh.*, 1982, **35** 398
103. USSR P. 1 373 707; Byull. Izobret., 1987, (6)
104. A I Kuznetsov, E B Basargin, M Kh Ba *Perspektivy Razvitiya Khimii Karkasnykh Soedinenii i Ikh Primenenie v Otraslyakhkk Promyshlennosti: Tezisy Dokladov* (Prospects for the Development of Skeletal Compounds and Their Applications in Different Branches of Industry: Abstracts of Reports), Kiev, 1986, p. 109
105. S Chiavarelli, L V Fennoy *J. Org. Chem.*, 1961, **26** 4895
106. P W Hickmott, S Wood, P Murray-Rust *J. Chem. Soc., Perkin Trans. 1*, 1985, 2033
107. B V Unkovskii, A I Kuznetsov, T D Sokolova, M Yu D'yakov *Perspektivy Razvitiya Khimii Karkasnykh Soedinenii i Ikh Primenenie v Otraslyakh Promyshlennosti: Tezisy Dokladov* (Prospects for the Development of Skeletal Compounds and Their Applications in Different Branches of Industry: Abstracts of Reports), Kiev, 1986, p. 110
108. W N Speckamp, J Dijkink, A W J D Dekkers *Tetrahedron Lett.*, 1974, 1853
109. W N Speckamp, A W J D Dekkers *Tetrahedron Lett.*, 1974 1857
110. A I Kuznetsov, V A Kosmakov, V A Tyurikov, et al. *Perspektivy Razvitiya Khimii Karkasnykh Soedinenii i Ikh Primenenie v Otraslyakh Promyshlennosti: Tezisy Dokladov* (Prospects for the Development of Skeletal Compounds and Their Applications in Different Branches of Industry: Abstracts of Reports), Kiev, 1986, p. 104
111. S Chiavarelli, G Settimj *Gazz. Chim. Ital.*, 1958, **88** 1253
112. S Chiavarelli, S Toffler, D Misiti *Ann. Ist. Super Sanita*, 1968, (4) 157
113. Ts E Agadzhanyan, G L Arutyunyan, G G Minasyan, R A Movsesyan *Arm. Khim. Zh.*, 1983, **36** 669
114. E V Dehmlow *Two-phase Reactions in Preparative Organic Chemistry. New Synthetic Methods. VI*, Verlag Chemie, Weinheim, 1975, p. 1
115. US P. 3 904 626; *Chem. Abs.*, 1976, **84** 5019
116. R L Vittory, G Settimj, E Gatta, et al. *Gazz. Chim. Ital.*, 1967, **97** 1294
117. D Misiti, S Chiavarelli *Gazz. Chim. Ital.*, 1966, **96** 1696
118. Ts E Agadzhanyan, G G Minasyan, R A Movsesyan *Arm. Khim. Zh.*, 1984, **37** 530
119. G G Minasyan, M B Mkrtchyan, Ts E Agadzhanyan *Arm. Khim. Zh.*, 1971, **24** 48
120. E N Kurkutova, A V Goncharov, N S Zefirov, V A Palyulin *Zh. Strukt. Khim.*, 1976, **17** 687
121. H Stetter, R Merten *Chem. Ber.*, 1957, **90** 868
122. A F Farminer, G A Webb *J. Chem. Soc., Perkin Trans. 1*, 1967, 940
123. A Edward, G A Webb *J. Chem. Soc.*, Perkin Trans. 1, 1977, 1989
124. J A Bell, I Dunstan *J. Chem. Soc. C*, 1969, 1559
125. N Blazévic, D Kolbah, B Belin, et al. *Synthesis*, 1979, 161
126. J Kuthan, J Palecek, L Musil *Collect. Czech. Chem. Commun.*, 1974, **39** 760
127. J Kuthan, J Palecek, L Musil *Collect. Czech. Chem. Commun.*, 1974, **39** 750
128. P Trska, M Hajek, Z Kafka, V Sklenar *Org. Magn. Res.*, 1984, **22** 352
129. I Morishima, K Yoshikawa, K Okada *J. Am. Chem. Soc.*, 1976, **98** 3787
130. H Duddeck, P Wolf *Org. Magn. Res.*, 1976, **8** 593
131. A W Dekkers, J W Werhoeven, W N Speckamp *Tetrahedron*, 1973, **29** 1691
132. A S Moskovkin, A I Kuznetsov, I V Miroshnichenko *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1985, **28**(10) 111
133. R C Cookson, J Henstock, J Hudec *J. Am. Chem. Soc.*, 1966, **88** 1060
134. R Hoffman, A Imamura, W J Hehz *J. Am. Chem. Soc.*, 1968, **90** 1499
135. C B Theissling, N M Nibbering *Adv. Mass. Spectrom.*, 1974, 725

136. R Gleiter, M Kobayushi, J Kuthan *Tetrahedron*, 1976, **32** 2775
137. P Pasman, J W Verhoeven, Th Boer *Tetrahedron*, 1976, **32** 2827
138. P Pasman, F Rob, J W Verhoeven *J. Am. Chem. Soc.*, 1982, **104** 5127
139. US P. 4 012 384; *Chem. Abs.*, 1978, **89** 43 493
140. BRD P. 2 545 292; *Chem. Abs.*, 1977, **87** 24 201
141. L A Meilakhs, R A Gorelik, I T Gridunov, B V Unkovskii, USSR P. 658 150; *Byull. Izobret.*, 1979, (15)
142. L A Meilakhs, I T Gridunov, A I Kuznetsov, USSR P. 810 738; *Byull. Izobret.*, 1981, (9)
143. I T Gridunov, E L Tatarinova, A I Kuznetsov, L I Meilakhs *Kauchuk i Rezina*, 1977, (2) 19
144. I T Gridunov, E L Tatarinova, L A Meilakhs, B V Unkovskii *Proizvodstvo Shin, Rezinotekhnicheskikh i Asbestotekhnicheskikh Izdelii*, 1976, (12) 1
145. G A Blokh *Organicheskie Uskoriteli Vulkanizatsii i Vulkanizuyushchie Sistemy dlya Elastomerov* (Organic Accelerators of the Vulcanisation of and Vulcanising Systems for Elastomers), Izd. Khimiya, Leningrad, 1978, p. 61
146. G V Benevolenskaya, A I Kuznetsov, Z Ya Perevozchikova, USSR P. 638 352; *Byull. Izobret.*, 1978, (7)
147. G V Benevolenskaya, Z Ya Perebozchikova, A I Kuznetsov *Podgotovka i Pererabotka Gaza i Gazovogo Kondensata* (Preparation and Processing of [Natural] Gas and Gas Condensate), Izd. VNIIEgazprom, Moscow, 1978, No. 7, p. 13
148. S Chiavarelli, L V Fennoy, G Settimj, L De-Barun *J. Med. Pharm. Chem.*, 1962, **5** 1293
149. Europ. P. 76 755; *Chem. Abs.*, 1983, **99** 88 055
150. French P. 2 543 954; *Chem. Abs.*, 1985, **102** 131 937
151. S A Vichkanova, L V Goryunova, A I Kuznetsov, et al. *Farmakologiya i Toksikologiya*, 1974, **37** 76
152. N P Obrosova-Serova, N L Pushkarskaya, S V Lavrov, A I Kuznetsov *Vopr. Virusologii*, 1976, 689

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Reactions involving the addition of *N*-halogenoamides to unsaturated compounds

N N Labeish, A A Petrov

ABSTRACT. The literature data on the reactions involving the addition of *N*-halogeno- and *NN*-dihalogeno-amides of carboxylic sulphonic, sulphuric, and phosphoric acids as well as the esters of *N*-halogeno- and *NN*-dihalogeno-carbamic acids to various types of unsaturated compounds are surveyed. In many cases, the addition takes place with a different regiospecificity than for other compounds with *N*-halogen bonds, which has been explained by differences between the reaction mechanisms. The adducts of halogeno-amides with unsaturated compounds can be used in organic synthesis, especially in the synthesis of amides, aziridines, and other heterocyclic compounds.

The bibliography includes 113 references.

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I. Introduction

Highly reactive and readily available *N*-halogenoamides have long attracted the attention of investigators as effective halogenating agents. The chemistry of *N*-halogen-containing compounds, many representatives of which were already synthesised in the past century, began to develop vigorously during the last 30 years. The chemistry of *N*-chloroamines and *NN*-dichloroamines with various alkyl substituents, of *N*-halogeno- and *NN*-dihalogeno-amides of sulphonic, carboxylic, phosphonic, and sulphuric acids, as well as *N*-halogeno- and *NN*-dihalogeno-carbamic acid esters was investigated during this period. Reactions involving unsaturated compounds, which have now been investigated in relation to many examples, are of special interest because they lead to new possibilities for the introduction of functional groups into unsaturated organic compounds.

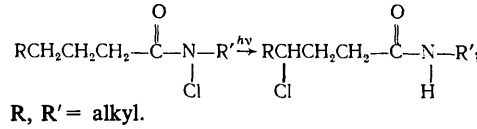
In the present review, which is devoted to the reactions involving the addition of *N*-halogenoamides to unsaturated compounds of different classes, we attempted to survey the available experimental data and to analyse the problems arising in their interpretation.

It is noteworthy that the previously published monographs and reviews by non-Soviet authors, in which this problem was dealt with in one way or another, inadequately reflect the modern advances in this field and hardly take into account the work of Soviet chemists.

II. Aliphatic alkenes

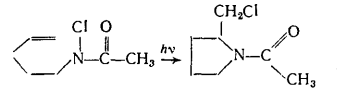
The reactions of alkenes with *N*-halogeno-substituted amides, carbamates, isocyanates, sulphonamides, and phosphoramides have been described in the literature.

The addition of *N*-halogenoamides to alkenes is usually carried out in neutral media under irradiation. Photolysis in the presence of alkenes proceeds via two pathways: with formation of adducts of the products of the substitution of the allyl hydrogen atom by the halogen. The reduction of temperature promotes an increase in the relative yield of the adducts.[1,2] It is noteworthy that, on irradiation, *N*-halogenoamides can rearrange (the Hoffmann–Loeffler reaction). For example, in the case of amides with three and more methylene groups, the following reaction occurs:[3]



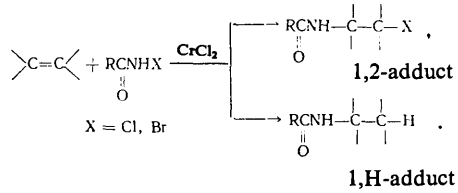
R, R′ = alkyl.

Unsaturated *N*-chloroamides can also react intramolecularly:[4]



A number of studies have been devoted to reactions of this type.[5–8]

The study of the one-electron reduction of *N*-halogenoamides by low-valence transition metal salts led to the conclusion that amidyl radicals can be generated without the accompanying formation of halogen atoms.[9–12] For example, a fairly effective method has been developed for the addition of *N*-halogenoamides to alkenes with participation of chromium(II) chloride. Two types of products are obtained: *N*-(2-halogenoalkyl)amides (1,2-adducts) and *N*-alkylamides (1,H-adducts).



X = Cl, Br

1,2-adduct

1,H-adduct

The overall yield of the adducts, the ratios of the yields of the 1,2- and 1,H-adducts, as well as the ratio of the *cis*- and *trans*-isomers depend on the nature of the alkene, the halogen, and the structure of the group R.

In the case of trisubstituted alkenes, 1,H-adducts have not been detected, whereas conjugated dienes afford exclusively 1,H-adducts. The following features have been observed for *N*-chloroamides:

(1) an increase in the overall capacity for 1,2-addition when R is varied in the sequence $CCl_3 < CH_3 < CF_3 < CH_2Cl < OAlk$;

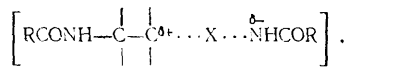
(2) an increase in the ratio of the 1,2- and 1,H-adducts in the sequence $CH_3 < CH_2Cl < OAlk < CCl_3 \leqslant CF_2$;

(3) an increase in the ratio of the *cis*- and *trans*-products in the sequence $CF_3 \simeq CCl_3 \leqslant CH_3 \simeq CH_2Cl < OAlk$.

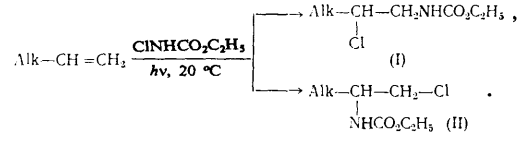
Thus both the best yields of the adducts and high selectivity of the reaction are obtained when *N*-chlorocarbamates are used.[11]

The influence of the structure of R on the yield of the adducts, on the ratio of the 1,2- and 1,H-adducts, and on the ratio of the *cis*- and *trans*-isomers is less significant when *N*-bromoamides are used. It is noteworthy that the competing electrophilic bromination (20–35%) in experiments with *N*-bromocarbamates lowers the yield of the adducts and thereby reduces the synthetic value of these reagents.

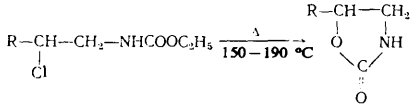
A radical mechanism has been proposed for the reactions described above.[12,13] The best chain transfer agent gives rise to the highest ratio of the 1,2- and 1,H-adducts for the given alkenes. Indeed, the *N*-bromoamide (the bromine atom is the actual chain transfer agent) is a better chain transfer agent than the *N*-chloroamide (where the chlorine atom is the actual chain transfer agent). On the other hand, the activity of the *N*-halogenoamide as a chain transfer agent increases as the electron-accepting capacity of the acyl residue (RCO) is enhanced as a result of the stabilisation of the polar transition state:



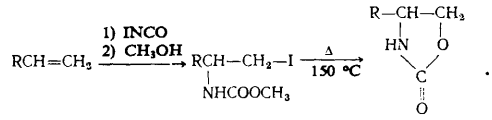
In the first studies on the addition of *NN*-dichlorocarbamate to a double bond,[14] it was already shown that the reaction proceeds with formation mainly of the adduct (contrary to the Markovnikov rule), i.e. with fixation of the nitrogen atom at the terminal carbon atom of the terminal double bond.[15,16] The UV-induced addition of *N*-chlorourethane proceeds with formation of a mixture of products (I) and (II) in proportions of 33 : 1:[17]



The position of the carbamate group was demonstrated both spectroscopically by ^1H NMR and chemically by pyrolysing the adduct with formation of 5-alkyl-2-oxazolidones:



The alternative formation of 4-alkyl-2-oxazolidinones has been observed in the pyrolysis of α-iodocarbamates obtained from iodine isocyanate and alkenes of a type similar to that described above:[18,19]

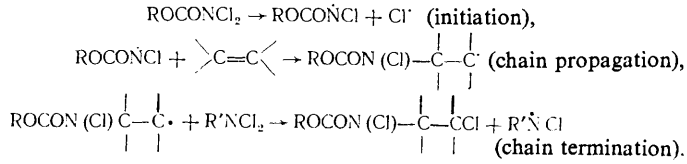


It is noteworthy that iodine isocyanate is a pseudohalogen and adds heterolytically. As a result of the electrophilic character of iodine isocyanate,[20] the iodine atom attacks the least substituted carbon atom, i.e. the adduct is formed "in conformity with the Markovnikov rule" (in contrast to the homolytic addition of *NN*-dichlorocarbamate).[21,22] The electrophilic addition of iodine isocyanate to a *cis*-alkene takes place *trans*-stereospecifically with formation of the *threo*-iodine isocyanate, which is converted into a carbamate without change of configuration. Treatment of this carbamate with base leads to a *cis*-aziridine, i.e. an intramolecular nucleophilic substitution takes place with inversion of configuration. A *trans*-aziridine is obtained similarly, albeit with lower yields than in the case of the *cis*-aziridine, from a *trans*-alkene via the *erythro*-iodine isocyanate.[19]

Homolytic addition of *NN*-dichlorocarbamates to alkyl-substituted alkenes proceeds non-stereospecifically with formation of a mixture of *erythro*- and *threo*-isomers[15] regardless of the geometrical configuration of the alkene. The lack of stereo-specificity in the UV-initiated addition of *N*-chlorourethane to but-2-ene is associated with the impossibility of the formation of a bridged structure.[23]

The most thorough information concerning the effect of steric factors on the rate of addition of *NN*-dichlorocarbamates to alkenes has been obtained in a study of its reactions with isomeric hexenes. Hex-1-ene reacts in less than 1 h quantitatively with formation of only the adduct. 2-Methylpent-2-ene is even more reactive, i.e. the electron-donating effect of the methyl group at the double bond overcomes its steric effect. 2,3-Dimethylbut-1-ene reacts much more slowly. 3,3-Dimethylbut-1-ene reacts on being refluxed for 4–5 h, while in the case of 2,3-dimethylbut-2-ene the addition to the double bond is not observed at all. Furthermore, the number of hydrogen atoms subjected to allylic attack changes simultaneously with the change in the steric parameters. Whereas hex-1-ene forms predominantly the 1,2-adduct with *NN*-dichlorourethane, 2,3-dimethylbut-1-ene and 2,3-dimethylbut-2-ene afford the allylic monochlorination products in 25 and 45% yields respectively.[24] Thus the yields of the main products diminish and those of side products increase with increase in the number of allyl hydrogen atoms.[25] As stated above, at low temperatures 1,2-addition predominates over the abstraction of an allyl hydrogen atom.[19]

The interaction of unsaturated compounds with *N*-halogeno-carbamates, which proceeds without the use of initiators (transition metal salts) or UV irradiation has all the features of a spontaneously initiated free-radical chain reaction, the sequence of the stages of which can be represented as folllows:



An inducation period is observed in this reaction and is followed by a rapid exothermic process; light accelerates the latter while free-radical reaction inhibitors retard it; the addition takes place also non-stereospecifically and contrary to the Markovnikov rule, the yields of the adducts diminish, and the yields of the side products (urethane, monochlorourethane) increase with increase in the number and activity of allyl hydrogen atoms. It is noteworthy that the radicals formed in the initiation stage are capable of abstracting an allyl hydrogen atom. This results in the appearance of a stable allyl radical, which subsequently participates in chain propagation.[15,19] The addition reactions are not then accompanied by vinyl polymerisation. Consequently in the formation of the primary radical, the monoadduct is produced at a rate much higher than the rate at which the polymerisation chain can be propagated. A concerted but non-synchronous molecularly induced homolysis (four-centre attack), in which the transition state is of a free-radical type, has therefore been proposed for the reaction considered. However, the impossibility of achieving the stereospecific addition to *trans*-hex-3-ene and stilbene constitutes evidence against the fully concerted homolysis.[24]

The reactions of alkenes with *NN*-dihalogenoarenesulphonamides are of considerable interest. Likhosherstov and co-workers[26–29] were the first to describe the interaction of *NN*-dichloroarene-sulphonamides with but-2-ene and isobutene in the presence of alcohols, phenols, or lower carboxylic acids in order to obtain β-chloroesters. In the reaction with but-2-ene, two racemic diastereoisomeric forms of *N*-(β-chlorobutyl)benzenesulphonamide and the corresponding aziridines were isolated as side products. The mode and mechanism of the addition reaction were not determined. The authors assumed that the reactions which they investigated are heterolytic.

There have been several communications containing contradictory data concerning the mode and mechanism of the addition of *N*-mono- and *NN*-di-halogenoarenesulphonamides to alkenes. In one of these communications,[30] it has been stated that *N*-bromo-*N*-methylarenesulphonamides add to alkenes and give rise to products in which the bromine atom occupies the same position as in the normal addition, i.e. in accordance with the Markovnikov rule, of HBr to these alkenes:

$$CH_3—CH=CH_2 + BrN(CH_3)SO_2Ar \rightarrow CH_3—CH(Br)CH_2—N(CH_3)SO_2Ar.$$

On the other hand, *NN*-dibromoarenesulphonamides add in the reverse order. However, here no account was taken of the different polarisations of the bromine atom in HBr and *N*-bromoamides. The structure of the product was demonstrated by a series of chemical conversions into known compounds.

In their reaction with propene, *NN*-dichloroarenesulphonamides give rise to two isomers, (III) and (IV), in proportions of 85 : 15.[31]

$$CH_3—CH=CH_2 + Cl_2NSO_2R \rightarrow \begin{cases} CH_3—CH(Cl)CH_2—N(Cl)SO_2R, & (III) \\ ClCH_2—CH(CH_3)N(Cl)SO_2R, & (IV) \end{cases}$$

It has been suggested that compound (III) is formed by a radical mechanism, similarly to the addition of *NN*-dichlorocarbamate,[31] while compound (IV) adds via the competing ionic mechanism. On the other hand, the product (IV) can be obtained, according to the authors, also via a radical mechanism, since the difference between the stabilities of the two possible radicals in the first chain propagation stage is not very great.

The reaction with isobutene proceeds quite differently. Mainly the allylic chlorination product (V) was isolated, its amount being equivalent to that of the benzenesulphonamide isolated. The formation of compound (VI) (in a low yield) takes place, according to the authors, via the cyclic chloronium intermediate (VII), i.e. via an ionic mechanism:

$$(CH_3)_2C=CH_2 + Cl_2NSO_2C_6H_5 \rightarrow (CH_3)_2C(\overset{+}{Cl})CH_2 + C_6H_5SO_2\bar{N}Cl \rightarrow$$
(VII)

$$\rightarrow ClCH_2—C(CH_3)=CH_2 + C_6H_5SO_2NHCl,$$
(V)

$$2\,C_6H_5SO_2NHCl \rightleftharpoons C_6H_5SO_2NCl_2 + C_6H_5SO_2NH_2,$$

$$(CH_3)_2C(\overset{+}{Cl})CH_2\cdot + C_6H_5SO_2NH_2 \rightarrow C_6H_5SO_2NHC(CH_3)_2CH_2Cl + H^{+}.$$
(VII) (VI)

Another communication describes the oxygen-inhibited radical addition of *NN*-dichloroarenesulphonamide to ethylene and hex-1-ene. In contrast to the example described above, the amide radical attacks the less substituted, i.e. the terminal, carbon atom.[32] However, an ionic reaction pathway involving atmospheric oxygen, in which a mixture of products with the opposite orientation is formed, is also possible.

The attack on the more substituted carbon atom by the amide radical in the reaction of *NN*-dibromoarenesulphonamide with 2,3-dimethylbut-1-ene and 2-methylpent-2-ene shows that *NN*-dibromoarenesulphonamide is less sensitive to steric factors than *NN*-dichlorocarbamate.[33] However, the structure of the adducts was not rigorously demonstrated.

The reaction of *NN*-dichloroarenesulphonamide with *cis*- and *trans*-but-2-enes is not sensitive to radical process inhibitors and proceeds equally well both in the dark in an oxygen atmosphere and in nitrogen under the usual illumination. The *trans*-stereospecific addition via the ionic mechanism leads, according to the authors, to the formation of a new type of β-chloroalkyliminosulphonate derivative (VIII) together with the β-chloroalkanesulphonamide adduct:[34]

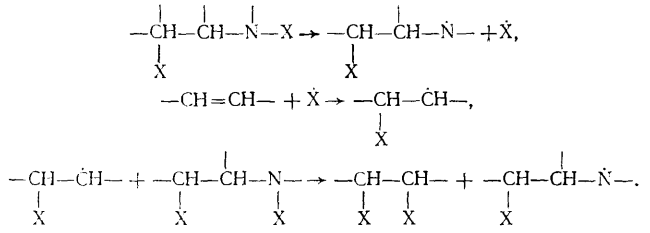
$$CH_3CH=CHCH_3 \xrightarrow[2)\ Na_2SO_3]{1)\ Cl_2NSO_2C_6H_5} \begin{cases} CH_3CH(Cl)CH(NHSO_2C_6H_5)CH_3, \\ CH_3CH(Cl)CH(CH_3)O—S(=O)(=NH)—C_6H_5 \quad (VIII) \end{cases}$$

The intermediate bridged chloronium ion is attacked either by the nitrogen atom or the oxygen atom of the *N*-chlorobenzene-sulphonamide anion. The high nucleophilicity of the oxygen atom is in this case completely unusual and conflicts with the available literature data on this problem.[34]

The *trans*-stereoselectivity of the addition of *NN*-dibromoarene-sulphonamide has been demonstrated in reactions with *cis*- and *trans*-hex-3-enes, *cis*-hept-2-ene, etc.[35] The formation of dibromo-derivatives and bromohydrins together with monoadducts has been observed:

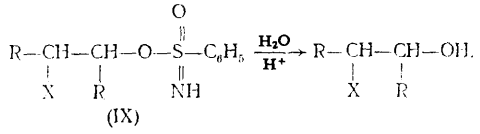
$$C_2H_5CH(Br)CH(NHSO_2C_6H_5)C_2H_5, \quad C_2H_5CH(Br)CH(Br)C_2H_5, \quad C_2H_5CH(Br)CH(OH)C_2H_5.$$

Judging from the observed stereoselectivity, the reaction proceeds via an ionic mechanism. The formation of dibromo-derivatives is a result of the radical reaction of *N*-bromo-*N*(β-bromoalkyl)-arenesulphonamide with a second substrate molecule:



It is striking that, as in the case of cyclohexene, allylic bromination products were not detected in the reaction.

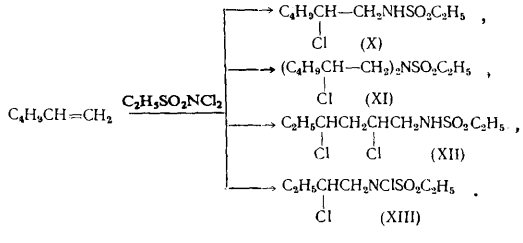
The elucidation of the pathways leading to the formation of bromohydrins was difficult. One of the possible pathways, namely the attack by water on the intermediate bromonium ion, is unlikely since the reaction is carried out under anhydrous conditions and the decomposition with bisulphite is performed in the complete absence of the alkene. An alternative possibility involves the hydrolysis of the iminosulphonate derivative (IX) which might have been formed in a reaction similar to that examined above:[34]



(IX)

However, all attempts to isolate compound (IX) were unsuccessful and a final conclusion about the mechanism of the formation of bromohydrins was not reached.

In the photoinitiated addition of *N*-chloro-*N*-methyl- and *NN*-dichloro-ethanesulphonamide to hex-1-ene, the nitrogen atom is attached to the terminal carbon atom of the alkene.[36] The formation of the products (X)–(XII) is described by the usual free-radical addition mechanism. Under these conditions, competition is observed between the abstraction of the allyl hydrogen atom from hex-1-ene and the rearrangement of the adduct (XIII) formed initially to (XII):



In a somewhat later study by the same workers,[37] it was observed that the mode of addition depends on the reaction conditions, while the yields vary with the alkene/*N*-chlorosulphonamide molar ratio. The data in Table 1 indicate a high regioselectivity of the addition only in photoinitiation. Under the usual illumination, the process competes with the radical reaction. The latter is slightly inhibited by oxygen and benzoquinone. It is of interest that virtually equal amounts of products with opposite orientations are obtained in a nitrogen atmosphere.

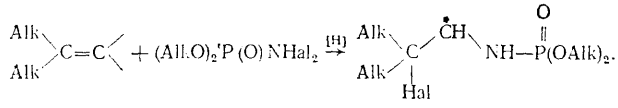
Table 1. The yields of the isomeric adducts in the reaction of *NN*-dichloroethanesulphonamide with hex-1-ene.[36,37]

Reaction conditions	1:1 adduct, %	
	C_4H_9–CH–CH_2Cl | $HNSO_2C_2H_5$	C_4H_9CH–CH_2 | | Cl $HNSO_2C_2H_5$
Photoinitiation, N_2	traces	100
Normal illumination	60	40
O_2 atmosphere, in the dark	67	33
In the presenceof $AlCl_3$	69	31
In the presenceof *p*-benzoquinone	68	32
Normal illumination, N_2	55	45

Rearrangements resembling the Hoffmann–Loeffler reaction for *N*-halogenoamides have been investigated in relation to *N*-alkyl-*N*-chloroarenesulphonamides[38] and *N*-chloroalkane sulphonamides[39] on photoinitiation or heat treatment.

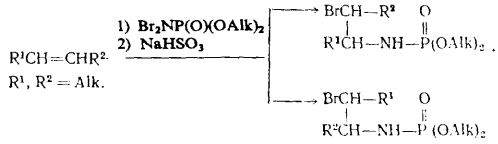
Thus there is no unanimity among investigators concerning the mechanism and order of the addition of *NN*-dihalogeno-sulphonamides to alkenes, which apparently depend both on the experimental conditions and on the nature of the halogen and the structure of the alkene. The wide variety of conditions under which the reactions were carried out and hence the wide range of products, which are in addition obtained via different mechanisms, preclude the comparison of the results of experiments of different workers.

The addition of *NN*-dichloro- and *NN*-dibromophosphoramidates to a series of alkenes with a terminal double bond has been studied recently.[40–45] The reactions take place in boiling benzene or methylene chloride or on photochemical initiation, depending on the reactivities of the reagents:



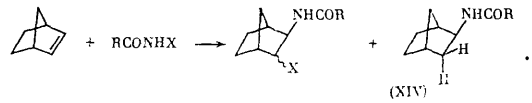
As in the example described above, the reaction of *NN*-dichloro-phosphoramidates is regiospecific and takes place with formation of a product in which the addition has taken place contrary to the Markovnikov rule. A radical mechanism has been proposed.

The heterolytic addition of *NN*-dibromophosphoramidate takes place in the presence of stoichiometric amounts of boron trifluoride etherate with formation of a mixture of products with opposite orientations:



III. Alicyclic alkenes

The regiospecificity of *N*-halogenoamides in the presence of chromium(II) chloride can be illustrated in relation to 1-methylcyclohexene and norbornene.[11] As might have been expected, the amido-group attacks the less substituted carbon atom. A small amount (up to 7%) of the 1,2-adduct with the opposite mode of addition was detected in the case of *N*-chlorocarbamate and *N*-bromoacetamide. The amide radical attacks norbornene exclusively in the *exo*-position in conformity with the generally accepted mechanism of the free-radical addition to norbornene:



An appreciable amount of the 1-*H*-adduct (XIV) was isolated in the above reaction, in contrast to the reaction involving 1-methylcyclohexene, which does not afford the 1,*H*-adduct even if the other reactant is *N*-chloroacetamide, producing the greatest amount of this adduct in its reactions with other alkenes. The ratio of the 1,2- and 1,*H*-adducts increases for cyclohexene and norbornene when R is varied in the sequence $CH_3 < CH_2Cl < OC_2H_5$.

The reaction involving ionic bromination by *N*-bromocarbamate, competing with the 1,2-addition, has been noted only for cyclohexene. According to the authors, in this instance the brominating agent is *NN*-dibromocarbamate arising as a result of the disproportionation of the initial reagent:

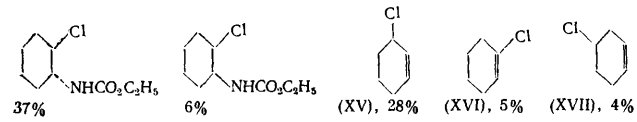
$$2ROCONHBr \rightleftharpoons ROCONBr_2 + ROCONH_2.$$

For *N*-bromoamides, this equilibrium is displaced to the left and the yields of the adducts are comparable to those for *N*-chlorocarbamates. Norbornene is unique in the series of monoolefins: in its reactions with *N*-chloroamides, it gives rise predominantly to the 1,*H*-adducts. On the other hand, in the reactions with *N*-bromo-amides, norbornene and cyclohexene afford comparable amounts of the 1,*H*-adducts. In the reactions involving the addition of *N*-halogenoamides to 1-methylcyclohexene and norbornene, the ratio of the *cis*- and *trans*-isomers increases in the sequence $CH_3 < CH_2Cl < OC_2H_5$. It is greater for *N*-chloroamides than for *N*-bromoamides and differs from the sequence observed for the reaction with cyclohexene. The addition to 1-methylcyclohexene is more stereoselective and that to norbornene is less stereoselective than the addition to cyclohexene. *N*-Alkyl-*N*-halogenocarbamates do not form 1,2- or 1,*H*-adducts in their reactions with cyclohexene. Small amounts of bicyclohexenyl (5%) and the corresponding alkyl carbamates have been isolated in such reactions. Table 2, compiled on the basis of the results of Driguez et al.,[11] summarises the relations examined above.

The UV-initiated addition of *N*-chlorocarbamates to cyclic alkenes proceeds with formation of a mixture of *cis*- and *trans*-products in proportions of 7 : 1. The predominance of the *cis*-configuration is a fairly rare phenomenon in radical addition reactions.[17]

The interaction of *NN*-dichlorocarbamate with cyclopentene can serve as an example of a *cis*-stereospecific radical reaction. In contrast to cyclohexenes, for five-membered cyclic alkenes there is a possibility of an intramolecular 1,3-transfer of a chlorine atom in the radical formed initially. On heating, the *cis*-isomer is converted into the *trans*-isomer.[46]

In contrast to the reaction examined above,[11] the *trans*-isomer predominates in the UV-initiated addition of *N*-chlorourethane to norbornene. It is noteworthy that the *cis*- and *trans*-isomers were isolated in this instance and the demonstration of the structure was based on the chemical conversion of the adducts into known compounds and also of the analysis of the ^1H NMR spectra of the isomers and their reaction products.[47] The overall yield of the adducts was high (93%) and the *trans*/*cis* ratio was 1.95, rising to 2.45 when a radical addition initiator was used. The reaction of *NN*-dichlorocarbamate with cyclohexene produces a complex mixture of products:[15]



In addition to the above set of products, monochlorourethane was detected in another study (4–5%).[48] It is of interest to compare this reaction with the chlorination of cyclohexene, where the products (XVIII), (XV), and (XVII) are obtained in proportions of 2 : 1 : 0.6, the formation of compounds (XV) and (XVIII) being the result of both radical reactions and the competing ionic reactions:

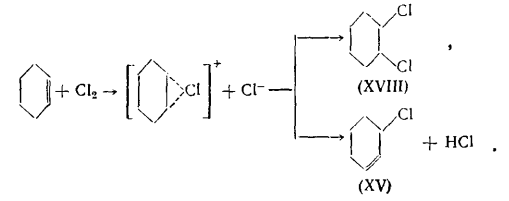


Table 2. The yields (%) of the products of the addition of *N*-halogenoamides to cyclohexene, 1-methylcyclohexene, and norbornene.[11]

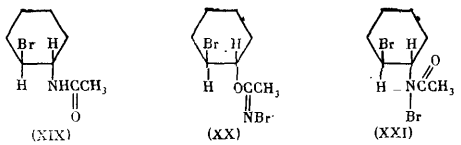
N-Halogenoamide	1-Methylcyclohexene		Norbornene			Cyclohexene		
	cis + *trans*	*cis*/*trans*	*cis* + *trans*	*cis*/*trans*	(XIV)	*cis* + *trans*	*cis*/*trans*	1,*H*
$CH_3CH_2OCONHCl$	80	25	41	5.8	54	87	6.7	6
$CH_3CONHCl$	74	6.4	1.6	*cis* only	93	34	2.1	36
$ClCH_2CONHCl$	77	5.5	33	2.8	55	75	2.0	13
$CH_3CH_2OCONHBr$	75	2.0	76	1.9	2	71	1.5	10.5
$CH_3CONHBr$	60	2.0	91	1.0	4	67	1.1	9
$ClCH_2CONHBr$	77	2.5	88	1.8	2.5	74	1.3	4

The mechanism of the formation of the product (XVII) in the reaction with *NN*-dichlorocarbamate is therefore not very clear. It could have been obtained as a result of the elimination of a hydrogen chloride molecule from the dihalogeno-derivative (XVIII), which, however, was not detected in the reaction with *NN*-dichlorocarbamate. The mechanism of the formation of

compound (XVI) as well as other chlorocyclohexenes was not discussed by Foglia and Swern[15] and Bal'on and Moskaleva.[48] On the other hand, it has been suggested that the 1,2-adduct is formed via free-radical mechanism.

In contrast to the addition of *N*-chloroamides to olefins, including alicyclic olefins, *N*-bromo- and *NN*-dibromo-carbamates add to cyclohexene stereospecifically (mainly by *trans*-addition). The structure of the product obtained was demonstrated by analysing the ^{1}H NMR spectra and by converting it into 8,9-*cis*-perhydrobenzoxazol-2-one. It had been established earlier that only the corresponding *trans*-compounds are capable of entering into similar reactions.[49] The lack of any side products whatever, in contrast to other reactions of *N*-bromocarbamate with alkenes, is striking.[11,15] The products of allylic bromination were not observed either on treating cyclohexene with *N*-bromo-acetamide.[50] Nevertheless, it is well known that bromoamides show a greater tendency than chloroamides to undergo allylic halogenation reactions and are used as specific brominating agents.[51,52] One of these widely used reagents is, for example, *N*-bromosuccinimide.[53] However, for *N*-bromosuccinimide also, experimental conditions have been found under which it (and *N*-chlorosuccinimide) add to cyclohexenes, producing adducts in yields up to 20%.[12]

The photoinitiated reaction of cyclohexene with *N*-bromo-acetamide, already mentioned above, is completely unexpected. Together with the formation of only 1% of the 1,2-*trans*-adduct (XIX), 36% of the *trans*-adduct (XX) and the isomeric product (XXI) were obtained:[50]



The *N*-bromoamidyl radical is generated via reactions (2) and (3), which are followed by the rapid reactions (4) and (5). The last of these explains, according to the authors, the absence of dibromo-derivatives and unsaturated bromo-derivatives as well as the formation of the products of the reaction of *NN*-dibromoacetamide with cyclohexene:

$$CH_3CONHBr \rightarrow CH_3CO\dot{N}H + \dot{B}r, \quad (1)$$

$$CH_3CO\dot{N}H + CH_3CONHBr \rightarrow CH_3CONH_2 + CH_3CO\dot{N}Br, \quad (2)$$

$$\dot{B}r + CH_3CONHBr \rightarrow CH_3CO\dot{N}Br + HBr, \quad (3)$$

$$HBr + CH_3CONHBr \rightarrow Br_2 + CH_3CONH_2, \quad (4)$$

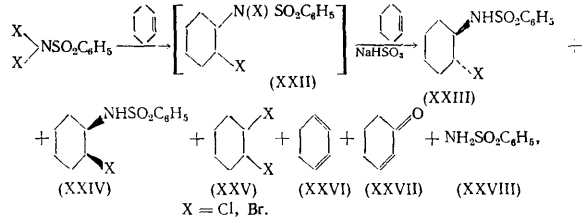
$$Br_2 + CH_3CO\dot{N}Br \rightarrow \dot{B}r + CH_3CONBr_2, \quad (5)$$

$$CH_3CO\dot{N}Br + CH_3CONHBr \rightarrow CH_3CONBr_2 + CH_3CO\dot{N}H. \quad (6)$$

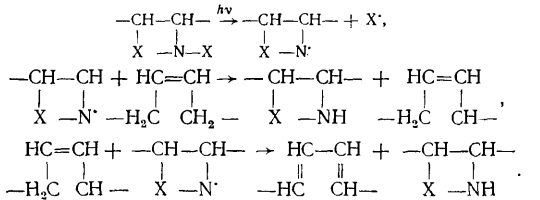
We may note that *N*-chloroiminosulphonates similar to compound (XX) are formed in the reaction of but-2-ene with chloramine B via an ionic pathway. The set of equations (1)–(6) quoted by the authors do not explain, in our view, the observed distribution of the yields of the products and leave open the question of both the reaction mechanism and of the "brominating" properties of mono- and dibromo-acetamides.

Asymmetrically substituted cyclohexenes have been investigated in the reaction involving the addition of iodine isocyanates.[54] It has been established that 1-ethyl-, 1-isopropyl-, and 1-phenyl-1-(α-naphthyl)cyclohex-1-enes react smoothly with formation of α-iodo-β-isocyanato-derivatives "in accordance with the Markovnikov rule". On acid hydrolysis, the adducts give rise to the corresponding salts of β-iodoamines in 30–40% yield. Among similar reactions, we may note the addition of iodine isocyanate to Δ^1-dihydronaphthalene.[55] Urea derivatives, aziridines, iodine carbamates, as well as amine hydrochlorides have been obtained from products of similar reactions (β-iodoisocyanates).

As already stated above, the addition of *NN*-dihalogeno-sulphonamides to alkenes proceeds via a free-radical or ionic mechanism depending on the experimental conditions. The reactions of cyclohexene with *NN*-dihalogenoarenesulphonamides afford similar sets of products for *NN*-dichloro- and *NN*-dibromo-benzenesulphonamides:[56–58]



Two reaction steps have been proposed: the intermediate (XXII) is formed in the first step and subsequently interacts with new cyclohexene molecules, giving rise to the reaction products indicated above. This hypothesis is confirmed by the results of the study of the reaction of compound (XXII) [obtained by brominating the adduct (XXIII) in the presence of alkali] with cyclohexene: the products (XXIV)–(XXVIII) are formed. On this basis, the authors postulated the absence of adducts in the reaction of *N*-alkyl-*N*-halogenobenzenesulphonamides with cyclohexene, which was in fact the case. The authors explain the formation of the dihalogeno-derivative (XXV) by invoking the well known mechanism of the bromination by *N*-bromosuccinimide.[59] However, the formation of cyclohexadiene via the free-radical abstraction of a hydrogen atom from the cyclohexenyl radical appears unlikely:



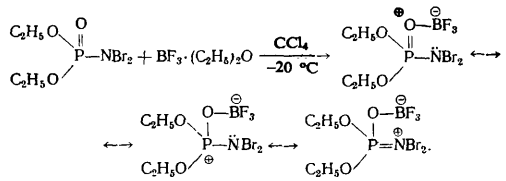
Thus the mechanism of the formation of cyclohexadiene and especially of cyclohexenone (XXVII) as well as the absence of products of allylic bromination from the reaction mixtures remain unexplained. On the other hand, competition between the halogen atom and the sulphonamide radical, which depends on their relative reactivities, can lead to the preferential formation of allylic bromination products and not products resulting from the addition of the halogen molecule. In confirmation of this, one may quote the results of a study of the reaction of *NN*-dichlorobenzene-sulphonamide with cyclohexene at 20 °C. A product of type (XXII)

was obtained (the reaction is non-stereospecific). It reacts with boiling carbon tetrachloride with a mixed cyclohexene molecule, affording the product of the allylic chlorination of cyclohexene together with compounds (XXIII) and (XXIV).[60] This course of the process is the opposite of the reactions described above.[56]

Two studies[61,62] were devoted to the reactions involving the addition of *NN*-dibromobenzenesulphonamides to norbornene and a series of bicyclic olefins, which occur, according to the authors, via an ionic mechanism. The principal pathway involved the formation of a nortricyclene bromo-derivative together with adducts, among which dibromo-derivatives and bromohydrins were detected. This was also observed in the reaction, discussed previously, of aliphatic alkenes, with *NN*-dibromobenzenesulphonamide and also in the reaction of *NN*-dichlorocarbamate with norbornene, which results in the formation of 3-chloronortricyclene in 45% yield.[15]

The reactions in which alkenes are subjected to *cis*-stereospecific hydroxyamination by chloramine T in the presence of catalytic amounts of osmium tetrachloride have been investigated vigorously in recent years.[63] In the above study, certain synthetic possibilities of this reaction and the practical applications of the product were investigated.

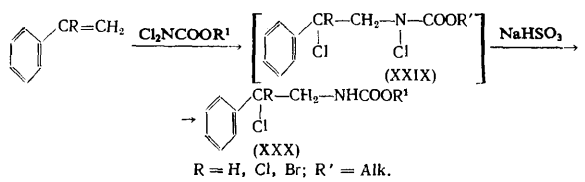
The ionic addition of *NN*-dibromophosphoramidate to cycloalkenes has been studied in relation to indene, cyclopentene, etc. The process has a *trans*-stereospecific character and proceeds rapidly at low temperatures without an induction period, in contrast to the radical reactions described above. Boron trifluoride etherate plays the role of an ionising agent for the dibromophosphoramidate molecule.[45] The electrophilic character of the bromine atom in the complex form leads to the heterolytic cleavage of the N—Br bond and ionic addition to the double bond.



IV. Arylalkenes

The reactions involving the addition of *N*-halogenoamides to aromatic alkenes exhibit the same features as the reactions with aliphatic and alicyclic alkenes.

As was to be expected, the addition of *NN*-dichlorocarbamate to styrene leads to the formation of the monoadduct (XXX) in which the carbamate group is attached to the less substituted carbon atom:[15]



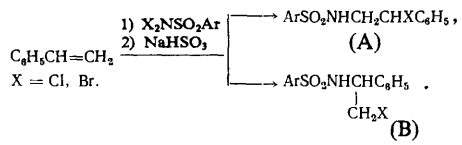
In this reaction it was possible to isolate the intermediate (XXIX).[48,64] Interesting series of reactions have been carried out in order to obtain various styrenes with functional group substituents.[65,66] These reactions as well as the synthesis of 5-alkyl-2-oxazolidinones from the adducts undoubtedly indicate that the carbamate group occupies the terminal position.[15,64] The addition of *NN*-dichlorourethane to bromostyrene proceeds similarly. The use of catalytic amounts of copper powder increases the yield of the adduct from 30 to 90%.[67]

In its reaction with *trans*-stilbene, dichlorocarbamate gives rise to an 11:9 mixture of the *erythro*- and *threo*-forms. The substances synthesised have been used to obtain 2-chloro-1,2-diphenylethyl isocyanate, 2-chloro-1,2-diphenylethylamine, 2,3-diphenylaziridine, and *NN*-disubstituted amides.[68]

The high regio- and stereo-specificities of the addition of *N*-bromocarbamates to styrene (a nitrogen-containing radical attacks the carbon atom, forming *trans*-adducts) has been demonstrated.[48]

The reactions of aromatic alkenes with *NN*-dihalogenoarenesulphonamides are of greatest interest, as for the olefins described above. The mechanism and mode of addition have been the subject of studies.

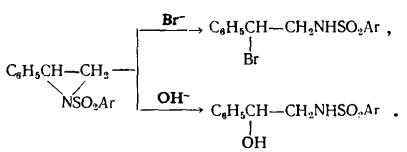
In the reaction with styrene, there is a possibility, in principle, of the formation of two isomers (A) and (B), which was already noted in one of the first studies on the addition of *N*-bromo-*N*-methylbenzenesulphonamide:[69]



The addition of dichloroarenesulphonamide to styrene in an inert gas atmosphere without an initiator leads to compound (A), while in the presence of equimolar amounts of aluminium chloride the product is compound (B). The authors believe that compound (A) is formed by a free-radical mechanism, while compound (B) is produced by an ionic mechanism via the complex $Cl^+[AlCl_3(NClSO_2Ar)]^-$ formed initially.[70]

A group of Soviet chemists have also shown that compound (A) is formed by a radical mechanism in a nitrogen atmosphere. However, in the presence of atmospheric oxygen, the reaction proceeds via an ionic pathway and the higher-melting adduct (B) is obtained.[71,72]

Japanese workers state that the reaction with styrene yields larger amounts of the product (A) formed "contrary to the Markovnikov rule" than in reactions with alkenes, where approximately equal amounts of adducts involving the opposite modes of addition were found in the case of *NN*-dichloroarenesulphonamides.[73] At the same time, it has been discovered that the reaction of *NN*-dibromoarenesulphonamide with styrene in the absence of catalysts gives rise to the product (B),[74] in contrast to *N*-bromo-*N*-methylarenesulphonamides, which, as for aliphatic alkenes, afford adducts formed contrary to the Markovnikov rule.[30] This can be illustrated by the formation of a bisadduct as a result of the addition of the brominated product (B) to a new styrene molecule. It is of interest to note that the opening of the ring of the aziridine obtained from compound (B) leads to the formation of a product in which the disposition of the substituents is the opposite to that in the initial compound.[68] This has also been noted in other studies:[75,76]

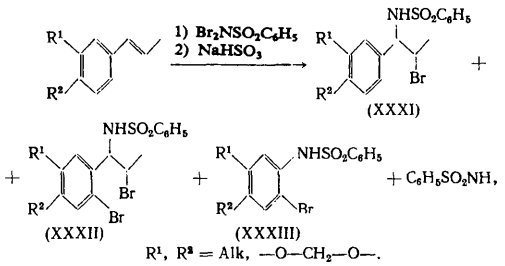


The adducts obtained were reduced to the corresponding amines, demonstrating rigorously thereby that the sulphonamide group occupies the initial position.

The ionic telomerisation of styrene by *NN*-dichloro-*p*-chlorobenzenesulphonamide leads to telomers of the following type:[77]

$$n\text{-}ClC_6H_4SO_2NH(C_8H_8)_nCl,\quad n=1,2,3;$$
$$n\text{-}ClC_6H_4SO_2N\begin{matrix}(C_8H_8)_mCl\\(C_8H_8)_{n-m}Cl\end{matrix}\quad n=2,5,6,14;\ m=1\ .$$

The addition of *NN*-dibromoarenesulphonamide to propenylbenzene derivatives proceeds *trans*-stereospecifically with formation of a mixture of products (XXXI)–(XXXIII):



R^1, R^2 = Alk, —O—CH_2—O—.

The formation of the product (XXIII) as a result of the elimination of the C_3 fragment from the adduct (XXXI), which occurs for 3,4-dialkoxypropenylbenzene, is of greatest interest according to the authors.[76,78] The fate of the C_3 fragment was not investigated. In the similar reaction with safrole (R^1, R^2 = —O—CH_2—O—) the products of the rearrangement predominate over the normal adducts for any reactant ratios.[79] The rearrangement proceeds via the phenonium ion (migration of the methylenedioxyphenyl group to the electron-deficient β-carbon atom of the safrole chain). Safrole and the rearranged products are brominated by an excess of *NN*-dibromoarenesulphonamide or the molecular bromine formed from it.

Thus *NN*-dibromoarenesulphonamides as a rule differ from their chloro-substituted analogues or *NN*-dichlorocarbamate in the mode of addition, which in the case of non-aromatic olefins depends on the experimental conditions.

NN-Dichlorophosphoramidates add to styrene and its analogues contrary to the Markovnikov rule, non-stereospecifically, and by the radical mechanism.[44,80] A vinyl chlorination product is also formed in the reaction of 1,1-di(*p*-methoxyphenyl)ethylene. *trans*-Stilbene reacts in the course of several hours, affording a low yield of adducts (33.5%). The products of allylic chlorination or vinyl polymerisation were not detected in the reactions with styrene, (*E*)- and (*Z*)-1-phenylpropenes and α-methyl styrene. In the presence of equimolar amounts of boron trifluoride etherate, adducts are formed in accordance with the Markovnikov rule (by an ionic mechanism).[45]

V. Substituted alkenes

1. Halogenoalkenes

The addition of *N*-chlorocarbamate to 1-chlorocyclohexene in the presence of chromium(II) chloride leads to smaller amounts of the 1,2- and 1,*H*-adducts than in the case of cyclohexene.[11]

Vinylidene chloride combines with *NN*-dichlorocarbamate fairly rapidly, giving good yields of the adducts,[24,81] which can be explained, according to the authors, by the stabilisation of the $CCl_2CH_2N(Cl)CCOR$ group as a result of the possibility of the delocalisation of the unpaired electron over the two chlorine atoms, which compensates to a large extent for their electron-accepting effect. Treatment of the adduct with alcoholic alkali leads to the formation of *N*-(1-alkoxy-2,2-dichloroethyl)-carbamic acid esters:

$$\dot{C}Cl_3CH_2NHCOR \xrightarrow[CH_3OH]{KOH} [CCl_2{=}CHNHCOR \rightleftarrows CHCl_2CH{=}NCOR] \rightarrow$$
$$\rightarrow CHCl_2CH(OCH_3)NHCOOR.$$

The increased reactivity of dichlorovinylamides is attributed to the possible enamide–*N*-acylimine tautomerism and the high reactivity of the *N*-acylimine form in nucleophilic addition reactions.[81]

When *NN*-dichlorourethanes are heated with trichloroethylene,[82] the adduct formed initially with the carbamate group at the less substituted carbon atom is readily dechlorinated, being converted into the *N*-acylimine:

$$CCl_2{=}CHCl + Cl_2NCOOR \rightarrow [CCl_3CHClN(Cl)COOR] \xrightarrow[-Cl_2]{30\ ^\circ C}$$
(XXXIV)
$$\rightarrow CCl_3CH{=}NCOOR.$$
(XXXV)

Together with the liberation of chlorine, the formation of pentachloroethane was detected in the given reaction[83] and the bisadduct $(C_2H_5OCONH)_2CHCCl_3$ was isolated. It is suggested, in contrast to the data of Mirskova et al.,[83] that the adduct (XXXIV) is not formed under the reaction conditions, while the azomethine (XXXV), isolated in the form of compound (XXXVI), is obtained as a result of the elimination of a chlorine atom from the radical (C) generated in the first stage of chain propagation:

$$C_2H_5OCONCl_2 \rightarrow C_2H_5OCO\dot{N}Cl + \dot{C}l,$$
$$C_2H_5OCO\dot{N}Cl + CHCl{=}CCl_2 \rightarrow C_2H_5OCON(Cl)CHCl{-}\dot{C}Cl_2,$$
(C)
$$(C) \rightarrow C_2H_5OCO\dot{N}CHClCCl_3 \xrightarrow{-\dot{C}l} C_2H_5OCON{=}CHCCl_3,$$
(XXXV)
$$(C) \xrightarrow{-\dot{C}l} C_2H_5OCONClCH{=}CCl_2 \rightarrow C_2H_5OCON{=}CHCCl_3,$$
(D) (XXXV)
$$(D) \rightarrow C_2H_5OCONCl_2 \rightarrow (C_2H_5OCONCl)_2CHCCl_3 \xrightarrow{H_2O} \rightarrow$$
(XXXV)
$$\rightarrow (C_2H_5OCONH)_2CHCCl_3 \xrightarrow{H_2O} C_2H_5O\overset{O}{\overset{\|}{C}}NH\overset{OH}{\overset{|}{C}}HCCl_3.$$
(XXXVI)

Chloral imines are obtained from trichloroethylene and *NN*-dichloroacetamide or *NN*-dichlorobenzamide, also with the intermediate formation of a type (C) radical-adduct, its rearrangement, the 1,3-migration of a chlorine atom, and the elimination of chlorine from the α-position.[84] Trichloroethylene reacts in the same way with *NN*-dichloroarenesulphonamides.[85–88] The saturated adducts $CCl_3CHClNClSO_2Ar$ are not formed under any reaction conditions. The reaction is accompanied by the liberation of chlorine and leads to trichloroethylidenearenesulphonamides.

The influence of Lewis acids on the mode of reaction of *NN*-dichloroarenesulphonamides with trichloroethylene and on the yield of its products[88] has also been studied. It has been shown that, in the presence of $SnCl_4$ or $AlCl_3$ under conditions ruling out to the maximum extent the free-radical reaction, the interaction of the above reactants proceeds in the same way as under the conditions of thermal and photochemical initiation.

The mechanism has been studied by CINP and EPR and the presence of radical stages in the photochemical reaction of *NN*-dichlorobenzenesulphonamide and *NN*-dichlorourethane with trichloroethylene was demonstrated.[89] The possible pathways leading to the formation of the final products were suggested.

1,1,2-Tribromo-1,2-dichloroethane has been detected, together with the liberation of gaseous chlorine and bromine, in the reaction of dichloroarenesulphonamide with tribromoethylene.[90] The rearrangement of the intermediate radical-adduct $C_6H_5SO_2NClCHBr\dot{C}Br_2$ (if it occurs) is achieved via the 1,3- and not the 1,2-migration of a chlorine atom. The elimination of a bromine atom with formation of the enamide $CBr_2=CHNClSO_2C_6H_5$ and its subsequent isomerisation appear to the authors to be less probable because of the greater ease of the homolytic dissociation of the N–Cl bond compared with C–Br.

In contrast to trichloro- and tribromo-ethylenes, vinylidene chloride[91] as well as other compounds containing the dichlorovinyl group[92] afford a 1 : 1 adduct with *NN*-dichloroarenesulphonamide, and in the last case the adducts obtained under ionic and radical conditions have the same structure (in contrast to the reaction of styrene).

The addition to ethylene, styrene, and allyl chloride of the product of the reaction of dichloroarenesulphonamide with vinylidene chloride has been investigated. Ionic reactions do not occur in this case and in the radical process the nitrogen atom adds to the styrene fragment contrary to the Markovnikov rule:

$$p\text{-}ClC_6H_4SO_2\overset{Cl}{\underset{|}{N}}CH_2CCl_3 + CH_2=CHR \rightarrow R\overset{Cl}{\underset{|}{C}}H-CH_2-\overset{SO_2C_6H_4Cl\text{-}p}{\underset{|}{N}}-CH_2CCl_3;$$
$$R = H,\ C_6H_5,\ CH_2Cl.$$

Such reactions proceed with much more difficulty than the analogous reactions with *NN*-dichloroarenesulphonamides.[94]

2. Alkenes with functional group substituents

The interactions of monochlorourethanes [in the presence of chromium(II) chloride] with methyl acrylate and methyl vinyl ketone do not afford 1,2-adducts.[11] A two fold excess of the reagent leads to the formation of small amounts of 1,*H*-adducts.

The yields of the products of the addition of *NN*-dichlorocarbamates to alkenes with functional group substituents are high regardless of whether electron-donating or electron-accepting groups adjoin the double bond. The polar effects of the substituents do, however, affect the rate of addition. The reaction of diethyl maleate with *NN*-dichlorocarbamate is slow (more than 30 h), while ethyl vinyl sulphone does not react even on refluxing in benzene for 72 h. Methyl acrylate reacts with dichlorocarbamate more slowly than does methyl vinyl ketone, while acrylonitrile reacts still more slowly.[24] In all these reactions, the carbamate group attacks the less substituted carbon atom; a free-radical mechanism of the addition reaction has been proposed. When they combine with *NN*-dichlorourethane on heating in benzene, vinyl ethers give rise to adducts with the opposite mode of addition (in accordance with the Markovnikov rule),[95] in contrast to vinyl acetate, which produces an adduct with the carbamate group in the terminal position regardless of the method of initiation.[24,96]

The use of a univalent copper salt or copper powder as the catalyst in the addition of *NN*-dichlorocarbamate to acrylic acid derivatives shortens the reaction from 4–5 h to 30–40 min and increases the yield and purity of the adducts.[97] It has been suggested that the reaction has a radical character:

$$AlkOCONCl_2 \xrightarrow[-CuCl]{Cu} AlkOCO\dot{N}Cl,$$
$$AlkOCONCl_2 \xrightarrow[-CuCl_2]{CuCl} AlkOCONCl \xrightarrow{CH_2=CHR}$$
$$\rightarrow AlkOCON(Cl)CH_2\dot{C}HR \xrightarrow[-CuCl]{CuCl_2} AlkOCON(Cl)CH_2CH(R)Cl\ .$$

It follows from the scheme presented that the copper(II) chloride formed in the initiation stage terminates the chain, which promotes, according to the authors,[98] an increase in the yield of the main reaction products. The formation of 5-alkyloxazolidinone, as in the case of aliphatic alkenes,[24] demonstrates the terminal position of the carbamate group.

NN-Dichloroarenesulphonamides add to the double bond in alkenes containing electron-accepting groups in the presence of peroxide catalysts or under UV irradiation.[71] The proposed initiation system (univalent copper salt and tetraethylammonium bromide) promotes an increase in the yield of adducts in these reactions and a decrease in the reaction time.[98] The role of the second additive (tetraethylammonium bromide) consists, in the authors' view, in generating the bromine atoms which initiate the addition reaction.

The reaction of *NN*-dichlorobenzenesulphonamide with alkyl 2,2-dichlorovinyl ketone results in the formation of 1,1-adducts $C_6H_5SO_2N(Cl)-CH(COAlk)CCl_3$, which are converted into *N*-(1-acyl-2,2,2-trichloroethyl)benzenesulphonamides on exposure to atmospheric moisture. On treatment with alkali the sulphonamides eliminate HCl and afford *N*-(1-acyl-2,2-dichlorovinyl)benzenesulphonamides:[99]

$$C_6H_5SO_2NHCH(COAlk)CCl_3 \xrightarrow{OH^-} C_6H_5SO_2\underset{H}{\underset{|}{N}}-\underset{CCl_2}{\underset{\|}{C}}-COAlk.$$

In conclusion, it is of interest to note that *NN*-dibromoarenesulphonamides, which add to asymmetric alkenes in accordance with the Markovnikov rule, in contrast to *NN*-dichlorourethane, react with αβ-unsaturated carboxylic acid esters similarly to *NN*-dichlorourethanes, in such a way that the bromine atom enters a position adjoining the carbonyl group ("contrary to the Markovnikov rule").

VI. Alkadienes

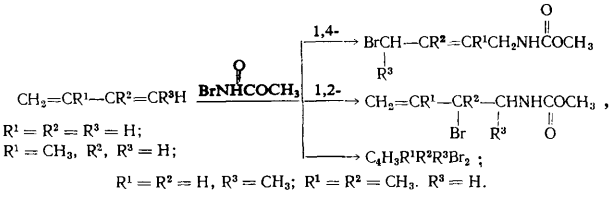
The order of the addition of various reagents to alkadienes depends greatly on their structure and its determination therefore permits additional conclusions concerning the reaction mechanism. On the other hand, the possibility of the formation in this case of a mixture of 1,2- and 1,4-isomers hinders the isolation and identification of the adducts.

The addition of various *N*-halogenoamides to buta-1,3-diene, isoprene, piperylene, cyclohexadiene, chloroprene, etc. has been investigated.

The photochemical decomposition of *N*-halogeneamides (including urethanes) is inhibited by cyclohexa-1,3-diene. After irradiation for 45 h, the reaction mixture still contains 94% of the active halogen.[25] On the other hand, the addition to norbornadiene proceeds readily and affords three isomeric 3,5-disubstituted nortricyclenes in 66% yield and 7% of the 1,2-adduct. Only linear adducts are formed in the photoinitiated addition of *N*-halogenoamides to non-conjugated dienes. In the reaction of cycloocta-1,5-diene, bicyclic derivatives — the products of the "transannular cycloaddition" of the primary radical — were not detected.[25]

NN-Dichlorocarbamates add to butadiene with formation of a mixture of the 1,4-*trans*-adduct (86%) and the 1,2-adduct (14%).[100] The reactions with chloroprene and 2,3-dimethylbuta-1,3-diene result in the exclusive formation of 1,4-adducts. In the case of isoprene, the 1,4-adduct $ClH_2C-C(CH_3)=CHCH_2NHCOOR$ was isolated (selectivity 85%). The formation of the products of the reverse 4,1-addition has also been postulated from ^1H NMR data. A mixture of three isomeric adducts, the 1,2-adduct (26%), the 1,4-adduct (44%), and the 4,1-adduct (30%), is formed in the reaction of *NN*-dichlorocarbamate with piperylene.[100]

The *trans*-1,4-adducts are formed predominantly in all cases in the interaction of *N*-bromocarbamates with conjugated alkadienes under the same conditions as for *NN*-dichlorocarbamates[100] (Table 3):



Dibromo-derivatives, whose formation may be induced by the disproportionation of the reagent with formation of carbamate and *NN*-dibromocarbamate, were identified as side products. The *NN*-dibromocarbamate functions as a brominating agent (as in the formation of dibromo-derivatives in the reactions of *N*-bromocarbamates with alkenes).[11]

Table 3. The isomeric composition of the products of the addition of *N*-halogenocarbamates to alkadienes.[100,101]

Hydrocarbon	$Cl_3NCOOCH_3$*			$BrHNCOOCH_3$		
	1,4-	4,1-	1,2-	1,4-	1,2-	dibromo-derivatives
$H_2C=CH-CH=CH_2$	90	—	10	70	20	10
$H_2C=C(CH_3)C(CH_3)=CH_2$	100	—	—	68	—	32
$H_2C=C(CH_3)CH=CH_2$	85	15		71	—	24
$H_2C=CH-CH=CH-CH_3$	44	30	26	66**	8	24

* According to the results of Daniher and Butler.[100]
** 1,4- and 4,1-isomers in proportions of ~1 : 1.

Thus the regio- and stereo-specificity of the addition of *N*-bromocarbamate hardly differs from that for *NN*-dichlorocarbamate. The reaction is not inhibited by oxygen (in contrast to the addition of dichlorocarbamate), while the ratio of the isomers depends little on the experimental conditions. A decrease in temperature promotes the formation of small amounts of dibromo-derivatives. The low selectivity of the addition reaction in the case of piperylene can be explained by the approximately equal stabilities of the two allyl radicals formed. The complete absence from the reaction mixtures of products resulting from chlorination and substitution of hydrogen atoms is noteworthy.[101]

The reactions of iodine isocyanate with alkadienes have also been investigated.[102] Aliphatic alkadienes with isolated double bonds combine with two moles of iodine isocyanate per mole of the substrate, in contrast to conjugated alkadienes which afford 1,4-mono-adducts; when the adducts are treated with methanol, the corresponding iodine carbamates are produced. Methylallene also combines slowly with one mole of iodine isocyanate; the structure of the adduct has not been demonstrated. With the exception of cycloocta-1,3-diene, alicyclic alkadienes react extremely rapidly, similarly to alkadienes with isolated multiple bonds. Contrary to expectation, cyclohexa-1,4-diene combines with only one mole of iodine isocyanate. Analysis of the ^1H NMR and IR spectra led to a tricyclic structure being attributed to the products of the addition of one mole of iodine isocyanate to norbornadiene.

NN-Dichloroarenesulphonamides add readily and exothermically to buta-1,3-diene and chloroprene. 1,4-Adducts are then formed in high yields.[31] The oxygen-inhibited reaction proceeds via a free-radical mechanism, like the addition of *NN*-dichlorocarbamate.

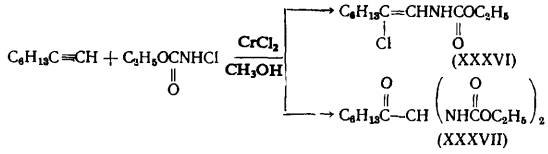
In their reactions with *NN*-dihalogenoarenesulphonamides (but not with dichlorocarbamate), alka-1,4-dienes afford, together with open-chain products, small amounts of cyclic adducts, mainly pyrrolidine derivatives. However, cyclohexa-1,4-diene does not form an azabicyclic compound, in contrast to *cis,cis*-cycloocta-1,5-diene, which produces such a compound in its reaction with *NN*-dibromotoluene-*p*-sulphonamide.[103] 1,4-Diphenylbuta-1,3-diene reacts with *NN*-dibromobenzenesulphonamide to form a pyrrolidine derivative and 1,2,3,4-tetrabromo-1,4-diphenylbutane in low yields. The authors attributed a symmetrical structure to the cyclic products of the addition of *NN*-dibromobenzenesulphonamide to hexa-1,5-diene, which does not agree with the firmly established mode of addition of halogenoamides to alkenes.[104]

The addition of diethyl *NN*-dichlorophosphoramidate to conjugated alka-1,3-dienes (butadiene, isoprene, 2,3-dimethylbutadiene) proceeds regiospecifically with formation of an (*E*)-1,4-adduct. The addition to cyclohexa-1,3-diene takes place in the same way. *trans*-Piperylene, 4-methylpenta-1,3-diene, 2,5-dimethylhexa-2,4-diene, and 1,4-diphenylbuta-1,3-diene usually give rise to a mixture of products. As in the case of other *NN*-dichloroamides, the reaction proceeds via a free-radical mechanism.[105]

VII. Acetylenes

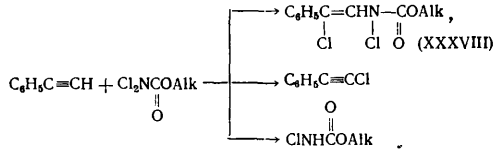
The reactions of acetylenes with *N*-halogenoamides have been least investigated. As a result of the high lability of enamines or enamides, obtained as a result of the addition reaction, the authors of the few studies which have been carried out succeeded in isolating either the products of further reactions or the true adducts in low yields. Only oct-1-yne and phenylacetylene were introduced into the reaction.

The addition of *N*-chlorocarbamate to oct-1-yne gives rise to a complex mixture of products, from which the adduct (XXXVI) and the *NN*-di(ethoxycarbonylamino)ketone (XXXVII), formed evidently as a result of the hydrolysis of the 2:1 adduct, were isolated. However, completely different proportions of the products (XXXVI) and (XXXVII) were obtained in two experiments (respectively 28 and 9% in one and traces and 13% in the other):

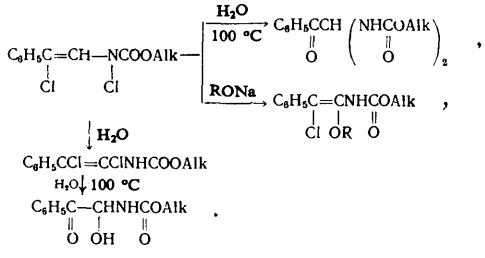


Unfortunately, the physicochemical constants and the methods used to isolate the above compounds are not quoted, which gives rise to some doubt as to the reliability of the results.[11]

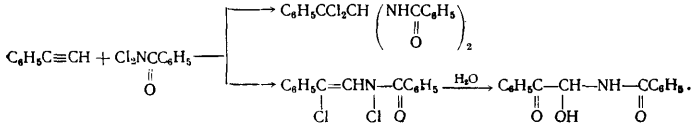
The addition of *NN*-dichloroamides to phenylacetylene has been studied:[106,107]



The *N*-chloro-*N*-(β-chlorostyryl)urethanes (XXXVIII) obtained are a mixture of geometrical isomers in proportions of 7:3; after storage for 24 h they rearrange to $C_6H_5CCl=CClNHCOOAlk$, which in our view is not an entirely usual behaviour. A number of chemical reactions of the compounds isolated demonstrate, according to the authors, the structure of the adducts formed initially:

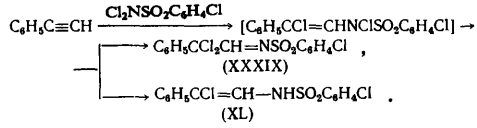


NN-Dichlorobenzamide adds in the same way to phenylacetylene:[108]



However, in both cases the hydrolysis and interaction of compound (XXXVIII) with sodium alkoxide are open to doubt. The lack of spectroscopic data for the NCl-adducts isolated and also the very high, in our view, chemical shift of the proton at the nitrogen atom in compound (XXXVIII) (9.05, 9.25 p.p.m.) suggest the possibility that the interaction of *NN*-dichloroamides with phenylacetylene proceeds differently than has been suggested.[106] *N*-Bromoamides have not been introduced into similar reactions.

The reaction of *NN*-dichloro-4-chlorobenzenesulphonamide with phenylacetylene afforded a high yield of the azomethine (XXXIX):[109]



Thus the previously uninvestigated "halogenotropism", i.e. the 1,3-migration of chlorine (most probably intramolecular) in the molecule of the NCl-adduct formed initially, occurs in this instance. Treatment of the reaction mixture with a solution of sodium bisulphite leads to a complex mixture of products, from which the adduct (XL) was isolated in a low yield (5%).

The addition of iodine isocyanate to acetylenes is complicated by the formation of diiodo-derivatives as side products. The pure reaction product cannot be obtained.[102] Ony the product derived from oct-4-yne by the addition of iodine isocyanate followed by treatment with methanol was isolated (yield 20%).

VIII. Alkenynes

The reactions involving the addition of *NN*-dihalogenoamides to conjugated alkenynes have been investigated in relation to vinylacetylene and its homologues.[101,109] The reactions of *NN*-dichlorocarbamates were performed in an argon atmosphere at a reduced temperature:

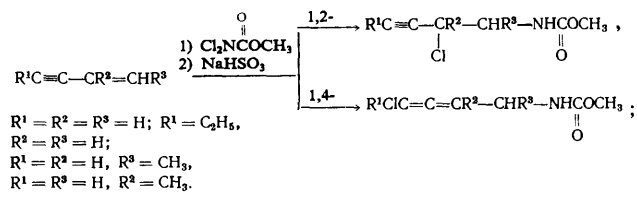


Table 4. The isomeric composition of the products of the addition of *N*-halogenocarbamates to alk-1-en-3-ynes.[101,112]

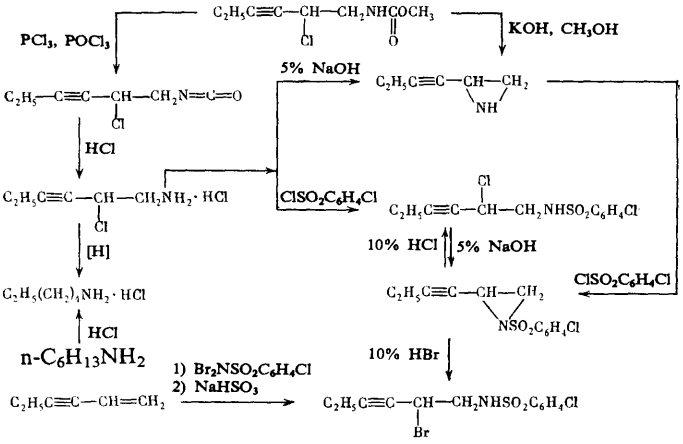
Hydrocarbon	$Cl_2NCOOCH_3$		$BrNHCOOCH_3$	
	1,2-	1,4-	1,2-	1,4-
$HC\equiv C-CH=CH_2$	30	70	70	30
$C_2H_5-C\equiv C-CH=CH_2$	100	—	95	5
$HC\equiv C-C(CH_3)=CH_2$	15	85	—	100
$HC\equiv C-CH=CH-CH_3$	60	40	20	80

It has been established that vinylacetylene and its closest homologues are attacked by *NN*-dichlorocarbamate only at the terminal atom of the ethylene bond and in the case of monosubstituted acetylenes the 1,4-adduct is formed preferentially. The amount of the 1,2-isomer in the case of propenylacetylene is

much greater than for isopropenyl- and vinyl-acetylenes. In the reaction of vinylethylacetylene, only the 1,2-adduct is formed (Table 4).

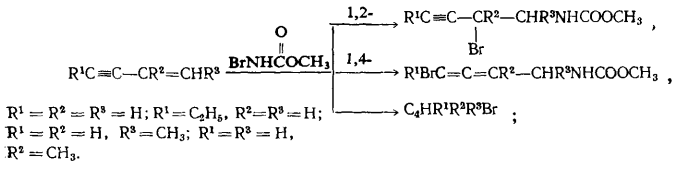
Attack by the carbamate group on the extreme ethylenic atom of the 1,3-enyne system was demonstrated in the last case not only from a study of the NMR spectra but also by means of chemical reactions (Scheme 1). The allenic (acetylenic) carbamates obtained do not isomerise to 1,3-dienes or acetylenes (allenes) either in the presence of copper(I) chloride or on treatment with alkali.

Scheme 1



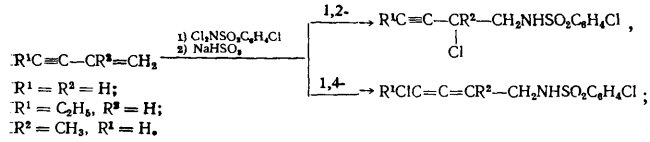
The inability of the compounds indicated to isomerise supports the view that the 1,2- and 1,4-isomers are obtained independently via a single mechanism, i.e. their addition reaction begins with attack by the carbamate group on the terminal ethylenic atom and not with attack by the chlorine atom on the extreme carbon atom of the triple bond with a subsequent allene–acetylene rearrangement.

In the reactions of *N*-bromocarbamate with alk-1-en-3-ynes, the amide moiety added to the ethylenic end of the molecule with rigorous selectivity, as in the reaction described above:[101]



However, the amount of 1,2-adducts in these reactions is smaller than in the reactions with *NN*-dichlorocarbamates. Vinylacetylene, for which the ratio of the isomers is reversed on replacement of *NN*-dichlorocarbamate by *N*-bromocarbamate, is an exception (Table 4). The reaction of *N*-bromocarbamate with alk-1-en-3-ynes results in the formation, as in the reaction with 1,3-dienes, of a considerable amount of dibromo-derivatives as side products (up to 25%) (the mechanism of this reaction was examined in detail above).

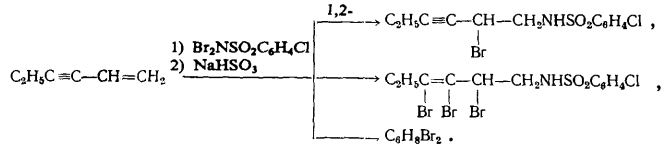
It has also been established that the regioselectivity of the addition of *NN*,4-trichlorobenzenesulphonamide to conjugated vinylacetylenes is similar to that for halogenocarbamates regardless of the experimental conditions:[109,110]



The terminal position of the sulphonamide group has been confirmed, apart from spectroscopic evidence, by a series of chemical reactions (presented in Scheme 1) in relation to 2-chloro-1-(4-chlorobenzenesulphonamido)hex-3-yne.

Trialkylsilyl-substituted vinylacetylenes combine with aromatic *NN*-dichlorosulphonamides at the double bond in the 1,4-position. The chlorine-containing adducts formed are unstable and are converted, already under the conditions of the addition reaction, into the corresponding alkadienyl(chloroalkynyl)sulphonamides. The addition is accompanied by the chlorination of the initial unsaturated compounds.[111]

The addition of *NN*-dibromo-4-chlorobenzenesulphonamide has been studied only in relation to vinylethylacetylene. The reaction mixture contained up to 40–45% of dibromo-derivatives, which were determined chromatographically. A tribromo-derivative was isolated from the reaction mixure as the main product. It was converted into the corresponding aziridine, which was also obtained by unambiguous synthesis. The monoadduct was identified by comparison with the authentic *N*-bromosulphonamide obtained as a result of the opening of the aziridine ring (Scheme 1):



Thus the view expressed in the literature that the order of the addition of *NN*-dihalogenoarenesulphonamides to unsaturated compounds depends on the experimental conditions and also that *NN*-dibromoarenesulphonamides add preferentially in accordance with the Markovnikov rule in reactions involving the addition of 4-chloro-*NN*-dibromobenzenesulphonamide to alk-1-ene-3-ynes has not been confirmed.[112] The structures of all the products obtained (the amide part of the reagent is attached exclusively or mainly to the extreme ethylenic atom) is convincing evidence in support of a radical reaction mechanism. This is also indicted by the absence of an appreciable influence of the solvent polarity on the mode of addition (the reaction with vinyl-acetylene was carried out in hexane, chloroform, and ether) and by the spontaneity and exothermicity of the process.[113] The amidyl radical formed as a result of the homolytic dissociation of the N–halogen bond attacks mainly the terminal atom of the double bond with formation of a more stable resonance-stabilised secondary propargyl radical. The attack on the terminal acetylenic atom with formation of a vinyl radical is less likely, since the electrophilic amidyl radical tends to attack the more nucleophilic double bond. Thus the preferential or exclusive formation of allenic or acetylenic isomers depends on the structure of the initial hydrocarbon and on the nature of the halogen in the reagent.

—o0o—

Summarising the analysis of the literature data for the addition of *N*-halogenoamides to unsaturated compounds, one may conclude that, despite some conflict between the results of the studies described, *N*-halogenamides can add to multiple bonds via both radical and ionic mechanisms depending on the conditions. In the former case, adducts are formed contrary to the Markovnikov rule, while in the latter the reaction proceeds in conformity with the Markovnikov rule. The most promising application of the reaction involving the addition of halogenoamides is the synthesis of aziridines.

References

1. D Touchard, J Lessard *Tetrahedron Lett.*, 1971, 4425
2. D Touchard, J Lessard *Tetrahedron Lett.*, 1973, 3827
3. R S Neale, N L Marcus, R G Schepers *J. Am. Chem. Soc.*, 1966, **88** 3051
4. M E Kuehne, D A Horne *J. Org. Chem.*, 1975, **40** 1287
5. R S Neale *Synthesis*, 1971, 1
6. M E Wolf *Chem. Rev.*, 1963, **63** 55
7. J Lessard, R Cote *J. Org. Chem.*, 1978, **43** 3750
8. R H Hesse *Adv. Free-Radical Chem.*, Acad. Press, New York, 1969, Vol. 3, p. 83
9. J Lessard, J M Paton *Tetrahedron Lett.*, 1970, 4883
10. J Lessard, H Driguez, J P Vermes *Tetrahedron Lett.*, 1970, 4887
11. H Driguez, J M Paton, J Lessard *Can. J. Chem.*, 1977, **55** 700
12. H Driguez, J Lessard *Can. J. Chem.*, 1977, **55** 720
13. M Mondon, J Lessard *Can. J. Chem.*, 1978, **56** 2590
14. P Chabrier *Ann. Chim.*, 1942, **17** 353
15. T A Foglia, D Swern *J. Org. Chem.*, 1966, **31** 3625
16. Ya G Bal'on, R N Moskaleva *Zh. Org. Khim.*, 1975, **11** 2497
17. K Schrage *Tetrahedron Lett.*, 1966, 5795
18. T A Foglia, D Swern *J. Org. Chem.*, 1967, **32** 75
19. D Swern *Ann. N.Y. Acad. Sci.*, 1969, 163
20. C G Gebelein, D Swern *Chem. Ind.*, 1965, 1462
21. S Rosen, D Swern *Anal. Chem.*, 1966, **38** 1392
22. A Hassner, M E Gorber *J. Org. Chem.*, 1967, **32** 540
23. K Schrage *Tetrahedron*, 1967, 3039
24. T A Foglia, D Swern *J. Org. Chem.*, 1968, **33** 766
25. J Lessard, D Touchard *Chem. J. Chem.*, 1981, **59** 431
26. M V Likhosherstov, R A Arkhangel'skaya *Zh. Obshch. Khim.*, 1937, **7** 1914
27. M V Likhosherstov, T V Shalaeva *Zh. Obshch. Khim.*, 1938, **8** 370
28. M V Likhosherstov, V E Zhabotinskaya, L D Pavlovskaya *Zh. Obshch. Khim.*, 1938, **8** 997
29. M V Likhosherstov, A A Petrov *Zh. Obshch. Khim.*, 1939, **9** 2000
30. M S Karasch, H M Priestley *J. Am. Chem. Soc.*, 1939, **61** 3425
31. F A Daniher, P E Butler *J. Org. Chem.*, 1968, **33** 4336
32. N A Rybakova, P V Petrovskii, P O Okulevich, P Kh Freidlina *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1970, 1577
33. H Terauchi, A Yamasaki, S Takemura *Chem. Pharm. Bull.*, 1975, **23** 3162
34. F A Daniher, M T Melchior, P E Butler *J. Chem. Soc., Chem. Commun.*, 1968, 931
35. T A Foglia, E T Haeberer, G Maerker *J. Am. Oil Chem. Soc.*, 1970, **47** 27
36. T Ohashi, M Sugie, M Okahara, S Komori *Tetrahedron Lett.*, 1968, 4195
37. T Ohashi, M Sugie, M Okahara, S Komori *Tetrahedron*, 1969, **25** 5349
38. G H Coleman *Proc. Iowa Acad. Sci.*, 1939, **46** 217
39. M Okahara, T Ohashi, S Komori *J. Org. Chem.*, 1968, **33** 3066
40. A Zwierzak, A Koziara *Tetrahedron*, 1970, **26** 3521
41. A Zwierzak, S Zawadzki *Synthesis*, 1971, 323
42. A Zwierzak, S Zawadzki *Synthesis*, 1972, 416
43. S Zawadzki, A Zwierzak *Tetrahedron*, 1973, **29** 315
44. S Zawadzki, A Zwierzak *Tetrahedron*, 1981, **37** 2675
45. K Osowska-Pacewicka, A Zwierzak *Tetrahedron*, 1985, **41** 4417
46. B J Walker, P J Wrobel *J. Chem. Soc., Chem. Commun.*, 1980, 462
47. K Schrage *Tetrahedron*, 1967, **23** 3033
48. Ya G Bal'on, R N Moskaleva *Zh. Org. Khim.*, 1978, **14** 1462
49. N I Filenko, V B Mochalin *Zh. Org. Khim.*, 1979, **15** 475
50. S Wolfe, D V C Awang *J. Am. Chem. Soc.*, 1967, **89** 5286
51. J D Park, H J Gerjovich, W R Lycan, J R Lacher *J. Am. Chem. Soc.*, 1952, **74** 2189
52. R E Buckles, R C Johnson *J. Org. Chem.*, 1957, **22** 55
53. W A Pryor *Free Radicals* (Translated into Russian), Atomizdat, Moscow, 1970, p. 333
54. G Drefahl, K Ponsold, G Köllner *J. Prakt. Chem.*, 1964, **23** 136
55. K Ponsold, G Drefahl *Chem. Ber.*, 1960, **93** 519
56. J Ueno *Chem. Pharm. Bull.*, 1965, **13** 1369
57. J Ueno, S Takemura, J Ando, H Terauchi *Chem. Pharm. Bull.*, 1967, **15** 1193
58. J Ueno, S Takemura, J Ando *Chem. Pharm. Bull.*, 1967, **15** 1198
59. J Adam, P A Gosselain, P Goldfinger *Bull. Soc. Chim. Belg.*, 1956, **65** 523
60. W Theilacker, H Wessel *Liebigs. Ann. Chem.*, 1967, **703** 34
61. A C Oehlschlager, L H Zalkov *Tetrahedron Lett.*, 1964, 2663
62. A C Oehlschlager, C D Kennedy, L H Zalkow *J. Org. Chem.*, 1966, **31** 1682
63. J E Bäckvall, K Oshimov, R E Palermo, K B Sharpless *J. Org. Chem.*, 1979, **44** 1953
64. Ya G Bal'on, R N Moskaleva *Zh. Org. Khim.*, 1979, **15** 1207
65. Ya G Bal'on, R N Moskaleva *Ukr. Khim. Zh.*, 1977, (7) 775
66. Ya G Bal'on *Zh. Org. Khim.*, 1974, **10** 408
67. Ya G Bal'on *Zh. Org. Khim.*, 1980, **16** 2606
68. Ya G Bal'on, R N Moskaleva *Zh. Org. Khim.*, 1980, **16** 2599
69. Z Földi *Ber.*, 1930, **63** 2257
70. T P Leden, P W Turner *J. Chem. Soc. C*, 1968, 876
71. N A Rybakova, P V Petrovskii, P O Okulevich *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1970, 1577
72. R Kh Freidlina, N A Rybakova, G K Semin, E A Kravchenko *Dokl. Akad. Nauk SSSR*, 1967, **176** 352
73. H Terauchi, S Takemura, J Ueno *Chem. Pharm. Bull.*, 1975, **23** 640
74. R E Buckles, W J Probst *J. Org. Chem.*, 1957, **22** 1728
75. H Terauchi, S Takemura *Chem. Pharm. Bull.*, 1975, **23** 2410
76. K Otsuki, T Irino *Chem. Pharm. Bull.*, 1975, **23** 2410
77. N A Rybakova, R Kh Freidlina *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1971, 429
78. T Adachi, K Otsuki *Chem. Pharm. Bull.*, 1976, **24** 2803
79. K Otsuki, T Irino *Chem. Pharm. Bull.*, 1975, **23** 482
80. A Zwierzak, A Koziara *Tetrahedron*, 1970, **26** 3527
81. Ya G Bal'on, V E Paranyuk *Zh. Org. Khim.*, 1976, **12** 522

82. Ya G Bal'on, V E Paranyuk *Zh. Org. Khim.*, 1983, **19** 1346
83. A N Mirskova, G G Levkovskaya, I T Gogoberidze, et al. *Zh. Org. Khim.*, 1983, **19** 1110
84. A N Mirskova, G G Levkovskaya, I T Gogoberidze, et al. *Zh. Org. Khim.*, 1985, **21** 269
85. A N Mirskova, G G Levkovskaya, T I Drozdova, et al. *Zh. Org. Khim.*, 1982, **18** 452
86. I T Gogoberidze, G G Levkovskaya, A N Mirskova, et al. *Zh. Org. Khim.*, 1985, **21** 633
87. A N Mirskova, G G Levkovskaya, A A Bryuzgin, et al. *Zh. Org. Khim.*, 1986, **22** 377
88. A N Mirskova, T I Drozdova, G G Levkovskaya, et al. *Zh. Org. Khim.*, 1986, **22** 763
89. M B Taraban, V I Mar'yasova, T V Leshina, et al. *Zh. Org. Khim.*, 1986, **22** 925
90. A N Mirskova, G G Levkovskaya, T I Drozdova, et al. *Zh. Org. Khim.*, 1982, **18** 1632
91. A N Mirskova, G G Levkovskaya, T I Drozdova, et al. *Zh. Org. Khim.*, 1981, **17** 1101
92. A N Mirskova, T I Drozdova, G G Levkovskaya, et al. *Zh. Org. Khim.*, 1981, **17** 1108
93. N A Rybakova, N A Pochkailo, L N Kiseleva *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 2793
94. N A Rybakova, V I Dostavalova, N A Slepushkina, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 359
95. Ya G Bal'on, V E Paranyuk *Zh. Org. Khim.*, 1980, **16** 2246
96. Ya G Bal'on, V E Paranyuk *Zh. Org. Khim.*, 1979, **15** 1203
97. Ya G Bal'on, V E Paranyuk *Zh. Org. Khim.*, 1980, **16** 556
98. V I Markov, V A Doroshenko *Zh. Org. Khim.*, 1972, **8** 1251
99. G G Levkovskaya, A N Mirskova, T I Drozdova, et al. *Zh. Org. Khim.*, 1985, **21** 620
100. F A Daniher, P E Butler *J. Org. Chem.*, 1968, **33** 2637
101. N N Labeish, Yu I Porfir'eva, A A Petrov *Zh. Org. Khim.*, 1984, **20** 477
102. B E Grinwood, D Swern *J. Org. Chem.*, 1967, **32** 3655
103. H Stetter, K Heckel *Chem. Ber.*, 1973, **106** 339
104. A Jamasaki, H Terauchi, S Takemura *Chem. Pharm. Bull.*, 1976, **24** 2841
105. T Gajda, A Zwierzak *Tetrahedron*, 1985, **41** 4953
106. Ya G Bal'on, R N Moskaleva *Zh. Org. Khim.*, 1977, **13** 664
107. Ya G Bal'on, R N Moskaleva *Zh. Org. Khim.*, 1978, **14** 147
108. Ya G Bal'on, R N Moskaleva *Zh. Org. Khim.*, 1983, **19** 2456
109. N N Labeish, Yu I Porfir'eva, A A Petrov *Zh. Org. Khim.*, 1983, **19** 1540
110. N N Labeish, Yu I Porfir'eva, A A Petrov *Zh. Org. Khim.*, 1984, **20** 447
111. I S Vorob'eva, M D Stadnichuk *Zh. Obshch. Khim.*, 1983, **54** 2731
112. N N Labeish, Candidate's Thesis, Lensovet Leningrad Technological Institute, Leningrad, 1984
113. P Mackiewicz, R Furstoss *Tetrahedron*, 1978, **34** 3241

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Phosphorus-containing alkyl, alkenyl, aryl, acyl, and sulphonyl isocyanates

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ABSTRACT. In this review the information in the literature on the methods of synthesis, physicochemical properties, and application of phosphorus-containing alkyl, alkenyl, aryl, acyl, and sulphonyl isocyanates has been classified and correlated.

The bibliography includes 143 references.

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I. Introduction

Alkyl and aryl isocyanates have been known for over a hundred years. The first examples of phosphorus-containing organic isocyanates were not synthesised until 1956.[1] In recent years a considerable number of new types of alkyl and aryl isocyanates containing one or more phosphorus atoms in the molecule have been obtained and some of their properties have been studied. In 1973 a short review was published on phosphorus-containing alkyl, aryl, acyl, and sulphonyl isocyanates, including studies carried out before 1971;[2] it is now out of date. It is therefore of interest to correlate both the old and new information on the methods of synthesis and properties of phosphorus-containing organic isocyanates.

II. Methods of synthesis

1. Phosphorus-containing alkyl, alkenyl, and aryl isocyanates

(a) Reactions of chloroalkyl phosphates and chlorophosphoramidates with silver cyanate

On heating tris(trichloromethyl)phosphate with silver cyanate in benzene, tris(isocyanatomethyl)phosphate is formed:[3]

$$OP(OCH_2Cl)_3 + 3AgOCN \rightarrow 3AgCl + OP(OCH_2NCO)_3.$$

Diethyl 1,2,2,2-tetrachloroethylphosphoramidate reacts with silver cyanate by a similar route, but it is not possible to obtain the resulting diethyl 1-isocyanato-2,2,2-trichloroethylphosphoramidate in a pure form.[4]

(b) Phosgenation of phosphorus-containing amines and *N*-phosphorylated amidines

Diesters of α-aminoalkylphosphonic and α-aminoalkylphosphonothioic acids react fairly readily with phosgene, and depending on the concentration of the reactants they form either diesters of α-isocyanato-substituted alkylphosponic and alkylphosphonothioic acids or *N*,*N*′-bis[α-(dialkoxyphosphoryl)alkyl]ureas:[1,5]

$$(C_2H_5O)_2P(X)CRR^1NH_2 \xrightarrow{COCl_2} \begin{cases} \xrightarrow[X=O,\,S]{3:1} (C_2H_5O)_2P(X)CRR^1NCO \\ \xrightarrow[X=O]{4:1} [(C_2H_5O)_2P(X)CRR^1NH]_2CO \end{cases}$$

X = O: R = R^1 = CH_3 or R = H, R^1 = C_6H_5; X = S: R = R^1 = CH_3.

The aminophosphonate and aminophosphonothioate diesters required for these syntheses are obtained from dialkyl phosphites (or dialkyl phosphorothioites), aldehydes (or ketones), and ammonia:[5–7]

$$(C_2H_5O)_2P(X)H + RC(O)R^1 + NH_3 \rightarrow (C_2H_5O)_2P(X)CRR^1NH_2.$$

Esters of α-(dialkoxyphosphoryl)aminoacetic acid react with phosgene in a similar manner[8] to form the corresponding isocyanates.[9]

Treatment of (*S*)-(−)-α-(diethoxyphosphoryl)benzylamine with phosgene[10–12] in the presence of pyridine resulted in the synthesis of the first example of optically active α-phosphorylated organic isocyanates—(*S*)-(+)-α-(diethoxyphosphoryl)benzyl isocyanate ($[\alpha]_D^{20}$ + 35.5°, *c* = 2, CCl_4).[12–14]

When aminoaryl esters of phosphoric, phosphorothioic, phosphonic, phosphonothioic, and phosphinothioic acids are reacted with phosgene in inert organic solvents at 50–120 °C, isocyanatoaryl esters of the corresponding phosphorus acids are obtained:[15–23]

$$XP(OC_6H_4NCO\text{-}4)_3,\quad (C_2H_5O)_2P(X)OC_6H_4NCO\text{-}4 \quad (\text{where } X = O, S),$$

$$C_6H_5N(CH_3)P(O)(OC_6H_4NCO\text{-}4)_2,\quad C\left[\begin{array}{c}CH_2O\\ \diagdown\\ \diagup\\ CH_2O\end{array}\!\!>P(O)OC_6H_4NCO\text{-}4\right]_2,$$

$$C_6H_5CH{=}CHP(O)(OC_6H_3CH_3\text{-}4\text{-}NCO\text{-}3)_2,$$

$$(CH_3)_nP(S)(OC_6H_3CH_3\text{-}4\text{-}NCO\text{-}3)_{3-n}.$$

When *O*,*O*′-bis(4-aminophenyl)-*N*,*N*-dimethylphosphoramidate is treated with phosgene, cleavage of the P–N bond occurs together with phosgenation of the amino group and *O*,*O*′-bis(4-isocyanatophenyl)phosphorochloridate is formed:[20]

$$(CH_3)_2NP(O)(OC_6H_4NH_2\text{-}4)_2 \xrightarrow[-4HCl]{COCl_2} ClP(O)(OC_6H_4NCO\text{-}4)_2 + (CH_3)_2NCOCl.$$

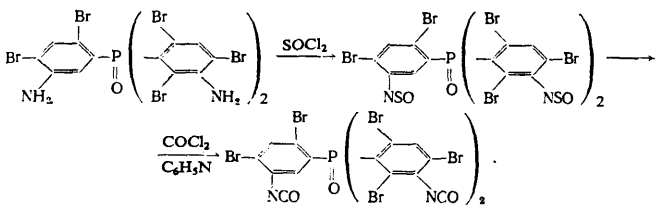
When phosgene reacts with aminoaryl phosphites the P—O bond is cleaved and isocyanatoaryl phosphites are not formed.[20]

Aminoaryl esters of phosphorus acids are obtained by reduction of the corresponding nitroaryl esters, by reaction of phosphorus acid chlorides with aminophenol, or by oxidation of aminoaryl phosphites.[16–18,20,24,25] Tris(*p*-nitrophenyl) phosphate is obtained by nitration of triphenyl phosphate. Nitrophenyl esters of other phosphorus acids are obtained by reaction of phosphorus acid chlorides with nitrophenols.[17,18,20,24]

Hexa(4-isocyanatophenoxy)triphosphonitrile is synthesised by phosgenation of hexa(4-aminophenoxy)triphosphonitrile:[26]

$$(P_3N_3)(OC_6H_4NH_2\text{-}4)_6 \xrightarrow{COCl_2} (P_3N_3)(OC_6H_4NCO\text{-}4)_6.$$

The conversion of aminoarylphosphine oxides to isocyanatoarylphosphine oxides by phosgenation of the intermediate $-N=S=O$ compounds has been reported:[27]



When *N*-(diphenoxyphosphoryl)benzamidine is boiled with phosgene, *N*-(diphenoxyphosphoryl)iminobenzoyl isocyanate $C_6H_5C[=NP(O)(OC_5H_5)_2]NCO$ is obtained.[28]

(c) Reaction of haloalkyl isocyanates with alkyl esters of trivalent phosphorus acids

Trialkyl phosphites and alkyl phosphinites undergo an Arbuzov rearrangement with chloromethyl isocyanate at –20 °C to form dialkoxy-, dialkyl-, or diaryl-phosphorylmethyl isocyanates.[29–32] When chloromethyl isocyanate reacts with alkyl phosphoro-dichloridites, alkyl phosphorodifluoridites, dialkyl phosphorochloridites, and dialkyl phosphorofluoridites, dihalophosphoryl- and alkoxy-halophosphoryl-methyl isocyanates are obtained. Reactions with dialkyl phosphorohalidites occur both in the presence of catalytic quantities of $FeCl_3$ and without it, while alkyl phosphorodihalidites react only in the presence of a catalyst.[30,32–35] Bromomethyl isocyanate also reacts in a similar manner with trialkyl phosphites, dialkyl phosphorohalidites, and alkyl phosphorodihalidites, but the reaction takes place under milder conditions:[14,35,36]

$$R_2POR^1 + XCH_2NCO \longrightarrow [R_2(R^1O)PCH_2NCO]^+X^- \xrightarrow{-R^1X} R_2P(O)CH_2NCO,$$
$$R = AlkO,\ Alk,\ Ar;\quad X = Cl,\ Br;$$
$$ROPX_2 + YCH_2NCO \xrightarrow[-RY]{FeCl_3} X_2P(O)CH_2NCO;$$
$$(RO)_2PX + YCH_2NCO \xrightarrow{-RY} X(RO)P(O)CH_2NCO,$$
$$R = Alk;\quad X = Cl,\ F;\quad Y = Cl,\ Br.$$

α,β-Dichloro- and α,β-dibromo-methyl isocyanates react with trialkyl phosphites, dialkyl phosphorohalidites, and alkyl phosphorodihalidites to form only α-phosphorylated β-chloro- or β-bromo-ethyl isocyanates. The reaction with alkyl phosphoro-dihalidites only takes place in the presence of catalysts. The halogen atoms at the β-position of these isocyanates are much less active and do not undergo reaction.[14,35,37–40]

α-Chlorobenzyl isocyanate undergoes a reaction with trialkyl phosphites, dialkyl phosphorohalidites, and alkyl phosphoro-dihalidites in a similar manner to chloromethyl isocyanate but under slightly more severe conditions.[14,35,41]

Diphenylchloromethyl isocyanate exists as a tautomeric mixture with *N*-chlorocarbonyldiphenylketimine and on reacting with ethyl diaryl phosphites gives two isomeric products in approximately equal quantities—α-(diaryloxyphosphoryl)diphenylmethyl isocyanate and the *N*-benzhydrylidenamide of phosphonoformic acid:[14,42,43]

$$\begin{array}{l}(C_6H_5)_2C(Cl)NCO \\ \quad\uparrow\downarrow \\ (C_6H_5)_2C=NCOCl\end{array} \xrightarrow{C_2H_5OP(OAr)_2} (ArO)_2P(O)C(C_6H_5)_2NCO + \\ + (C_6H_5)_2C=NCOP(O)(OAr)_2.$$

In contrast to diphenylchloromethyl isocyanate, 1-chloro-1-phenyl-2,2,2-trifluoroethyl isocyanate exists only in the isocyanate form and when it reacts with triphenyl phosphite gives only the isocyanate:[44]

$$(C_2H_5O)_3P + C_6H_5CCl(CF_3)NCO \xrightarrow[-C_2H_5Cl]{} (C_2H_5O)_2P(O)C(C_6H_5)(CF_3)NCO.$$

It was reported[45] that when 1,2,2,2-tetrachloroethyl isocyanate is reacted with triethyl phosphite in carbon tetrachloride, 1-(diethoxy-phosphoryl)-2,2,2-trichloroethyl isocyanate is obtained in good yield. It was later established that when this isocyanate is reacted with trialkyl phosphites and dialkyl phosphorohalidites, a mixture of 1-(dialkoxyphosphoryl)- or 1-(alkoxyhalophosphoryl)-substituted 2,2,2-trichloroethyl and 2,2-dichlorovinyl isocyanates is formed:[46]

$$(RO)_2PX + CCl_3CHClNCO \rightarrow X(RO)P(O)CH(CCl_3)NCO + \\ + X(RO)P(O)C(=CCl_2)NCO,$$
$$X = RO,\ Cl,\ F;\quad R = Alk.$$

Unsaturated α-chlorovinyl isocyanate undergoes an Arbuzov reaction with triethyl phosphite in the same way as α-chloroalkyl isocyanates but the reaction takes place under more severe conditions:[47]

$$(C_2H_5O)_3P + CH_2=CClNCO \longrightarrow (C_2H_5O)_2P(O)C(=CH_2)NCO.$$

Dichloro- and trichloro-methyl isocyanates also readily undergo an Arbuzov rearrangement with phosphites, dialkyl phosphoro-halidites, and alkyl phosphorodihalidites. Under normal conditions dichloromethyl isocyanate exists as a tautomeric mixture with *N*-chloromethylenecarbamoyl chloride; this has been confirmed from its IR spectra. In the reaction with trialkyl phosphite nucleophilic attack by the phosphorus atom is directed on to both the carbon atom of the dichloromethyl group and the carbon atom of the chlorocarbonyl group so that a mixture of at least two products is formed. Only the isocyanate was isolated by vacuum fractionation:

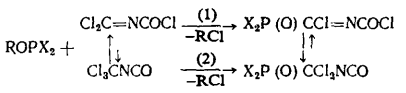
$$\begin{array}{l}Cl_2CHNCO \\ \quad\uparrow\downarrow \\ ClCH=NCOCl\end{array} \xrightarrow{(C_2H_5O)_3P} (C_2H_5O)_2P(O)CHClNCO + \\ + ClCH=NC(O)P(O)(OC_2H_5)_2.$$

Reaction of dichloromethyl isocyanate with 2 moles of triethyl phosphite results in the formation of the bis-phosphorylated methyl isocyanate $[(C_2H_5O)_2P(O)]_2CHNCO$.[32,48]

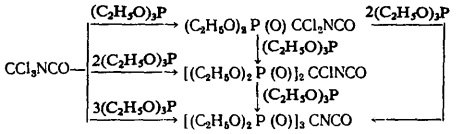
Diethyl phosphorofluoridite reacts with dichloromethyl isocyanate without a catalyst and depending on the ratio of the reactants (1 : 1 or 2 : 1) either ethoxyfluorophosphorylchloromethyl isocyanate or bis(ethoxyfluorophosphoryl)methyl isocyanate are formed.[32,35,49,50]

When dichloromethyl isocyanate reacts with diethyl phosphoro-chloridite, ethoxychlorophosphorylchloromethyl isocyanate is formed; in this case the second chlorine atom cannot be replaced by a phosphoryl group.[32,35,50] Dichloromethyl isocyanate reacts with alkyl phosphorodichloridites and phosphorodifluoridites in a similar manner to chloromethyl isocyanate, forming dihalophosphoryl-chloromethyl isocyanates.[32,35,50,51]

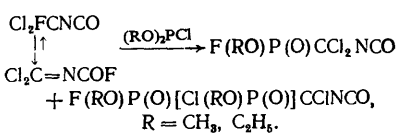
Under normal conditions trichloromethyl isocyanate exists in its tautomeric form—*N*-(dichloromethylene)carbamoyl chloride. On heating, the equilibrium is displaced towards the isocyanate form. When the tautomeric mixture reacts with alkyl phosphorodihalidites in the presence of catalytic quantities of $FeCl_3$, dihalophosphoryl-dichloromethyl isocyanates are obtained, and their formation can be represented by two routes.[32,52,53]



Depending on the ratio of the reactants (1 : 1 or 2 : 1), trichloromethyl isocyanate reacts with diethyl phosphorochloridite to form a mixture of mono- and bis-phosphorylated chloromethyl isocyanates or only bis-phosphorylated chloromethyl isocyanate. When diethyl phosphorofluoridite reacts with trichloromethyl isocyanate, only bis(ethoxyfluorophosphoryl)chloromethyl isocyanate can be isolated, whatever the ratio of the reactants (1 : 1, 2 : 1, or 3 : 1).[32,35,53] Trichloromethyl isocyanate reacts with one, two, and three moles of triethyl phosphite to form diethoxyphosphoryl-dichloromethyl, bis(diethoxyphosphoryl)chloromethyl, and tris(diethoxyphosphoryl)methyl isocyanates respectively. Bis- and tris-phosphorylated alkyl isocyanates are also obtained by reaction of mono- and bis-phosphorylated haloalkyl isocyanates with a suitable quantity of triethyl phosphite:[32,35,54]

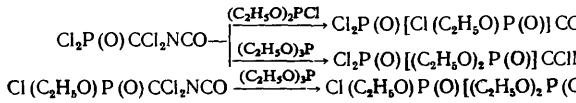


Dichlorofluoromethyl isocyanate, which exists mainly in the form of *N*-(dichloromethylene)carbamoyl fluoride (1 : 14), reacts with dialkyl phosphorochloridites in an interesting manner. In addition to formation of the expected alkoxychlorophosphorylchlorofluoro-methyl isocyanate and bis(alkoxychlorophosphoryl)fluoromethyl isocyanate, as in the case of the reaction with trichloromethyl isocyanate, a mixture of alkoxyfluorophosphoryldichloromethyl isocyanate and alkoxyfluorophosphoryl(alkoxychlorophosphoryl)chloromethyl isocyanate is formed with the latter predominating:[55]



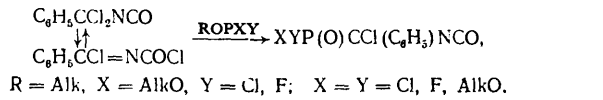
Tribromomethyl isocyanate reacts with trialkyl phosphites, dialkyl phosphorohalidites, and alkyl phosphorodihalidites in a similar manner to trichloromethyl isocyanate. However, it was only possible to isolate dichlorophosphoryldibromomethyl isocyanate $Cl_2P(O)CBr_2NCO$, tris(diethoxyphosphoryl)methyl isocyanate $[(C_2H_5O)_2P(O)]_3CNCO$, and difluorophosphoryldibromomethyl isocyanate $F_2P(O)CBr_2NCO$, in a pure form, with a small quantity of initial Br_3CNCO present.[40]

Dichlorophosphoryl- and ethoxychlorophosphoryl-dichloromethyl isocyanates also react with 1 mole of diethyl phosphorochloridite or triethyl phosphite to form mixed bis-phosphorylated chloromethyl isocyanates.[32,53]

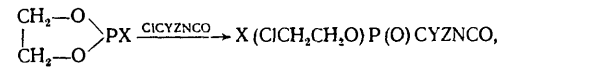


Ethoxyfluorophosphoryldichloromethyl isocyanate reacts with diethyl phosphorochloridite in a similar manner:[55]

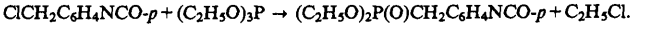
α,α-Dichlorobenzyl isocyanate reacts with esters and halide esters of trivalent phosphorus acids in a similar manner to α-chlorobenzyl isocyanate to form α-phosphorylated α-chlorobenzyl isocyanates. The reaction of α,α-dichlorobenzyl isocyanate with two (or more) moles of alkyl phosphorodichloridite or phosphorodifluoridite occurs with replacement of only a single chlorine atom by a dihalophosphoryl group, while when it is reacted with two moles of dialkyl phosphorohalidite or trialkyl phosphite a complex mixture is formed, from which pure compounds could not be isolated:[56]



The cyclic phosphites—2-chloro- and 2-fluoro-phospholanes—undergo an Arbuzov reaction with chloro-, dichloro-, and trichloro-methyl isocyanates with ring-opening:[32,35,57]

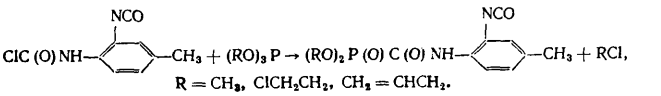


In contrast to α-chloroalkyl isocyanates, *p*-chloromethylphenyl isocyanate reacts with triethyl phosphite under more severe conditions (150–160 °C) without a solvent and *p*-(diethoxy-phosphorylmethyl)phenyl isocyanate is obtained in low yield:[30,31]

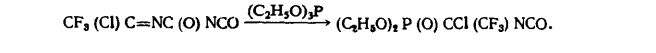


1-Chloromethyl- and 1-bromomethyl-2,4-diisocyanatobenzenes and bis(4-isocyanatophenyl)chloromethane also undergo an Arbuzov reaction with trialkyl phosphites but the corresponding isocyanates cannot be isolated as they probably polymerise in the presence of trialkyl phosphites.[20,58,59]

It should be mentioned that *N*-(isocyanatoaryl)carbamoyl chlorides also undergo a reaction with trialkyl phosphites, forming the corresponding phosphorus-containing aryl isocyanates:[20,60,61]



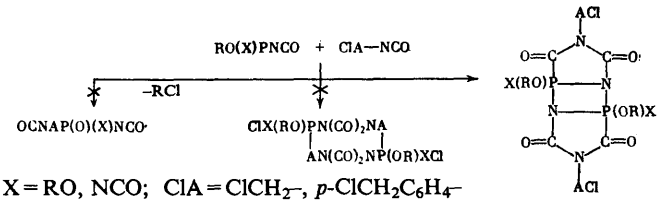
When *N*-(1-chloro-2,2,2-trifluoroethylidene)carbamoyl isocyanate reacts with triethyl phosphite, an isocyanate group rather than a chlorine atom is eliminated and 1-(diethoxyphosphoryl)-1-chloro-2,2,2-trifluoroethyl isocyanate is formed:[62,63]



N-(1-Methoxy-2,2,2-trifluoroethylidene)carbamoyl isocyanate reacts with triethyl phosphite in a similar manner.[62,63]

Chloromethyl isocyanate and *p*-chloromethylphenyl isocyanate also undergo a reaction with dialkyl phosphoroisocyanates and alkyl phosphorodiisocyanates but the products of Arbuzov rearrangement are not obtained. It was earlier suggested that quasiphosphonium compounds of dimeric structure are formed.[29,30,64] It was subsequently

established that tricyclic 1,3,2λ⁵4λ⁵-diazadiphosphetidine derivatives are obtained as a result of this reaction:[14,65–67]



X = RO, NCO; ClA = $ClCH_2$–, *p*-$ClCH_2C_6H_4$–

(d) Reaction of diaryl phosphites with α-chloroalkyl isocyanates

Diaryl phosphites readily react with a tautomeric mixture of diarylchloromethyl isocyanate with *N*-chlorocarbonyldiarylketimine in the presence of triethylamine to form diaryloxyphosphoryldiarylmethyl isocyanates:[42,43,68]

$$\begin{matrix} Ar_2C{=}NCOCl \\ \downarrow\uparrow \\ Ar_2C(Cl)NCO \end{matrix} + (Ar^1O)_2P(O)H \xrightarrow[-(C_2H_5)_3N{\cdot}HCl]{(C_2H_5)_3N} (Ar^1O)_2P(O)C(Ar)_2NCO.$$

(e) Reaction of chloroalkyl isocyanates with phosphorothioic acids

Chloromethyl isocyanate reacts with the potassium salts of *O,O'*-dialkylphosphorothioic and *O,O'*-dialkylphosphorodithioic acids to form the corresponding phosphorylated isocyanates:[29,69]

$$ClCH_2NCO + (RO)_2P(X)SK \rightarrow (RO)_2P(X)SCH_2NCO + KCl,$$
$$X = O, S.$$

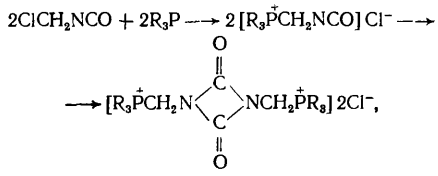
1-Chloro-1-phenyl-2,2,2-trifluoroethyl isocyanate reacts with *O,O'*-diisopropylphosphorodithioic acid in a similar manner.[44]

In contrast to chloromethyl and 1-chloro-1-phenyl-2,2,2-trifluoroethyl isocyanates, a tautomeric mixture of diphenylchloromethyl isocyanate and *N*-chlorocarbonyldiphenylketimine when reacted with *O,O'*-dialkylphosphorodithioic acids or their salts gives *O,O'*-dialkyl-*S*-(*N*-diphenylmethylenecarbamoyl)phosphorodithioates, which only in solution occur in tautomeric equilibrium with the corresponding isocyanates.[43,70]

$$\begin{matrix} (C_6H_5)_2C{=}NCOCl \\ \downarrow\uparrow \\ (C_6H_5)_2CClNCO \end{matrix} \xrightarrow{(RO)_2P(S)SH} \begin{matrix} (C_6H_5)_2C{=}N{-}C(O)SP(S)(OR)_2 \\ \downarrow\uparrow \\ (RO)_2P(S)SC(C_6H_5)_2NCO \end{matrix}$$

(f) Reaction of α-haloalkyl isocyanates with trialkyl- and triaryl-phosphines

Trialkyl- and triaryl-phosphines react very readily with chloromethyl isocyanate in inert solvents to form trialkyl- or triaryl-(isocyanatomethyl)phosphonium chlorides. Depending on the structure of the initial tertiary phosphines and also the reaction conditions and conditions for isolating the reaction products, either substituted isocyanatomethylphosphonium chlorides or their dimers can be obtained. In the case of triarylphosphines, both monomeric and dimeric products were obtained in a pure state, while in the case of trialkylphosphines only pure dimers were obtained:[29,71]



R = C_3H_7, C_8H_{17}, $C_{10}H_{21}$, C_6H_5, *p*-$CH_3OC_6H_4$, *p*-$CH_3C_6H_4$.

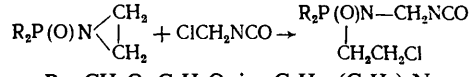
Bromomethyl isocyanate[36] and α-chlorobenzyl isocyanate[41,72] react in a similar manner with triphenylphosphine to form triphenyl(isocyanatomethyl)phosphonium bromide and triphenyl-(α-isocyanatobenzyl)phosphonium chloride.

It has not been possible to synthesise triaryl(isocyanatomethyl)-phosphonium iodides by this method since iodomethyl isocyanate, which is required for their synthesis, has not been prepared up to the present time. Attempts to obtain iodomethyl isocyanate demonstrated that it is very unstable and decomposes as it is being formed with considerable elimination of free iodine. Another method was used to synthesise triaryl(isocyanatomethyl)phosphonium iodides. On heating triaryl(isocyanatomethyl)phosphonium chlorides with methyl iodide in methylene chloride (45–60 °C, 1–2 h), chlorine is exchanged for iodine and triaryl(isocyanatomethyl)phosphonium iodides are obtained. For the purpose of preparative synthesis there is no need to obtain and isolate triaryl(isocyanatomethyl)phosphonium chlorides in a pure form. It is sufficient to add triarylphosphine to a mixture of chloromethyl isocyanate and methyl iodide and heat the reaction mixture:[73]

$$\left.\begin{matrix} [Ar_3\overset{+}{P}CH_2NCO]Cl^- + CH_3I \\ Ar_3P + ClCH_2NCO + CH_3I \end{matrix}\right\rbrace \rightarrow [Ar_3\overset{+}{P}CH_2NCO]I^- + CH_3Cl.$$

(g) Reaction of *N*-phosphorylated aziridines with chloromethyl isocyanate

When *N*-(dialkoxyphosphoryl)- and *N*-(tetraethyldiamino-phosphoryl)aziridines are reacted with chloromethyl isocyanate, the aziridine ring readily opens and *N*-phosphorylated aminomethyl isocyanates are formed:[74–76]



R = CH_3O, C_2H_5O, iso-C_3H_7, $(C_2H_5)_2N$.

(h) Reaction of phosphorus pentachloride with vinyl isocyanates

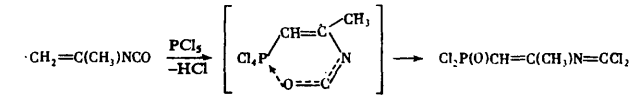
Vinyl isocyanate reacts with phosphorus pentachloride in the ratio 1 : 2 to form 2-(*N*-chlorocarbonylamino)vinyltrichloro-phosphonium hexachlorophosphorate, treatment of which with sulphur dioxide gives 2-(dichlorophosphoryl)vinylcarbamoyl chloride. The latter on heating under vacuum or by treatment with tertiary amines eliminates hydrogen chloride and is converted to 2-(dichlorophosphoryl)vinyl isocyanate:[77–80]

$$CH_2{=}CHNCO + PCl_4^+Cl^- \rightarrow [Cl_4PCH_2\overset{+}{C}HNCO]Cl^- \xrightarrow{-HCl}$$
$$\rightarrow [Cl_4PCH{=}CHNCO] \xrightarrow{PCl_5} [Cl_6\bar{P}Cl_3\overset{+}{P}CH{=}CHNCO] \xrightarrow{HCl}$$
$$\rightarrow [Cl_3PCH{=}CHNHCOCl]^+PCl_6^- \xrightarrow[-POCl_3,\ -SOCl_2]{SO_2}$$
$$\rightarrow Cl_2P(O)CH{=}CHNHCOCl \xrightarrow[-HCl]{} Cl_2P(O)CH{=}CHNCO.$$

When 2-(*N*-chlorocarbonylamino)vinyltrichlorophosphonium hexachlorophosphorate is treated with excess hydrogen sulphide or the calculated quantity of potassium xanthate, 2-(dichlorophosphoro-thioyl)vinyl isocyanate is obtained:[78,79]

$$[Cl_3PCH{=}CHNHCOCl]^+PCl_6^- \xrightarrow{H_2S \text{ or } CH_3OCSSK} Cl_2P(S)CH{=}CHNCO.$$

In contrast to vinyl isocyanate, 1-methylvinyl isocyanate reacts with phosphorus pentachloride in a 1 : 1 ratio of reactants to form *N*-[2-(dichlorophosphoryl)-1-methylvinyl]iminocarbonyl dichloride:[80,81]



It should be mentioned that the analogous dichloride is obtained on boiling 2-(*N*-chlorocarbonylamino)vinyltrichlorophosphonium hexachlorophosphorate in benzene or by treatment of it with methyl phosphorodichloridite at 60 °C:[80–82]

$$[Cl_3PCH{=}CHNHCOCl]^+PCl_6^- \xrightarrow{\Delta \text{ or } CH_3OPCl_2,\ 60\ ^\circ C} Cl_2P(O)CH{=}CHN{=}CCl_2.$$

When *N*-[2-(difluorophosphoryl)-1-methylvinyl]iminocarbonyl dichloride is treated with hexamethyldisiloxane, difluorophosphoryl-methylvinyl isocyanate is obtained:[83]

$$Cl_2P(O)CH{=}C(R)N{=}CCl_2 \xrightarrow{2C_2H_5OH} \rightarrow [Cl(C_2H_5O)P(O)CH{=}C(R)N{=}C(OC_2H_5)Cl] \rightarrow \rightarrow Cl(C_2H_5O)P(O)CH{=}C(R)NCO,$$
$$R = H,\ CH_3.$$

When *N*-[2-(difluorophosphoryl-1-methylvinyl]iminocarbonyl dichloride is treated with hexamethyldisiloxane, difluorophosphoryl-methylvinyl isocyanate is obtained:[83]

$$F_2P(O)CH{=}C(CH_3)N{=}CCl_2 \xrightarrow{[(CH_3)_3Si]_2O} F_2P(O)CH{=}C(CH_3)NCO.$$

(i) Reaction of dialkoxyphosphorylsulphenyl chlorides with vinyl and allyl isocyanates

Vinyl isocyanate undergoes a reaction with diethoxyphosphoryl-sulphenyl chloride to form *S*-(diethoxyphosphoryl)thiovinyl isocyanate:[77]

$$(C_2H_5O)_2P(O)SCl + CH_2{=}CHNCO \xrightarrow{-HCl} (C_2H_5O)_2P(O)SCH{=}CHNCO.$$

Dialkoxyphosphorylsulphenyl chloride readily adds on to the C=C double bond of allyl isocyanate in two directions to form a mixture of two isocyanates in the ratio 3 : 1:[84]

$$(RO)_2P(O)SCl + CH_2{=}CHCH_2NCO \rightarrow \rightarrow (RO)_2P(O)SCH_2CHClCH_2NCO + (RO)_2P(O)SCH(CH_2Cl)CH_2NCO.$$

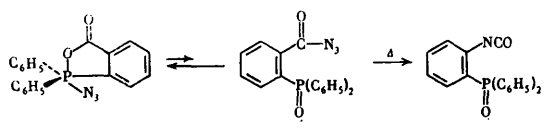
(j) Thermal decomposition of phosphorus-containing carboxylic acid azides

Thermal decomposition via the Curtius rearrangement of azides of phosphorus-containing fatty and aromatic carboxylic acids in toluene or without a solvent gives the corresponding phosphorus-containing alkyl and aryl isocyanates:[32,85–90]

$$R_2P(O)CH_2CH_2COCl \xrightarrow{NaN_3 \text{ or } (CH_3)_3SiN_3} \rightarrow [R_2P(O)CH_2CH_2CON_3] \xrightarrow[\text{toluene}]{\Delta} R_2P(O)CH_2CH_2NCO,$$
$$R = Cl,\ C_2H_5O,\ C_3H_7O,\ \text{iso-}C_3H_7O;$$
$$(RO)_2P(S)SCH_2CH_2COCl \xrightarrow{NaN_3 \text{ or } (CH_3)_3SiN_3} \rightarrow [(RO)_2P(S)SCH_2CH_2CON_3] \xrightarrow{\Delta} (RO)_2P(S)SCH_2CH_2NCO;$$

$$C_6H_5P(O)(C_6H_4COCl\text{-}p)_2 \xrightarrow{2NaN_3} [C_6H_5P(O)(C_6H_4CON_3\text{-}p)_2] \xrightarrow{\Delta} \rightarrow C_6H_5P(O)(C_6H_4NCO\text{-}p)_2;$$

$$(C_2H_5O)_2P(O)C(C_6H_5){=}C{=}O \xrightarrow{HN_3} (C_2H_5O)_2P(O)CH(C_6H_5)CON_3 \xrightarrow{\Delta} \rightarrow (C_2H_5O)_2P(O)CH(C_6H_5)NCO.$$



On boiling phosphorus-containing azides of aliphatic or aromatic carboxylic acids in absolute alcohol, nitrogen is eliminated and isocyanates are formed, immediately adding on alcohols and being converted to the corresponding urethanes $CH_3P(O)(C_6H_4NHCOOC_2H_5)_2$, $(C_6H_5)_2P(O)CH_2CH.(NHCOOC_2H_5)_2$, and $(C_6H_5)_2P(O)CH(NHCOOC_2H_5)(CH_2)_n.NHCOOC_2H_5$ (n = 1, 2).[63,92,93]

(k) Rearrangement of dialkyl- and diaryl-phosphinyl-acetohydroxamic acids and their *O*-benzoyl derivatives

On heating dialkyl- and diaryl-phosphinylhydroxamic acids with an excess of triethyl orthoformate, they rearrange to phosphorylated alkyl isocyanates, which are converted during reaction to *N,N'*-bis(diarylphosphinylmethyl)ureas and ethyl *N*-[dialkyl(diaryl)-phosphinylmethyl]carbamates:[92,94]

$$R_2P(O)CH_2CONHOH \xrightarrow[-2R'OH,\ -R'OC(O)H]{(R'O)_3CH} [R_2P(O)CH_2NCO] \rightarrow$$
$$\rightarrow \begin{cases} \xrightarrow{R'OH} R_2P(O)CH_2NHCOOR' \\ \xrightarrow{H_2O} R_2P(O)CH_2NH_2 \xrightarrow{R_2P(O)CH_2NCO} [R_2P(O)CH_2NH]_2CO, \end{cases}$$
$$R = C_2H_5,\ C_6H_5,\ p\text{-}CH_3C_6H_4,\ p\text{-}ClC_6H_4;\ R' = C_2H_5.$$

O-Benzoyl derivatives of diarylphosphinylacetohydroxamic acids when heated in aqueous alkaline solution also undergo the Lossen rearrangement to form phosphorylated methyl isocyanates, which are converted to symmetric *N,N'*-bis(diarylphosphinylmethyl)-ureas:[92,94]

$$R_2P(O)CH_2C(O)NHOC(O)C_6H_5 \xrightarrow[-H_2O]{KOH} \left[R_2P(O)CH_2C(=O)NOC(O)C_6H_5\right]^- K^+ \xrightarrow{-C_6H_5COOH}$$
$$\rightarrow \left[R_2P(O)CH_2C(=O)\ddot{N}:\right] \rightarrow R_2P(O)CH_2NCO \xrightarrow[-CO_2]{H_2O}$$
$$\rightarrow R_2P(O)CH_2NH_2 \xrightarrow{R_2P(O)CH_2NCO} [R_2P(O)CH_2NH]_2CO;$$
$$R = C_6H_5,\ p\text{-}CH_3C_6H_4,\ p\text{-}ClC_6H_4.$$

(l) Isomerisation of *O,O'*-dialkyl *S*-(ethyleniminocarbonyl)phosphoro-dithioate

When *O,O'*-dialkyl *S*-(chlorocarbonyl)phosphorodithioates are treated with ethylenimine in the presence of triethylamine, *O,O'*-dialkyl *S*-(ethyleniminocarbonyl)phosphorodithioates are formed, which on boiling in toluene undergo complete isomerisation to phosphorus-containing alkyl isocyanates:[87,95]

$$(RO)_2P(S)SC(O)Cl \xrightarrow{HN\langle CH_2\text{–}CH_2,\ (C_2H_5)_3N} (RO)_2P(S)SC(O)N\langle CH_2\text{–}CH_2 \xrightarrow[\text{toluene}]{\Delta} \rightarrow (RO)_2P(S)SCH_2CH_2NCO.$$

(m) Reaction of *N,N'*-bis(alkylidene)ureas with dialkyl phosphites and dialkylphosphorodithioic acids

When *N,N'*-bis(1-phenyl-2,2,2-trifluoroethylidene)urea is boiled with diethyl phosphite or *O,O'*-diisopropyl phosphorodithioate in benzene, the corresponding phosphorus-containing isocyanates are obtained:[96]

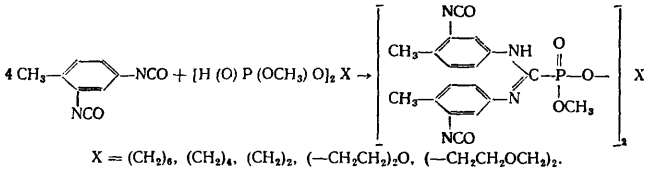
$$[C_6H_5(CF_3)C{=}N]_2CO \rightarrow$$
$$\rightarrow \begin{cases} \xrightarrow{(C_2H_5O)_2P(O)H} (C_2H_5O)_2P(O)C(C_6H_5)(CF_3)NCO \\ \xrightarrow{(\text{iso-}C_3H_7O)_2P(S)SH} (\text{iso-}C_3H_7O)_2P(S)SC(C_6H_5)(CF_3)NCO. \end{cases}$$

(n) Addition to 2,4-diisocyanatotoluene of phosphorus compounds containing active hydrogen atoms

2,4-Diisocyanatotoluene readily adds on 1 mole of dialkyl phosphite:[97–99]

$$(RO)_2P(O)H + CH_3C_6H_3(NCO)_2\text{-}2,4 \xrightarrow[\text{hexane}]{Na} \rightarrow (RO)_2P(O)C(O)NHC_6H_3NCO\text{-}3\text{-}CH_3\text{-}4.$$

Bis-phosphites react with excess 2,4-diisocyanatotoluene in the absence of catalysts to form phosphorus-containing aromatic isocyanates of complex structure:[100]



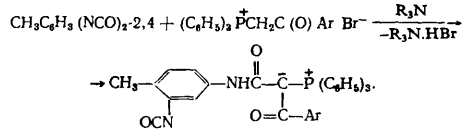
$X = (CH_2)_6,\ (CH_2)_4,\ (CH_2)_2,\ (-CH_2CH_2)_2O,\ (-CH_2CH_2OCH_2)_2.$

When 3 moles of 2,4-diisocyanatotoluene are reacted with tris(hydroxymethyl)phosphine or its oxide, aromatic isocyanates containing phosphorus are also obtained:[101]

$$XP(CH_2OH)_3 + CH_3C_6H_3(NCO)_2\text{-}2,4 \rightarrow XP[CH_2OC(O)NHC_6H_3NCO\text{-}3\text{-}.\ .CH_3\text{-}4]_3,$$

X = O or unshared electron pair.

2,4-Diisocyanatotoluene reacts with triphenylphenacylphosphonium bromides in the presence of ethyldiisopropylamine to form a phosphorus ylide containing a free isocyanate group:[102]



(o) Treatment of phosphorus-containing urethanes with phosphorus pentachloride

When methyl *N*-[1-(diethoxyphosphoryl)]-, *N*-([1-ethoxyphenylphosphonyl)]- and *N*-[1-diphenylphosphinyl)]-2,2-dichlorovinylcarbamates are heated with phosphorus pentachloride, the corresponding 1-phosphorylated 2,2-dichlorovinyl isocyanates are obtained:[103,104]

$$C_2H_5O(X)P(O)C(=CCl_2)NHCOOCH_3 \xrightarrow{n PCl_5} Cl(Y)P(O)C(=CCl_2)NCO,$$
$$X = C_2H_5O,\ Y = Cl,\ n = 3;\quad X = Y = C_6H_5,\ n = 2;$$
$$(C_6H_5)_2P(O)C(=CCl_2)NHCOOCH_3 \xrightarrow{PCl_5} (C_6H_5)_2P(O)C(=CCl_2)NCO.$$

(p) Reaction of trichlorophosphazotrichloromethane with *N,N',N''*-trichloroisocyanuric acid

Trichlorophosphazotrichloromethane readily reacts with *N,N',N''*-trichloroisocyanuric acid, whereupon a chlorine molecule is eliminated and 1-trichlorophosphazo-1,1-dichloromethyl isocyanate is formed, which exists in equilibrium with its acid chloride form:[105,106]

$$Cl_3P{=}NCCl_3 \xrightarrow[-Cl_2]{1/3(ClNCO)_3} Cl_3P{=}NCCl_2NCO \rightleftarrows Cl_3P{=}NCCl{=}NCOCl.$$

(q) Reaction of isocyanates of trivalent phosphorus acids with alkylene oxides

When ethylene oxide is reacted with triisocyanatophosphine in the presence of catalytic quantities of a tertiary amine, *O,O'*-bis(2-isocyanatoethyl) phosphorus isocyanate is obtained:[107]

$$P(NCO)_3 + 2CH_2{-}CH_2 \rightarrow OCNP(OCH_2CH_2NCO)_2.$$
$$\qquad\qquad\quad \backslash O /$$

(r) Halogenation of phosphorus-containing alkyl and vinyl isocyanates

When dichlorophosphorylmethyl isocyanate is chlorinated with the calculated quantity of chlorine in carbon tetrachloride in the presence of UV light, *N*-(dichlorophosphorylchloromethyl)carbamoyl chloride is formed, treatment of which with triethylamine gives dichlorophosphorylchloromethyl isocyanate:[51]

$$Cl_2P(O)CH_2NCO \xrightarrow[CCl_4,UV]{Cl_2} Cl_2P(O)CHClNHCOCl \xrightarrow[-(C_2H_5)_3N.HCl]{(C_2H_5)_3N} \rightarrow Cl_2P(O)CHClNCO.$$

2-[*S*-(Diethoxyphosphoryl)thio]vinyl isocyanate reacts with an equimolar quantity of chlorine in carbon tetrachloride (20 °C, 20 h) to form 2-[*S*-diethoxyphosphoryl)thio]-2-chlorovinyl isocyanate:[77]

$$(RO)_2P(O)SCH{=}CHNCO \xrightarrow{Cl_2} (RO)_2P(O)SC(Cl){=}CHNCO.$$

1-(Dihalophosphoryl)- and 1-(alkoxyhalophosphoryl)-vinyl isocyanates readily add on bromine to the double bond:[14,40]

$$XYP(O)C(=CH_2)NCO \xrightarrow{Br_2} XYP(O)CBr(CH_2Br)NCO,$$
$$X = Y = Cl,\ F;\quad X = Cl,\ F,\ Y = C_2H_5O.$$

When 2-(dichlorophosphoryl)- and 2-(difluorophosphoryl)-alkenyl isocyanates react with an equimolar quantity of chlorine or bromine at 0 °C, *N*-[2-dichloro(difluoro)phosphoryl-2-haloalkenyl]carbamoyl halides are obtained, which on heating under vacuum readily eliminate hydrogen halide, being converted to 2-(dichlorophosphoryl)- or 2-(difluorophosphoryl)-2-haloalkenyl isocyanates:[108]

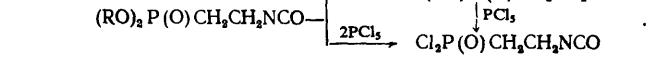
$$Y_2P(O)CH{=}C(R)NCO + X_2 \rightarrow [Y_2P(O)CHXCX(R)NCO] \xrightarrow{-HX} \rightarrow [Y_2P(O)CX{=}C(R)NCO] \xrightarrow{HX} Y_2P(O)CX{=}C(R)NHCOX \xrightarrow{-HX} \rightarrow Y_2P(O)CX{=}C(R)NCO,$$
$$R = H,\ CH_3;\quad Y = Cl,\ F;\quad X = Cl,\ Br.$$

2-(Dihalophosphoryl)alkenyl isocyanates react with excess chlorine according to the following scheme:[108]

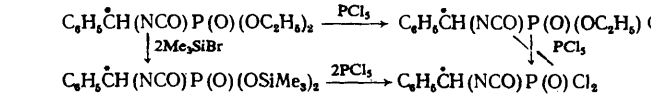
$$X_2P(O)CH{=}C(R)NCO \xrightarrow[25-50\ ^\circ C]{Cl_2} X_2P(O)CCl_2CCl(R)NCO \xrightarrow[100-120\ ^\circ C,\ UV]{Cl_2} \rightarrow X_2P(O)CCl_2CCl(R')NCO,$$
$$X = Cl,\ F;\quad R = H,\ CH_3;\quad R' = Cl,\ CCl_3.$$

(s) Treatment of β-(dialkoxyphosphoryl)- and β-(alkoxychlorophosphoryl)-alkyl isocyanates with phosphorus pentachloride

β-(Dialkoxyphosphoryl)ethyl isocyanates react with an equimolar quantity of phosphorus pentachloride at room temperature in carbon tetrachloride to form β-(alkoxychlorophosphoryl)ethyl isocyanates. When β-(dialkoxyphosphoryl)ethyl isocyanates are treated with 2 moles of phosphorus pentachloride or β-(alkoxychlorophosphoryl)-ethyl isocyanate is treated with 1 mole of phosphorus pentachloride, β-(dichlorophosphoryl)ether isocyanates are obtained:[86]



On treatment with 1 mole of phosphorus pentachloride, (*S*)-(+)-α(diethoxyphosphoryl)benzyl isocyanate is converted to (*S*)-(+)-α-(ethoxychlorophosphoryl)benzyl isocyanate. It is not possible to obtain optically active α-(dichlorophosphoryl)benzyl isocyanate by treating the above isocyanates with phosphorus pentachloride. Another method has been proposed for the synthesis of this compound:[12-14]



(t) Fluorination of dihalophosphorylalkyl, dihalophosphorylalkenyl, and alkoxychlorophosphorylalkyl isocyanates

Dichlorophosphorylalkyl, dichlorophosphorylalkenyl, and alkoxychlorophosphorylalkyl isocyanates are fluorinated with arsenic trifluoride[12–14,57,86] or antimony trifluoride:[37,38,53,83]

$$Cl_2P(O)—A—NCO \xrightarrow{AsF_3 \text{ or } SbF_3} F_2P(O)—A—NCO,$$
$$A=CH_2CH_2,\ CCl_2,\ C(=CH_2),\ CH=CH,\ CH(C_6H_5);$$
$$Cl(RO)P(O)CR^1R^2NCO \xrightarrow{AsF_3} F(RO)P(O)CR^1R^2NCO,$$
$$R^1=R^2=H,\ Cl;\ R^1=H,\ R^2=Cl,\ C_6H_5.$$

Reaction of difluorophosphorylalkenyl isocyanates with sulphur tetrafluoride gives 2-isocyanatoalkenyltetrafluorophosphoranes,[80,83] which are also formed when *N*-[dichloro(difluoro)phosphorylalkenyl]-iminocarbonyl dichloride is treated with sulphur tetrafluoride:[83]

$$F_2P(O)CH=C(R)NCO \xrightarrow{SF_4} F_4PCH=C(R)NCO$$
$$X_2P(O)CH=C(R)N=CCl_2 \xrightarrow{SF_4} [F_2P(O)CH=C(R)N=CF_2]$$
$$X=Cl,\ F;\ R=H,\ CH_3.$$

It should be mentioned that it is not possible to obtain 2-isocyanatoperchloroethyltetrafluorophosphorane by reaction of 2-dichlorophosphorylperchloroethyl isocyanate with sulphur tetrafluoride as cleavage of the P–C bond occurs:[108]

$$Cl_2P(O)CCl_2CCl_2NCO \xrightarrow{SF_4} Cl_3\overset{+}{S}\ P\overline{F}_6 + [F_3SCCl_2CClFNCO + S_2Cl_2].$$

(u) Elimination of chlorine, hydrogen chloride, or hydrogen bromide from phosphorylated haloalkyl isocyanates

When 1-(dihalophosphoryl)-, 1-(alkoxyhalophosphoryl)- and 1-(dialkoxyphosphoryl)-substituted 2-chloro- or 2-bromo-methyl isocyanates are treated with triethylamine, hydrogen chloride or bromide is readily eliminated and the corresponding phosphorylvinyl isocyanates are obtained.[14,38–40]

$$XYP(O)CH(CH_2Z)NCO \xrightarrow[-(C_2H_5)_3N.HZ]{(C_2H_5)_3N} XYP(O)C(=CH_2)NCO,$$
$$X=Y=Cl,\ F,\ OAlk,\ Z=Cl,\ Br;\ X=Cl,\ F,\ Y=C_2H_5O,\ Z=Br.$$

When 1-(dichlorophosphoryl)-1,2-dibromoethyl isocyanate is treated with triethylamine, (*E*)-1-(dichlorophosphoryl)-2-bromovinyl isocyanate is obtained.[14,40] When 2-(dichlorophosphoryl)tetrachloroethyl isocyanate is heated with methyl phosphorodichloridite, 2-(dichlorophosphoryl)-1,2-dichlorovinyl isocyanate is formed:[108]

$$Cl_2P(O)CCl_2CCl_2NCO \xrightarrow[-CH_3Cl,\ -POCl_3]{CH_3OPCl_2} Cl_2P(O)CCl=CClNCO.$$

(v) Reaction of 2-isocyanatoalkenyltetrafluorophosphoranes with hexamethyldisiloxane

On heating 2-isocyanatoalkenyltetrafluorophosphoranes with hexamethyldisiloxane, 2-(difluorophosphoryl)alkenyl isocyanates are obtained:[83]

$$F_4PCH=C(R)NCO \xrightarrow[-2(CH_3)_3SiF]{[(CH_3)_3Si]_2O} F_2P(O)CH=C(R)NCO,$$
$$R=H,\ CH_3.$$

(x) Cyclopolymerisation of diisocyanates in the presence of trialkyl phosphites

It has been shown[109] that when 2,4-toluylene diisocyanate, 1,6-hexamethylene diisocyanate, and 1,4-tetramethylene diisocyanate undergo cyclopolymerisation in the presence of trialkyl phosphites, phosphorylated isocyanates that contain isocyanurate rings are formed.

2. Phosphorus-containing acyl isocyanates

(a) Reaction of *N*-(diethoxyphosphoryl)-*N*-(2-chloroethyl)carbamoyl chloride with trimethylsilyl isocyanate

N-(Diethoxyphosphoryl)-*N*-(2-chloroethyl)carbamoyl chloride reacts with trimethylsilyl isocyanate on boiling for 30 h in the presence of the catalyst $(C_4H_9)_4NI$ to form *N*-(diethoxyphosphoryl)-*N*-(2-chloroethyl)carbamoyl isocyanate:[110]

$$(C_2H_5O)_2P(O)NC(O)Cl + (CH_3)_3SiNCO \xrightarrow{\text{Cat. } (C_4H_9)_4NI}$$
$$\rightarrow (C_2H_5O)_2P(O)NC(O)NCO + (CH_3)_3SiCl.$$
$$CH_2CH_2Cl \qquad\qquad CH_2CH_2Cl$$

(b) Reaction of dialkoxyphosphorylcarboxamides and *N*-phosphorylated ureas with oxalyl chloride

Dialkoxyphosphorylcarboxamides react in carbon tetrachloride or chloroform at a temperature of 60–70 °C with oxalyl chloride to form dialkoxyphosphorylacyl isocyanates:[111–113]

$$(AlkO)_2P(O)CRR^1CONH_2 + (COCl)_2 \rightarrow (AlkO)_2P(O)CRR^1CONCO + 2HCl + CO,$$
$$R=R^1=H,\ Cl,\ CH_3;\ R=H,\ R^1=CH_3.$$

N-(Diethoxyphosphoryl)-*N*-(2-chloroethyl)urea reacts in a similar manner:[110]

$$(C_2H_5O)_2P(O)NC(O)NH_2 + (COCl)_2 \rightarrow (C_2H_5O)_2P(O)NC(O)NCO.$$
$$CH_2CH_2Cl \qquad\qquad CH_2CH_2Cl$$

(c) Treatment of *O,O'*-dialkyl *N*-alkylphosphoramidates with chlorocarbonyl isocyanate

When *O,O'*-dialkyl *N*-alkylphosphoramidates are boiled with chlorocarbonyl isocyanate in carbon tetrachloride, *N*-alkyl-*N*-(dialkoxyphosphoryl)carbamoyl isocyanates are obtained:[114]

$$(RO)_2P(O)NHR^1 + ClC(O)NCO \rightarrow (RO)_2P(O)N(R^1)C(O)NCO + HCl,$$
$$R=C_2H_5,\ R^1=CH_3,\ C_2H_5;\ R=\text{iso-}C_3H_7,\ R^1=C_2H_5.$$

(d) Reaction of *N*-phosphorylated ethylenimines with chlorocarbonyl isocyanate and dichloromethylenecarbamoyl chloride

When *O,O'*-dialkyl phosphoroethylenamidates are treated with chlorocarbonyl isocyanate, opening of the ethylenimine ring occurs with formation of *N*-(dialkoxyphosphoryl)-*N*-(2-chloroethyl)-carbamoyl isocyanates,[76,110] which are also obtained by the action of dichloromethylenecarbamoyl chloride followed by treatment of the intermediate with methanesulphonic acid:[75]

$$(RO)_2P(O)N\begin{array}{l}CH_2\\|\\CH_2\end{array}\begin{array}{l}\xrightarrow{ClC(O)NCO}\ (RO)_2P(O)N(CH_2CH_2Cl)C(O)NCO\\ \qquad\qquad\qquad\qquad\qquad\uparrow CH_3SO_2OH\\ \xrightarrow{ClC(O)-CCl_2}\ (RO)_2P(O)N(CH_2CH_2Cl)C(O)N=CCl_2\end{array}.$$

3. Phosphorus-containing sulphonyl isocyanates

(a) Addition of dialkyl phosphites to sulphuryl diisocyanate

One mole of dialkyl phosphite in ether solution at 0 °C adds on to one isocyanate group of sulphuryl diisocyanate to form the corresponding sulphonyl isocyanate.[115] With excess dialkyl phosphite products from the addition to both isocyanate groups are formed:[115,116]

$$SO_2(NCO)_2\begin{array}{l}\xrightarrow{(RO)_2P(O)H}\ (RO)_2P(O)C(O)NHSO_2NCO\\ \xrightarrow{2(RO)_2P(O)H}\ [(RO)_2P(O)C(O)NH]_2SO_2\end{array}.$$

(b) Treatment of *N*-isopropyl-*N'*-(triphenylphosphazosulphonyl)urea with phosgene

When *N*-isopropyl-*N'*-(triphenylphosphazosulphonyl)urea is boiled with phosgene in chlorobenzene, triphenylphosphazosulphonyl isocyanate is obtained:[117]

$$(C_6H_5)_3P{=}NSO_2NHCONHC_3H_7\text{-iso} \xrightarrow{COCl_2} (C_6H_5)_3P{=}NSO_2NCO.$$

III. Chemical properties

Phosphorylated organic isocyanates which contain no other reactive groups apart from the isocyanate are similar in their chemical properties to normal organic isocyanates. They readily react with alcohols, phenols, amines, and other compounds with an active hydrogen atom, forming the corresponding derivatives in good yield. Phosphorus-containing organic isocyanates which have other reactive sites in addition to the isocyanate group can undergo a reaction with nucleophilic reagents on one or more reaction sites. Some reactions of phosphorus-containing organic isocyanates which do not affect the isocyanate group and which give other phosphorus-containing organic isocyanates have been described above.

1. Reaction with water

The majority of phosphorus-containing alkyl and aryl isocyanates are very readily hydrolysed by atmospheric moisture and react with water; but only in certain cases have the reaction products—the corresponding phosphorus-containing symmetrical ureas—been isolated:[9,46,91,94,98]

$$\{(C_2H_5O)_2P(O)C(=CCl_2)NH\}_2CO,$$
$$\{2\text{-}CH_3\text{-}4\text{-}[(C_2H_5O)_2P(O)C(O)NH]C_6H_3NH\}_2CO,$$
$$\{(C_6H_5)_2P(O)CH_2NH\}_2CO,\ \{(RO)_2P(O)CH(COOR^1)NH\}_2CO,$$
$$\{2\text{-}[(C_6H_5)_2P(O)]C_6H_4NH\}_2CO.$$

When α-(diethoxyphosphoryl)benzyl isocyanate [racemate or (*S*)-(+)-enantiomer] is exposed to atmospheric moisture or a stoichiometric quantity of water in ether, racemic or (*SS*)-(−)-*N*,*N'*-bis[α-(diethoxyphosphoryl)benzyl]urea is obtained.[12]

When (*S*)-(+)-α-[bis-(trimethylsiloxy)phosphoryl]benzyl isocyanate is treated with excess water, (*S*)-(−)-α-aminobenzylphosphonic acid is obtained:[12,56]

$$C_6H_5\dot{C}H(NCO)P(O)[OSi(CH_3)_3]_2 \xrightarrow{H_2O} C_6H_5\dot{C}H(NH_2)P(O)(OH)_2.$$

Diethoxyphosphorylcarbonylamidosulphonyl isocyanate is hydrolysed with water to diethoxyphosphorylcarbonylamidosulphonamide:[115]

$$(C_2H_5O)_2P(O)C(O)NHSO_2NCO \xrightarrow{H_2O} (C_2H_5O)_2P(O)C(O)NHSO_2NH_2.$$

When bis(diethoxyphosphoryl)chloromethyl isocyanate is reacted with 2 moles of water in acetone, a compound containing a carbonyl group is formed:[118]

$$\{(C_2H_5O)_2P(O)\}_2CClNCO \xrightarrow{H_2O} [(C_2H_5O)_2P(O)]_2CClNHCOOH \xrightarrow{-CO_2}$$
$$\rightarrow [(C_2H_5O)_2P(O)]_2CClNH_2 \rightarrow [(C_2H_5O)_2P(O)]_2C{=}NH\cdot HCl \xrightarrow{H_2O}$$
$$\rightarrow \{(C_2H_5O)_2P(O)\}_2C{=}O.$$

In contrast to mono- and bis-phosphorylated alkyl isocyanates, tris(diethoxyphosphoryl)methyl isocyanate reacts with water only with great difficulty. It remains unchanged on boiling for 2 hours with a stoichiometric quantity of water in acetone. Only on boiling with a tenfold excess of water in dioxan for 3 h does the molecule decompose to form products with an undetermined structure.[118]

2. Reaction with alcohols and phenols

Phosphorus-containing alkyl, alkenyl, and aryl isocyanates that do not contain other groups can react with alcohols and phenols; they have the properties of normal organic isocyanates and readily add on alcohols,[1,4,5,12,26,27,30–32,36–38,40–42, 45–47, 54,68,69,74,75,88,89,91–95,107,119] glycols,[3,20,26,58,59,88,101,119,120] cresol,[20,58,59] and cellulose and cellulose acetate[99] to the isocyanate group. The reactions are usually carried out in inert solvents without a catalyst or in the presence of catalytic quantities of a tertiary amine.

$$R_{3-n}P(X)(ANCO)_n + nR^1OH \rightarrow R_{3-n}P(X)(ANHCOOR^1)_n,$$

$n = 1-3$; X = O, S; A—different bridging groups (see Methods of Synthesis)

It should be mentioned that tris(diethoxyphosphoryl)methyl isocyanate does not react at 20 °C even with a large excess of alcohol over a period of 10–15 days. Even in the presence of a base the reaction is only complete after 15 days under these conditions:[40,54]

$$[(C_2H_5O)_2P(O)]_3CNCO \xrightarrow[\text{Cat. } (C_2H_5)_3N]{ROH} [(C_2H_5O)_2P(O)]_3CNHCOOR.$$

Trialkyl- and triaryl-(isocyanatomethyl)phosphonium halides readily add on alcohols to the isocyanate group. Phenols add on only in the presence of catalytic quantities of a tertiary amine.[36,71,73]

$$[R_3PCH_2NCO]^+X^- + R^1OH \rightarrow [R_3PCH_2NHCOOR^1]^+X^-,$$
R, R^1=Alk, Ar; X=Cl, Br, I.

Phosphorus-containing acyl isocyanates[110–112] and sulphonyl isocyanates[115,117] also readily add alcohols to the isocyanate group to form the corresponding urethanes:

$$(RO)_3P(O)CCl_2CONHCOOR^1,\ (C_2H_5O)_2P(O)N(CH_3CH_2Cl)C(O)NHCOOC_2H_5,$$
$$(C_6H_5)_3P{=}NSO_2NHCOOR^2,\ (C_2H_5O)_2P(O)C(O)NHSO_2NHCOOC_2H_5$$

(where R = C_2H_5, C_4H_9; R^1 = CH_3, C_2H_5, iso-C_3H_7; R^2 = CH_3, iso-C_3H_7, tert-C_4H_9, cyclo-C_6H_{11}).

Dihalo- and alkoxyhalo-phosphoryl-substituted alkyl and alkenyl isocyanates have two reaction sites—the carbon atom of the isocyanate group and the phosphorus atom. Depending on the structure of the phosphorylated isocyanate, the alcohol reacting with it, the solubility of the product formed, the reaction conditions, etc., either only the isocyanate group reacts with an equimolar quantity of alcohol or replacement of a halogen atom on phosphorus by an alkoxy group takes place at the same time as addition. Thus, addition products of alcohols only on the isocyanate group have been obtained for the following types of isocyanates:[30,32,34,40,41,64,78,81,83,86,108,121–123]

$$XYP(O)CH_2NCO\ (X{=}Y{=}Cl;\ X{=}F,\ Y{=}RO);\ Cl_2P(O)CH(CH_2Br)NCO;$$
$$Cl_2P(O)CH(C_6H_5)NCO;\ F(C_2H_5O)P(O)CH(C_6H_5)NCO;\ F_2P(O)CH_2CH_2NCO;$$
$$Cl(RO)P(O)CH{=}CHNCO;\ X_2P(Y)CH{=}C(R)NCO$$
$$(X = Cl, F;\ Y = O, S;\ R = H, CH_3);$$
$$Cl_2P(O)CX{=}CHNCO\ (X = Cl, Br).$$

It is not possible to obtain products from the addition of 1 mole of a primary alcohol only to the isocyanate group of difluorophosphorylmethyl, alkoxychlorophosphorylmethyl, 2-(dichlorophosphoryl)ethyl, 1-(dichlorophosphoryl)vinyl, α-(difluorophosphoryl)benzyl, and α-(alkoxychlorophosphoryl)benzyl isocyanates.[30,34,38,40,41,64,86] However, when tertiary butyl alcohol is reacted with 1-(dichlorophosphoryl)vinyl isocyanate, the urethane $Cl_2P(O)C(=CH_2)NHCOOC(CH_3)_3$ is obtained.[38]

When difluorophosphorylmethyl isocyanate is treated with 2 moles of alcohol, alkyl *N*-(alkoxyfluorophosphorylmethyl)carbamate is

obtained in good yield.[30,34,64] With excess alcohol in the presence of tertiary amines, all dihalophosphoryl- and alkoxyhalophosphoryl-substituted alkyl and alkenyl isocyanates give alkyl *N*-[dialkoxyphosphorylalkyl(alkenyl)]carbamates.[30,34,38,40,41,46,64,86,108]

When 1-dichlorophosphoryl-2-chloro(bromo)ethyl isocyanates react with excess alcohol in the presence of triethylamine, as well as addition of the alcohol to the isocyanate group and replacement of the chlorine atom on phosphorus there is elimination of hydrogen chloride or bromide to give alkyl *N*-(1-dialkoxyphosphorylvinyl)-carbamate;[38,40] the same esters are obtained when 1-(dialkoxyphosphoryl)-2-bromoethyl isocyanate is treated with 1 mole of alcohol in the presence of triethylamine:[40]

$$\left.\begin{array}{l} Cl_2P(O)CH(CH_2X)NCO \xrightarrow[3(C_2H_5)_3N]{3ROH} \\ X=Cl,\ Br \\ (RO)_2P(O)CH(CH_2Br)NCO \xrightarrow[(C_2H_5)_3N]{ROH} \end{array}\right| \rightarrow (RO)_2P(O)C(=CH_2)NHCOOR.$$

α-(Dialkoxyphosphoryl)-α-chlorobenzyl isocyanate has two reaction sites—the carbon atoms of the isocyanate group and the substituted methylene group. When α-(diethoxyphosphoryl)-α-chlorobenzyl isocyanate in ether solution is treated with an equimolar quantity of methanol it appears that addition of methanol to the isocyanate group mainly occurs, and methyl *N*-[α-(diethoxyphosphoryll)-α-chlorobenzyl]carbamate, which is soluble with difficulty in ether, can be isolated in 50% yield. In the presence of triethylamine, methyl *N*-[α-(diethoxyphosphoryl)-benzylidene]carbamate is obtained in high yield.[56]

$$C_6H_5CCl(NCO)P(O)(OC_2H_5)_2 \longrightarrow \left|\begin{array}{l} \xrightarrow{CH_3OH} C_6H_5CCl(NHCOOCH_3)P(O)(OC_2H_5)_2 \\ \xrightarrow[CH_3OH,\ (C_2H_5)_3N]{} C_6H_5C(=NCOOCH_3)P(O)(OC_2H_5)_2. \end{array}\right.$$

Diethoxy phosphoryldichloromethyl and bis(diethoxyphosphoryl)-chloromethyl isocyanates react in a similar manner:[32,54]

$$(RO)_2P(O)C(X)ClNCO \xrightarrow{R'OH} [(RO)_2P(O)C(X)ClNHCOOR'] \xrightarrow{[(C_2H_5)_3N]} \rightarrow (RO)_2P(O)C(X)=NCOOR',$$
$$X=Cl,\ (RO)_2P(O).$$

In the case of the halophosphoryl compounds $Hal(X)P(O)C(Hal)_2.NCO$ and $Hal(X)P(O)CH(Hal)NCO$ (X = Hal or OR) there is a third reaction site—the phosphorus atom.

Depending on the structure of the isocyanate and the nucleophilic reagent reacting with it as well as their stoichiometric ratio, initially only the isocyanate group participates, then the phosphorus atom and the halogen on the α-carbon atom, or all reaction sites simultaneously.

Dichloro- and difluoro-phosphorylchloromethyl isocyanates add 1 mole of alcohol to form crystalline alkyl *N*-(dihalophosphoryl-chloromethyl)carbamates:[50]

$$X_2P(O)CHClNCO \xrightarrow{ROH} X_2P(O)CHClNHCOOR,$$
$$X=Cl,\ F.$$

Dichlorophosphoryldichloromethyl isocyanate, and alkoxychloro-, alkoxyfluoro-phosphorylchloromethyl isocyanates also react with 1 mole of alcohol mainly on the isocyanate group alone. However, the urethanes formed are very unstable and on evaporating the solutions, vacuum distillation, or treatment with tertiary amines they readily eliminate a hydrogen chloride molecule and are converted to the corresponding compounds with a C=N bond. It was only possible to isolate the stable alkyl *N*-(dichlorophosphorylchloro-methylene)carbamates in a pure form.[50,52-54] Dichlorophosphoryl-dibromomethyl isocyanate reacts with alcohols in a similar manner:[40]

$$Cl_2P(O)CX_2NCO \xrightarrow{ROH} [Cl_2P(O)CX_2NHCOOR] \xrightarrow{(C_2H_5)_3N} \rightarrow Cl_2P(O)CX=NCOOR,$$
$$X=Cl,\ Br.$$

It should be mentioned that it is not possible to add 1 mole of alcohol to the isocyanate group of difluorophosphoryl- or alkoxyfluorophosphoryl-dichloromethyl isocyanate. Reaction takes place simultaneously on two reaction sites—the carbon atom of the NCO group and the phosphorus atom—and a mixture of products is formed, from which pure compounds could not be isolated.[53,118] However, in the case of 2-chloroethoxychlorophosphoryldichloro-methyl isocyanate, *N*-(2-chloroethoxychlorophosphorylchloro-methylene)carbamate was obtained.[57]

When dichloro- or alkoxychloro-phosphoryldichloromethyl isocyanate reacts with excess alcohol in the presence of a tertiary amine, alkyl *N*-(dialkoxyphosphorylchloromethylene)carbamates are obtained,[32,52,53] while dichloro- and alkoxychloro-phosphorylchloro-methyl isocyanates under the same conditions give alkyl *N*-[alkoxy-(dialkoxyphosphoryl)methyl]carbamates:[50]

$$Cl(X)P(O)CCl_2NCO \xrightarrow[(C_2H_5)_3N]{ROH} (RO)_2P(O)C(Cl)=NCOOR,$$
$$Cl(X)P(O)CHClNCO \xrightarrow[(C_2H_5)_3N]{ROH} (RO)_2P(O)CH(OR)NHCOOR,$$
$$X=Cl,\ RO.$$

α-(Dichlorophosphoryl)-α-chlorobenzyl isocyanate reacts with excess methanol in a similar manner to dichlorophosphoryldichloro-methyl isocyanate, forming the urethane $C_6H_5C(=NCOOCH_3)P(O).(OCH_3)_2$.[56]

When dichlorophosphoryldibromomethyl isocyanate is treated with 4 moles of sodium ethoxide in ethanol, ethyl *N*-[diethoxy-phosphoryl(ethoxy)methylene]carbamate is obtained:[40]

$$Cl_2P(O)CBr_2NCO \xrightarrow{4C_2H_5ONa} (C_2H_5O)_2P(O)C(OC_2H_5)=NCOOC_2H_5.$$

2-(Dichlorophosphoryl)perchloroethyl isocyanate reacts with alcohols in a similar manner to dichlorophosphoryldichloromethyl isocyanate, forming urethanes $(RO)_2P(O)CCl_2CCl=NCOOR$.[108]

When difluorophosphorylchloromethyl isocyanate is treated with 3 moles of alcohol or alkoxyfluorophosphorylchloromethyl isocyanate is treated with 2 moles of alcohol in the presence of triethylamine, alkyl *N*-[alkoxy(alkoxyfluorophosphoryl)methyl carbamates are obtained:[50]

$$\left.\begin{array}{l} F_2P(O)CHClNCO \xrightarrow[2(C_2H_5)_3N]{3\ ROH} \\ F(RO)P(O)CHClNCO \xrightarrow[(C_2H_5)_3N]{2ROH} \end{array}\right| \rightarrow F(RO)P(O)CH(OR)NHCOOR.$$

It is not possible to add 1 mole of alcohol just to the isocyanate group of bis(alkoxyfluorophosphoryl)chloromethyl isocyanate, and when the latter is treated with 3 moles of alcohol in the presence of triethylamine the reaction proceeds thus:[53]

$$[F(RO)P(O)]_2CClNCO \xrightarrow[3(C_2H_5)_3N]{3\ ROH} [(RO)_2P(O)]_2C=NCOOR.$$

Bis(alkoxyfluorophosphoryl)methyl isocyanate and its corresponding α-chloro-substituted compound when reacted with alcohols give urethanes.[50,53]

$$[F(RO)P(O)]_2CHNCO \xrightarrow{ROH} [F(RO)P(O)]_2CHNHCOOR,$$
$$[F(RO)P(O)]_2CClNCO \xrightarrow[(C_2H_5)_3N]{ROH} [F(RO)P(O)]_2C=NCOOR.$$

The addition of phenols and glucose tetraacetate to dichloro-phosphorylvinyl isocyanate has been reported.[121-123]

3. Reaction with thiols

Thiols add to phosphorylated alkyl isocyanates with much greater difficulty than alcohols. Thioethanol reacts with 1-diethoxyphosphoryl- and 1-diethoxyphosphorothioyl-1-methylethyl isocyanates only in the presence of triethylamine on heating in a sealed tube on a boiling water bath:[1,5]

$$(C_2H_5O)_2P(X)C(CH_3)_2NCO \xrightarrow[(C_2H_5)_3N]{C_2H_5SH} (C_2H_5O)_2P(X)C(CH_3)_2NHC(O)SC_2H_5$$
X=O, S.

4. Reactions with ammonia and amines

Dialkoxyphosphorylalkyl isocyanates, in the same way as alkyl and aryl isocyanates, readily react with ammonia to form *N*-(dialkoxyphosphorylalkyl)ureas:[1,5,31,75,90]

$$(RO)_2P(X)—A—NCO + NH_3 \rightarrow (RO)_2P(X)—A—NHCONH_2,$$
X=O: A=CH_2, $C(CH_3)_2$, $CH(C_6H_5)$, —N$(CH_2CH_2Cl)CH_2$—;
X=S: A=$C(CH_3)_2$.

N-(Diethoxyphosphoryl)-*N*-(2-chloroethyl)aminocarbonyl isocyanate[110] and triphenylphosphazosulphonyl isocyanate[117] add ammonia in a similar manner.

Phosphorus-containing alkyl,[1,4,5,9,12,30–32,36,37,41,42,45–48,54,68,74,75,85,88,92,94,95,124] alkenyl,[46,47] and aryl[30,31,89,98] isocyanates as well as isocyanates of *N*-phosphorylated iminocarboxylic acids[28] which apart from the isocyanate group have no other reaction sites very readily add primary[1,5,46] and secondary[30–32,54,72,75] aliphatic amines, phosphorylated alkylamines,[12,92,94] primary aromatic amines,[1,4,5,9,12,28,30–32,36,37,41,42,45–48,54,68,74,75,85,88,89,95,98,124] and morpholine[41,124] to form the respective ureas.

$$[R_2P(X)]_nANCO + R^1R^2NH \rightarrow [R_2P(X)]_nANHCONHR^1R^2,$$
n=1: R=Alk, Ar, AlkO, ArO; A=CH_2, $(CH_2)_2$, $\dot{C}H(C_6H_5)$, $\dot{C}H(C_6H_5)$, $CH(CH_2Cl)CH(CCl_3)$, $CHCOOR^3$, $C(CH_3)_2$, $C(C_6H_5)_2$, $C(C_{10}H_7\text{-}\alpha)_2$, $S(CH_2)_2$, —$CH_2C_6H_4$—, $C(=CH_2)$, $C(=CCl_2)$, N=$C(C_6H_5)$ etc.;
n = 2: R=AlkO, A=CH; n = 3, R=AlkO, A=C;

$$C_6H_5P(O)(C_6H_4NCO\text{-}p)_2 + 2C_6H_5NH_2 \rightarrow C_6H_5P(O)(C_6H_4NHCONHC_6H_5\text{-}p)_2.$$

Triaryl(isocyanatomethyl)phosphonium halides add 1 mole of an aromatic amine to the isocyanate group, forming compounds of the type $[Ar_3PCH_2NHCONHAr^1]^+X^-$ (X = Cl, Br, I).[36,73]

Phosphorus-containing acyl isocyanates[110–113] and sulphonyl isocyanates[115,117] also add primary aromatic amines,[110–113,115] and diethyl- and cyclohexyl-amine[117] to the isocyanate group, forming ureas

$$(AlkO)_2P(O)C(R)(R')CONHCONHAr,\ (C_6H_5)_3P{=}NSO_2NHCONRR',$$
$$(C_2H_5O)_2P(O)N(CH_2CH_2Cl)CONHCONHAr,$$
$$(C_2H_5O)_2P(O)C(O)NHSO_2NHCONHC_6H_5.$$

When dialkoxyphosphoryldichloro- or bis(dialkoxyphosphoryl)-chloro-methyl isocyanate is treated with 2 moles of an aromatic amine or 1 mole of an aromatic amine in the presence of triethylamine, hydrogen chloride is eliminated at the same time as addition of the amine to the isocyanate group:[48,54]

$$(RO)_2P(O)CXClNCO \xrightarrow[(C_2H_5)_3N]{ArNH_2} (RO)_2P(O)CX{=}NCONHAr,$$
X=Cl, $(RO)_2P(O)$.

One mole of a primary aromatic amine reacts with difluorophosphorylated alkyl and alkenyl isocyanates,[30,34,36,40,41,83,86] fluoroalkoxyphosphorylalkyl isocyanates,[30,34,36,41,57] and bis(ethoxyfluorophosphoryl)methyl isocyanate[50] only on the isocyanate group.

$$F_2P(O)ANCO + ArNH_2 \rightarrow F_2P(O)ANHCONHAr,$$
A=CH_2, $CHCH_2Br$, CHC_6H_5, $C(=CH_2)$, CH_2CH_2, CH=CH, $CH{=}C(CH_3)$;

$$F(AlkO)P(O)ANCO + ArNH_2 \rightarrow F(AlkO)P(O)ANHCONHAr,$$
A=CH_2, CHC_6H_5;

$$[F(C_2H_5O)P(O)_2CHNCO + p\text{-}ClC_6H_4NH_2 \rightarrow$$
$$\rightarrow [F(C_2H_5O)P(O)]_2CHNHCONHC_6H_4Cl\text{-}p.$$

2-(Dichlorophosphoryl)- and 2-(alkoxychlorophosphoryl)-vinyl isocyanates[78,79,81,108] as well as 2-(chlorazidophosphoryl)ethyl isocyanate[86] react in a similar manner.

It is not possible to add 1 mole of amine just to the isocyanate group of dichlorophosphorylalkyl, alkoxychlorophosphorylalkyl, 1-(dichlorophosphoryl)vinyl, 1-(dichlorophosphoryl)-2,2-dichlorovinyl and 1-(phenylchlorophosphonyl)-2,2-dichlorovinyl isocyanates or to isolate pure compounds. Reaction occurs simultaneously on the carbon atom of the isocyanate group and the phosphorus atom. With excess amine, as well as addition to the isocyanate group the chlorine atoms are completely replaced by amino groups[30,34,36,38,41,86,103,124] and the following ureas are formed: $(RR^1N)_2P(O)—A—NHCONRR^1$, $ArNH(R^2)P(O)—A—NHCONHAr$ [A = CH_2, CHC_6H_5, $(CH_2)_2$, $C(=CH_2)$, $C(=CCl_2)$, R^2 = AlkO, C_6H_5].

In the case of 1-(dichlorophosphoryl)- and 1-(phenylchlorophosphonyl)-2,2-dichlorovinyl isocyanates, treatment of the reaction mixture with water or alcohol gives products in which one chlorine atom on phosphorus has been replaced by a hydroxyl or alkoxyl group $R^2O(X)P(O)C(=CCl_2)NHCONRR^1$ (X = C_6H_5, RR^1N; R_2 = H, Alk).[103,124]

Depending on the structure of the isocyanate, α-halogen atoms are also replaced by an amino group or eliminated as hydrogen halides,[38,40,50,53,56] for example:

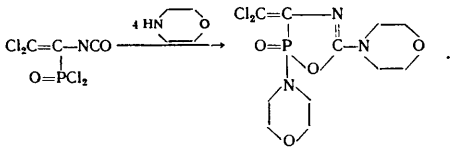
$$Cl_2P(O)CHClNCO \xrightarrow[3(C_2H_5)_3N]{4RR^1NH} (RR^1N)_2P(O)CH(NRR^1)NHCONRR^1,$$

$$[Cl(RO)P(O)]_2CClNCO \xrightarrow[3(C_2H_5)_3N]{3R^1R^2NH} [R^1R^2N(RO)P(O)]_2C{=}NCONR^1R^2.$$

In the case of bis(ethoxyfluorophosphoryl)chloromethyl isocyanate the fluorine atoms are not exchanged for amino groups under similar conditions:[53]

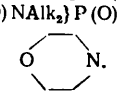
$$[F(C_2H_5O)P(O)]_2CClNCO \xrightarrow[(C_2H_5)_3N]{ArNH_2} [F(C_2H_5O)P(O)]_2C{=}NHCONHAr.$$

When 1-(dichlorophosphoryl)-2,2-dichlorovinyl isocyanate is reacted with 4 moles of morpholine, a cyclic compound—2,5-dimorpholino-4-dichloromethylene-5-oxo-5-phospha-2-oxazoline—is obtained:[103]



The addition of dialkyltrimethylsilylamines to α-(diethoxyphosphoryl)benzyl isocyanate and to triphenyl(α-isocyanatobenzyl)-phosphonium chloride has been reported:

$$C_6H_5CH(NCO)P(O)(OC_2H_5)_2 + Alk_2NSi(CH_3)_3 \rightarrow$$
$$\rightarrow C_6H_5CH\{N[Si(CH_3)_3]C(O)NAlk_2\}P(O)(OC_2H_5)_2,$$

$Alk_2N{=}(C_2H_5)_2N$,  .

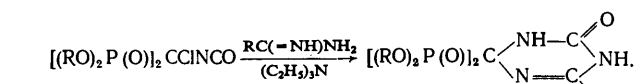
In the latter case the addition product decomposes immediately it is formed at 15–20 °C, so that azomethine, triphenylphosphine, and trimethylchlorosilane are obtained.[72]

Diphenylketimines react similarly to amines with $(RO)_2P(S)SCH_2.CH_2NCO$ [95] and triphenylphosphazohydride reacts similarly with $Cl(X)P(O)CH_2NCO$ (X = Cl, RO) and $Cl_2P(O)CH=CHNCO$.[125,126]

α-Isocyanatophosphonoacetates add on hydrazine and 2,4-dinitrophenylhydrazine to form the corresponding semicarbazides:[9]

$$(RO)_2P(O)CH(COOR^1)NCO + R^2NHNH_2 \rightarrow \rightarrow (RO)_2P(O)CH(COOR^1)NHCONHNHR^2.$$

When bis(dialkoxyphosphoryl)chloromethyl isocyanate is reacted with amidines in the presence of triethylamine, phosphorylated 1,3,5-triazine derivatives are obtained.[127]



5. Addition of hydrogen chloride and hydrazoic acid

When hydrogen chloride is passed through an ether solution of 2-(dichlorophosphoryl)ethyl isocyanate, *N*-[2-dichlorophosphoryl)-ethyl]carbamoyl chloride is obtained:[86]

$$Cl_2P(O)CH_2CH_2NCO \xrightarrow{HCl} Cl_2P(O)CH_2CH_2NHCOCl.$$

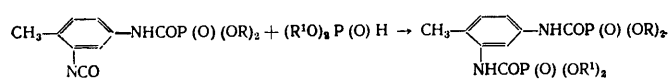
2-(Dichlorophosphoryl)vinyl isocyanate adds on hydrogen chloride when exposed to UV radiation, while 2-(dichlorophosphorothioyl)vinyl isocyanate does not react with hydrogen chloride under similar conditions.[78]

The addition of hydrazoic acid to diethoxyphosphoryldichloroacetyl isocyanate has been reported:[128]

$$(C_2H_5O)_2P(O)CCl_2C(O)NCO + HN_3 \rightarrow (C_2H_5O)_2P(O)CCl_2C(O)NHC(O)N_3.$$

6. Addition of dialkyl phosphites

2-Methyl-5-(dialkoxyphosphorylcarbonylamino)phenyl isocyanate in dioxan adds dialkyl phosphites:[98]



Diethoxyphosphorylcarbonylaminosulphonyl isocyanate adds diethyl phosphite to form *N*,*N*^{1}-bis(diethoxyphosphorylcarbonyl)-diamides of sulphuric acid:[115,116]

$$(C_2H_5O)_2P(O)C(O)NHSO_2NCO + (C_2H_5O)_2P(O)H \rightarrow \rightarrow [(C_2H_5O)_2P(O)C(O)NH]_2SO_2.$$

Similar compounds are obtained when sulphuryl diisocyanate is treated with 2 moles of dialkyl phosphite. The reaction evidently occurs in two stages.[115,116]

7. Reaction with phosphazo compounds

Phosphorylated alkyl isocyanates undergo the Staudinger reaction with triphenylphosphazo hydrocarbons to form phosphorylated carbodiimides.[62,129–131]

$$(RO)_2P(X)YC(CF_3)(C_6H_5)NCO + (C_6H_5)_3P=NR^1 \rightarrow \rightarrow (RO)_2P(X)YC(CF_3)(C_6H_5)N=C=NR^1 + (C_6H_5)_3PO,$$

X=O, Y–bond; X=Y=S.

8. Elimination of carbon dioxide from phosphorylated alkyl isocyanates

On heating the racemate of (*S*)-(+)-enantiomer of α-diethoxyphosphoryl)benzyl isocyanate for 1–2 h at 100–110 °C in the presence of a catalytic quantity of 1,3-dimethylphosphol-3-ene in anhydrous toluene, the corresponding racemic and optically active *N*,*N*′-bis[α-(diethoxyphosphoryl)benzyl]carbodiimides are obtained:[12]

$$2C_6H_5CH(NCO)P(O)(OC_2H_5)_2 \xrightarrow{\Delta} [(C_2H_5O)_2P(O)(C_6H_5)CHN=]_2C + CO_2.$$

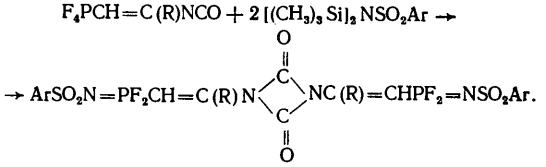
9. Reaction with chlorine

When dimethoxyphosphorothioylthiomethyl isocyanate is chlorinated, dimethyl phosphorochloridothioate and (probably) isocyanatomethylsulphenyl chloride are obtained:[69]

$$(RO)_2P(S)SCH_2NCO \xrightarrow{Cl_2} (RO)_2P(S)Cl + [ClSCH_2NCO].$$

10. Reaction with *N*,*N*-bis(trimethylsilyl)arenesulphonamides

2-Isocyanatoalkenyltetrafluorophosphoranes, when treated with *N*,*N*-bis(trimethylsilyl)arenesulphonamides, form phosphazo isocyanate dimers:[83]



IV. IR and NMR spectra

The IR spectra of phosphorus-containing alkyl, alkenyl, aryl, acyl, and sulphonyl isocyanates contain absorption bands that are characteristic of vibrations of the –N=C=O group. They are very intense in the region 2250–2280 cm^{-1} (asymmetric stretching vibrations),[4,9,12,28,31,34,36–38,40–50,52–57,62,69–71,75,78,81,83–85,86,88,90,91,93,95,96,102,103,106,108,110,112,114,115,117,120,132] weak in the region 1415 to 1470 cm^{-1} (symmetric stretching vibrations),[12,34,40,41,56,85,86,88] and strong in the region of about 600 cm^{-1} (bending vibrations).[12,41,56] The absorption bands from the asymmetric stretching vibrations of the isocyanate group in phosphorylated alkyl and alkenyl isocyanates are displaced to lower frequency by 10–25 cm^{-1} relative to the isocyanates of phosphorus acids and they occur in approximately the same region as for organic isocyanates not containing phosphorus substituents.[132,133] It was established by IR spectroscopy that the majority of α-chloro-substituted phosphorylated alkyl isocyanates occur solely in the isocyanate form, but some phosphorylated α,α-dichloroalkyl isocyanates exist in equilibrium with their chlorocarbonyl form:[54,106,108]

$$(C_2H_5O)_2P(O)CCl_2NCO \rightleftarrows (C_2H_5O)_2P(O)CCl=NCOCl,$$
$$Cl_2P(O)CCl_2CCl_2NCO \rightleftarrows Cl_2P(O)CCl_2CCl=NCOCl,$$
$$Cl_3P=NCCl_2NCO \rightleftarrows Cl_3P=NCCl=NCOCl.$$

In order to confirm the structure of phosphorus-containing alkyl, alkenyl, and aryl isocyanates, the ^1H NMR spectra of the following isocyanates were studied: $(RO)_2P(O)CH(NCO)COOR'$ (R = C_2H_5, iso-C_3H_7; R′ = CH_3, C_2H_5, iso-C_3H_7),[9] $Cl_2P(O)C(=CH_2)NCO$,[38] and $(C_2H_5O)_2P(S)SCH_2CH_2NCO$.[95]

The following isocyanates were studied using ^1H NMR and ^{31}P NMR: $Cl(X)P(O)CY(CH_2Br)NCO$ (X = Cl, C_2H_5O; Y = H, Br)

and $Cl_2P(O)C(=CHX)NCO$ (X = H, Br),[40] $C_6H_5CH(NCO)P(O)(OR)_2$ (R = CH_3, C_2H_5),[41,90] $C_6H_5CH(NCO)P(O)(X)Cl$ (X = Cl, C_2H_5O),[41] $(RO)_2P(O)CH(CCl_3)NCO$ and $(RO)_2P(O)C(=CCl_2)NCO$ (R = CH_3, C_2H_5),[46] $C_6H_5CCl(NCO)P(O)(OR)_2$ (R = CH_3, C_2H_5), $C_6H_5CCl(NCO)P(O)(X)Cl$ (X = Cl, C_2H_5O),[56] and $(C_2H_5O)_2P(S).SCH_2CH_2NCO$.[88]

The following isocyanates were studied using ^{31}P NMR: (*S*)-(+)-$C_6H_5CH(NCO)P(O)(OR)_2$ [R = C_2H_5, $Si(CH_3)_3$],[12] a mixture of $(RO)_2P(O)SCH_2CHClCH_2NCO$ and $(RO)_2P(O)SCH.(CH_2Cl)CH_2NCO$ (R = CH_3, iso-C_3H_7),[84] $X(C_2H_5O)P(O)CH_2CH_2.NCO$ (X = Cl, C_2H_5O),[86] and *o*-$(C_6H_5)_2P(O)C_6H_4NCO$.[91]

The following isocyanates were studied using ^{31}P and ^{19}F NMR: $F(X)P(O)C(=CH_2)NCO$ (X = F, C_2H_5O),[40] $F(RO)P(O)CCl_2NCO$ (R = CH_3, C_2H_5),[55] and $(C_2H_5O)_2P(O)C(CF_3)(R)NCO$ (R = Cl, CH_3O).[62]

^1H NMR was used to study the diastereotopicity of the hydrogen atoms of the CH_2Br group in the isocyanates $X_2P(O)CH(CH_2Br)NCO$ (X = Cl, F) [40] and also the methoxyl groups in the isocyanates $C_6H_5CH(NCO)P(O)(OCH_3)_2$ [41] and $C_6H_5CCl(NCO)P(O)(OCH_3)_2$.[56]

^{31}P, $^{31}P-\{^1H\}$, ^{19}F, and ^1H NMR were used to confirm the structure and study the diastereotopicity of the fluorine atoms on phosphorus in isocyanates with a chiral carbon atom: (*S*)-(−)-$C_6H_5\dot{C}H(NCO)P(O)F_2$,[12] $C_6H_5\dot{C}H(NCO)P(O)F_2$,[12,41] $F_2P(O)\dot{C}H(CH_2Br)NCO$,[39,40] $F_2P(O)\dot{C}Br(CH_2Br)NCO$,[40] $C_6H_5\dot{C}Cl(NCO)P(O)F_2$ [56] and the diastereomeric anisochronism of isocyanates with chiral phosphorus and carbon atoms:

$(S)(+)\text{-}C_6H_5\dot{C}H(NCO)\dot{P}(O)(OC_2H_5)F$ (Ref.12),

$C_6H_5\dot{C}H(NCO)\dot{P}(O)(OC_2H_5)F$ (Refs.12, 41),

$F(C_2H_5O)\dot{P}(O)\dot{C}H(CH_2Br)NCO$ (Refs.39, 40),

$F(C_2H_5O)\dot{P}(O)\dot{C}Br(CH_2Br)NCO$ (Ref.40),

$C_6H_5\dot{C}Cl(NCO)\dot{P}(O)(OC_2H_5)F$ (Ref.56).

In addition, $^{19}F-\{^1H\}$ and $^{31}P-\{^1H\}$ NMR were used to study the structure and diastereomeric anisochromism of bis-phosphorylated chloromethyl isocyanates with chiral phosphorus atoms:[55]

$F(RO)\dot{P}(O)[Cl(RO)\dot{P}(O)]\dot{C}ClNCO$ (R = CH_3, C_2H_5),

$[F(C_2H_5O)\dot{P}(O)]_2CClNCO$ и $[Cl(C_2H_5O)\dot{P}(O)]_2CClNCO$.

A quantum-chemical calculation using the Hofmann method was carried out on the isocyanates $F_4PCH=CHNCO$ and $Cl_4PCH=CHNCO$ and also their isomers $F_2P(O)CH=CHNCF_2$ and $Cl_2P(O)CH=CHNCCl_2$, and it was established that the phosphorane form is stable for fluorine-containing compounds while for chlorine-containing compounds the dichloride form is stable.[80]

V. Use of phosphorus-containing isocyanates for obtaining polymers

Phosphorylated organic isocyanates that contain several isocyanate groups in the molecule when reacted with polyfunctional compounds containing an active hydrogen atom (hydroxyl and amino groups, etc.) form fire-resistant, thermally stable polymers—polyurethanes, polyureas, polyurethanoureas, etc. These polymers are used for the production of rubbers, glues, varnish coatings, films, foamed plastics, moulded products, finishing materials for fabrics, etc. Phosphorus-containing organic isocyanates are used as additives for plastics and cellulose in order to impart fire-resistant properties or as vulcanising agents. Tris(*p*-isocyanatophenyl) phosphorothioate (Desmodur RF) has been used in West Germany as a cross-linking agent in adhesive rubber solutions.[3,15,18,20,26,58,61,89,99–101,107,109,119,120,134–139]

VI. Physiological activity of compounds obtained from phosphorus-containing isocyanates

Esters and amides of phosphorylated *N*-alkyl- and *N*-alkenylcarbamic acids possess high insecticidal, acaricidal, and fungicidal activity.[56,64,118,140,141] *N*-[2-Diethylenediamidophosphoryl)vinyl]-substituted urethanes and *N'*-arylureas exhibit antitumorigenic activity.[76,79,121,123] The phosphonium salt $[(C_6H_5)_3PCH_2NH.COOC_{10}H_{21}]^+Cl^-$ has antimicrobial properties.[142] The compounds $SO_2[NHC(O)P(O)(OR)_2]_2$, obtained from sulphuryl diisocyanate, have fungicidical, nematocidal, and herbicidal activity.[116]

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It is evident from the above that there has been an extensive development of the chemistry of phosphorus-containing alkyl, alkenyl, aryl, acyl, and sulphonyl isocyanates which are derivatives of synthetic and natural aminophosphonic acids[143] (the two hydrogen atoms on nitrogen replaced by a =C=O group), playing a definite role in biology. Phosphorus-containing organic isocyanates are starting to be used as raw materials for the synthesis of various types of aminophosphonic acids—analogues of aminocarboxylic acids. Moreover, phosphorus-containing organic isocyanates are very convenient and highly reactive compounds for introducing phosphorus into different organic products. They have already been used for the synthesis of phosphorus-containing polymers and biologically active compounds. From the theoretical point of view phosphorus-containing alkyl isocyanates have proved convenient subjects for studying the phenomena of diastereomeric anisochronism and diastereotopicity of atoms and groups in molecules with chiral carbon and phosphorus atoms.

References

1. T Ya Medved', M I Kabachnik *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1956, 634
2. V A Shokol *Uspekhi Khimii Fosfororganicheskikh i Seraorganicheskikh Soedinenii. Vypusk 3* (Progress in the Chemistry of Organophosphorus and Organosulphur Compounds. No. 3) (Edited by A V Kirsanov et al.), Izd. Naukova Dumka, Kiev, 1973, p. 6
3. H C Fielding, J M Pollack, B. P. 968 109; *Chem. Abs.*, 1964, **61** 14 864
4. B S Drach, A D Sinitsa, A V Kirsanov *Zh. Obshch. Khim.*, **1970, 40** 1933
5. T Ya Medved' *Khimiya i Primenenie Fosfororganicheskikh Soedinenii: Trudy I Konferentsii* (Proceedings of the Ist Conference on the Chemistry and Use of Organophosphorus Compounds) (Edited by A E Arbuzov), Izd. Akad. Nauk SSSR, Moscow, 1957, p. 262
6. M I Kabachnik, T Ya Medved' *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1953, 866
7. M I Kabachnik, T Ya Medved', T Ya Mastryukova *Dokl. Akad. Nauk SSSR*, 1953, **92** 890

8. P S Khokhlov, B A Kashemirov, A D Mikityuk, Yu A Strepikheev *Zh. Obshch. Khim.*, 1983, **53** 2146
9. P S Khokhlov, B A Kashemirov, A D Mikityuk, et al. *Zh. Obshch. Khim.*, 1984, **54** 2237
10. S V Rogozhin, V A Davankov, Yu P Belov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 955
11. Yu P Belov, V A Davankov, V A Tsyryapkin, S V Rogozhin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975, 1619
12. B N Kozhushko, A V Lomakina, Yu A Paliichuk, V A Shokol *Zh. Obshch. Khim.*, 1983, **53** 1960
13. B N Kozhushko, V A Shokol, Yu A Paliichuk, et al. *Tezisy Dokladov VIII Vsesoyuznoi Konferentsii po Khimii Fosfororganicheskikh Soedinenii, Posvyashchennoi 80-letiyu Reaktsii A E Arbuzova* (Abstracts of Reports at the VIIIth All-Union Conference on the Chemistry of Organophosphorus Compounds, Dedicated to the 80th Anniversary of the A E Arbuzov Reaction), Kazan', 1985, Part 2, p. 98
14. V A Shokol, B N Kozhushko, Yu A Paliichuk, et al. *Khimiya i Primenenie Fosfororganicheskikh Soedinenii: Trudy VII Konferentsii* (Proceedings of the VIIth Conference on the Chemistry and Use of Organophosphorus Compounds) (Edited by M I Kabachnik), Izd. Nauka, Leningrad, 1987, p. 231
15. H Holtschmidt, BRD P. 1 126 379; *Chem. Abs.*, 1962, **57** 7169
16. H Holtschmidt, BRD P. 1 129 149; *Chem. Abs.*, 1962, **57** 11 238
17. H Holtschmidt, US P. 3 013 048; *Chem. Abs.*, 1962, **57** 11 105
18. H Holtschmidt, US P. 3 136 806; *Chem. Abs.*, 1964, **61** 5565
19. B. P. 891 654; *Chem. Abs.*, 1962, **57** 11 108
20. H Holtschmidt, G Oertel *Angew. Chem.*, 1962, **74** 795
21. R F W Rätz, US P. 3 299 187
22. M Soga, P Yamomoto, A Takagi, M Sakian, Japanese Appl. 57-40 451; *Ref. Zh. Khim.*, 1983, 9H186
23. M Soga, T Yamamoto, K Takaki, M Torisu, Japanese Appl. 57-59 849; *Ref. Zh. Khim.*, 1983, 9H185
24. H Holtschmidt, W Hugo, BRD P. 1 122 075
25. J Holtschmidt, W Hugo, US P. 3 013 049; *Chem. Abs.*, 1962, **57** 4594
26. G Ottmann, H Lederle, H Hooks, E Kober *Inorg. Chem.*, 1967, **6** 394
27. H Gerber, M Halman, D Vofsi *Phosphorus*, 1976, **6** 111
28. L I Samarai, V A Bondar', G I Derkach *Zh. Org. Khim.*, 1969, **5** 119
29. V A Shokol, V V Doroshenko, G I Derkach *Zh. Obshch. Khim.*, 1969, **39** 214
30. V O Shokol, V V Doroshenko, G I Derkach *Dopov. Akad. Nauk Ukr. RSR, Ser. B*, 1969, 818
31. V A Shokol, V V Doroshenko, G I Derkach *Zh. Obshch. Khim.*, 1970, **40** 1458
32. V A Shokol, V V Doroshenko, B N Kozhushko, E A Stukalo *Khimiya i Premenenie Fosfororganicheskikh Soedinenii: Trudy V Konferentsii* (Proceedings of the Vth Conference on the Chemistry and Use of Organophosphorus Compounds) (Edited by M I Kabachnik et al.), Izd. Nauka, Moscow, 1974, p. 54
33. V A Shokol, V V Doroshenko, G I Derkach *Zh. Obshch. Khim.*, 1969, **39** 938
34. V A Shokol, V V Doroshenko, G I Derkach *Zh. Obshch. Khim.*, 1970, **40** 535
35. V A Shokol, B N Kozhushko *Usp. Khim.*, 1985, **54**(1) 162 [English translation in *Russ. Chem. Rev.*, 1985(1)]
36. V A Shokol, E B Silina, B N Kozhushko, G A Golik *Zh. Obshch. Khim.*, 1979, **49** 312
37. N K Mikhailyuchenko, V A Shokol *Zh. Obshch. Khim.*, 1977, **47** 2203
38. E A Stukalo, E M Yur'eva, L N Markovskii *Zh. Obshch. Khim.*, 1980, **50** 343
39. B N Kozhushko, E B Silina, V A Shokol *Zh. Obshch. Khim.*, 1979, **49** 2153
40. E B Silina, B N Kozhushko, V A Shokol *Zh. Obshch. Khim.*, 1989, **59** 571
41. B N Kozhushko, A V Gumenyuk, N K Mikhailyuchenko, V A Shokol *Zh. Obshch. Khim.*, 1980, **50** 541
42. V I Gorbatenko, L I Kruglik, L I Samarai *Zh. Obshch. Khim.*, 1973, **43** 1043
43. V I Gorbatenko, L I Samarai, I E Boldeskul *Khimiya i Premenenie Fosfororganicheskikh Soedinenii: Trudy V Konferentsii* (Proceedings of the Vth Conference on the Chemistry and Use of Organophosphorus Compounds (Edited by M I Kabachnik et al.), Izd. Nauka, Moscow, 1974, p. 56
44. V N Fetyukhin, A S Koretskii, V I Gorbatenko, L I Samarai *Zh. Org. Khim.*, 1977, **13** 271
45. H Ulrich, B Tucker *J. Org. Chem.*, 1968, **33** 2887
46. N K Mikhailyuchenko, B N Kozhushko, V A Shokol *Zh. Obshch. Khim.*, 1983, **53** 548
47. V A Shokol, N K Mikhailyuchenko *Zh. Obshch. Khim.*, 1977, **47** 75
48. V A Shokol, B N Kozhushko, V V Doroshenko, A V Kirsanov *Zh. Obshch. Khim.*, 1973, **43** 12
49. V A Shokol, B N Kozhushko *Zh. Obshch. Khim.*, 1972, **42** 2346
50. V A Shokol, B N Kozhushko *Zh. Obshch. Khim.*, 1977, **47** 321
51. V V Doroshenko, B N Kozhushko, E A Stukalo, V A Shokol *Zh. Obshch. Khim.*, 1972, **42** 484
52. V V Doroshenko, E A Stukalo, V A Shokol, B N Kozhushko *Zh. Obshch. Khim.*, 1971, **41** 2155
53. V A Shokol, B N Kozhushko, A V Gumenyuk *Zh. Obshch. Khim.*, 1975, **45** 1965
54. V A Shokol, B N Kozhushko, A V Kirsanov *Zh. Obshch. Khim.*, 1973, **43** 544
55. B N Kozhushko, V A Shokol *Zh. Obshch. Khim.*, 1988, **58** 1516
56. A V Lomakina, Candidate's Thesis in Chemical Sciences, Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev, 1983, p. 179
57. B N Kozhushko, A V Gumenyuk, V A Shokol *Zh. Obshch. Khim.*, 1977, **47** 2766
58. H Holtschmidt, E Degener, G Braun, BRD P. 1 154 106
59. H Holtschmidt, E Degener, G Braun, French P. 1 307 007; *Chem. Zbl.*, 1965, 12-2711
60. H Holtschmidt, P Fischer, Belgian P. 61 225; *Chem. Abs.*, 1962, **57** 1554
61. P Fischer, H Holtschmidt, G Oertel, G Braun, Belgian P. 618 027; *Chem. Abs.*, 1963, **58** 6995
62. V I Gorbatenko, M N Gertsyuk, L I Samarai *Zh. Org. Khim.*, 1979, **15** 2047
63. L I Samarai, V I Gorbatenko, V N Fetyukhin, et al. *Tezisy Dokladov VII Vsesoyuznoi Konferentsii po Khimii Fosfororganicheskikh Soedinenii* (Abstracts of Reports at the VIIth All-Union Conference on the Chemistry of Organophosphorus Compounds), Leningrad, 1982, p. 174
64. V V Doroshenko, Candidate's Thesis in Chemical Sciences, Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev, 1969, p. 161

65. B N Kozhushko, E B Silina, M I Povolotskii, V A Shokol *Zh. Obshch. Khim.*, 1982, **52** 443
66. B N Kozhushko, E B Silina, V V Doroshenko, et al. *Zh. Obshch. Khim.*, 1986, **56** 1758
67. B N Kozhushko, N K Mikhailyuchenko, E B Silina, et al. *Zh. Obshch. Khim.*, 1987, **57** 1092
68. V I Gorbatenko, L I Kruglik, L I Samarai, USSR P. 423 803; *Byull. Izobret.*, 1974, (14) 83; *Ref. Zh. Khim.*, 1976, 60377
69. V A Shokol, V V Doroshenko, G I Derkach *Zh. Obshch. Khim.*, 1970, **40** 1692
70. L I Samarai, V I Gorbatenko, L I Kruglik, et al. *Zh. Obshch. Khim.*, 1972, **42** 1169
71. B N Kozhushko, A V Gumenyuk, Yu A Paliichuk, V A Shokol *Zh. Obshch. Khim.*, 1977, **47** 333
72. A D Sinitsa, N A Parkhomenko, L N Markovskii *Zh. Obshch. Khim.*, 1983, **53** 354
73. B N Kozhushko, E B Silina, A V Gumenyuk, et al. *Zh. Obshch. Khim.*, 1980, **50** 2210
74. E S Gubnitskaya, Z T Semashko *Zh. Obshch. Khim.*, 1975, **45** 489
75. E S Gubnitskaya, Z T Semashko *Zh. Obshch. Khim.*, 1978, **48** 2007
76. E S Gubnitskaya, Z T Semashko *Tezisy Dokladov Vsesoyuznoi Konferentsii "Sintez i Mekhanizm Deistviya Fiziologicheski Aktivnykh Veshchestv"* (Abstracts of Reports at the All-Union Conference "The Synthesis and Mechanism of the Action of Physiologically Active Compounds"), Odessa, 1976, p. 67
77. V V Doroshenko, E A Stukalo, A V Kirsanov *Zh. Obshch. Khim.*, 1971, **41** 1645
78. V V Doroshenko, E A Stukalo, A V Kirsanov *Zh. Obshch. Khim.*, 1974, **44** 69
79. E S Gubnitskaya, I M Loseva, E A Stukalo *Khim.-farm. Zh.*, 1974, **8** 13
80. A A Kisilenko, Yu P Egorov, E A Stukalo, L N Markovskii *Zh. Obshch. Khim.*, 1975, **45** 1722
81. V V Doroshenko, E A Stukalo, L N Markovskii *Zh. Obshch. Khim.*, 1974, **44** 2135
82. E A Stukalo, V V Doroshenko, L N Markovskii *Zh. Obshch. Khim.*, 1975, **45** 2166
83. L N Markovskii, E A Stukalo *Phosphorus*, 1974, **4** 237
84. G A Kutyrev, O S Korolev, R A Cherkasov, A N Pudovik *Zh. Obshch. Khim.*, 1985, **55** 996
85. V A Shokol, V F Gamaleya, L I Molyavko *Zh. Obshch. Khim.*, 1974, **44** 90
86. V F Gamaleya, V A Shokol *Zh. Obshch. Khim.*, 1977, **47** 2759
87. E S Gubnitskaya, V F Gamaleya, V A Shokol *Zh. Obshch. Khim.*, 1972, **42** 2112
88. V F Gamaleya, L I Molyavko, V A Shokol *Zh. Obshch. Khim.*, 1976, **46** 51
89. V A Shokol, V V Doroshenko, G I Derkach *Zh. Obshch. Khim.*, 1975, **45** 1713
90. O I Kolodyazhnyi, V N Yakovlev, V P Kukhar' *Zh. Obshch. Khim.*, 1980, **50** 1418
91. A Baceiredo, G Bertrand, J-P Majoral, et al. *J. Am. Chem. Soc.*, 1984, **106** 7065
92. O A Mukhacheva, V G Nikolaeva, R L Yafarova, et al. *Zh. Obshch. Khim.*, 1975, **45** 526
93. L I Razumov, R K Ismagilov, R L Yafarova, T A Tarzivolova *Zh. Obshch. Khim.*, 1977, **47** 41
94. O A Mukhacheva, V G Nikolaeva, L I Razumov *Zh. Obshch. Khim.*, 1971, **41** 1873
95. E S Gubnitskaya, L A Zolotareva, Z T Semashko *Zh. Obshch. Khim.*, 1976, **46** 2233
96. V N Fetyukhin, M V Vovk, L I Samarai *Zh. Org. Khim.*, 1981, **17** 1420
97. M I Bakhitov, E V Kuznetsov, R A Mirgazizova, USSR P. 278 690; *Byull. Izobret.*, 1970, (26) 24; *Ref. Zhur. Khim.*, 1971, 22H124
98. M I Bakhitov, E V Kuznetsov, R A Mirgazizova, L A Emikh *Sintez i Fizikokhimiya Polimerov. Vypusk 8* (The Synthesis and Physical Chemistry of Polymers. No. 8) (Edited by Yu S Lipatov et al.), Izd. Naukova Dumka, Kiev, 1971, p. 36
99. Yu L Pogosov, M I Bakhitov, E N Ratnikov, M M Shaimardanova *Zh. Prikl. Khim.*, 1972, **45** 924
100. G Borisov, K Troev *Izv. Otd. Khim. Nauki, B''lg. Akad. Nauk*, 1972, **5** 545
101. M I Bakhitov, M Ya Obryadina, E V Kuznetsov, USSR P. 572 465; *Byull. Izobret.*, 1977, (34) 55; *Ref. Zh. Khim.*, 1978, 17H158
102. H Wittmann, F A Peteo *Z. Naturforsch., B*, 1974, **29b** 765
103. B S Drach, O P Lobanov, V A Kovalev, A V Kirsanov *Dokl. Akad. Nauk Ukr. SSR, Ser. B*, 1978, 1102
104. B S Drach, O P Lobanov, E P Sviridov *Khimiya i Primenenie Fosfororganicheskikh Soedinenii: Trudy Yubileinoi VI Konferentsii* (Proceedings of the Anniversary VIth Conference on the Chemistry and Use of Organophosphorus Compounds) (Edited by A V Kirsanov et al.), Izd. Naukova Dumka, Kiev, 1981, p. 333
105. V P Kukhar', A V Kirsanov, N A Kirsanova, USSR P. 407 889; *Byull. Izobret.*, 1973, (47) 81; *Ref. Zh. Khim.*, 1974, 23H321
106. V Ya Semenii, A P Boiko, G F Solodushchenko, et al. *Zh. Obshch. Khim.*, 1974, **44** 1251
107. H C Fielding, J M Pollack, B. P. 923 581
108. E A Stukalo, V V Doroshenko, L N Markovskii *Zh. Obshch. Khim.*, 1975, **45** 1022
109. M I Bakhitov, L Sh Zainutdinova, E V Kuznetsov, F L Kligman *Sintez Poliuretanov* (The Synthesis of Polyurethanes) (Edited by S I Omel'chenko et al.), Izd. Naukova Dumka, Kiev, 1981, p. 114
110. E S Gubnitskaya, Z T Semashko, V I Gorbatenko *Zh. Org. Khim.*, 1978, **14** 2268
111. G I Derkach, V V Malovik, N D Bodnarchuk *Z. Naturforsch., B*, 1969, **24b** 139
112. N D Bodnarchuk, V V Malovik, G I Derkach *Zh. Obshch. Khim.*, 1969, **39** 1707
113. N D Bodnarchuk, V V Malovik, G I Derkach *Zh. Obshch. Khim.*, 1970, **40** 1210
114. V I Gorbatenko, L F Lur'e, L I Samarai *Zh. Obshch. Khim.*, 1977, **47** 2388
115. Z Arnold, B Fiszer *Rocz. Chem.*, 1969, **43** 1443
116. J J Kohler, US P. 3 401 214
117. D E Arrington *J. Chem. Res. (S)*, 1978, 330
118. B N Kozhushko, Candidate's Thesis in Chemical Sciences, Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev, 1973, p. 161
119. H C Fielding, J M Pollack, N H Rey, B. P. 923 583; *Chem. Abs.*, 1964, **60** 2758
120. C Fefer, S E Molis, S L Hsu, W J MacKnight *Macromolecules*, 1984, **17** 1830

121. L D Protsenko, E A Stukalo, I S Trokhimenko, et al., USSR P. 476 272; *Byull. Izobret.*, 1975, (25) 75; *Ref. Zh. Khim.*, 1977, 10 080
122. I S Trokhimenko *Zh. Obshch. Khim.*, 1977, **47** 1039
123. L D Protsenko, I I Kuz'menko, N Ya Skul'skaya, et al. *Tezisy Dokladov Vsesoyuznoi Konferentsii "Sintez i Mekhanizm Deistviya Fiziologicheski Aktivnykh Veshchestv"* (Abstracts of Reports at the All-Union Conference "The Synthesis and Mechanism of the Action of Physiologically Active Compounds"), Odessa, 1976, p. 65
124. A P Martynyuk, V S Brovarets, O P Lobanov, B S Drach *Zh. Obshch. Khim.*, 1984, **54** 2186
125. A S Shtepanek, V V Doroshenko, V A Zasorina, et al. *Zh. Obshch. Khim.*, 1974, **44** 2130
126. A S Shtepanek, V A Zasorina, E N Tkachenko, L M Tochilkina *Khimiya i Primenenie Fosfororganicheskikh Soedinenii: Trudy V Konferentsii* (Proceedings of the Vth Conference on the Chemistry and Use of Organophosphorus Compounds) (Edited by M I Kabachnik et al.), Izd. Nauka, Moscow, 1974, p. 59
127. V A Shokol, B N Kozhushko, A M Kolesnikov *Zh. Obshch. Khim.*, 1975, **45** 2093
128. R Neidlein, W Friederich *Arch. Pharm. (Weinheim, Ger.)*, 1977, **310** 614
129. V I Gorbatenko, N V Mel'nichenko, L I Samarai *Zh. Obshch. Khim.*, 1978, **48** 1425
130. V I Gorbatenko, N V Mel'nichenko, L I Samarai, A V Kirsanov *Tezisy Dokladov VI Yubileinoi Konferentsii po Khimii Fosfororganicheskikh Soedinenii, Posvyashchennoi 100-letiyu so Dnya Rozhdeniya Akademika A E Arbuzova* (Abstracts of Reports at the VIth Anniversary Conference on the Chemistry of Organophosphorus Compounds, Dedicated to the 100th Anniversary of the Birth of Academician A E Arbuzov), Kiev, 1977, p. 94
131. V N Fetyukhin, M K Vovk *Zh. Obshch. Khim.*, 1983, **53** 1763
132. Yu P Egorov, A A Kisilenko, V A Shokol *Zh. Strukt. Khim.*, 1973, **14** 240
133. L Bellamy *Infrared Spectra of Complex Molecules* (Translated into Russian), Izd. Inostr. Lit., 1963, p. 590
134. H Holtschmidt, G Braun, BRD P. 1 092 190
135. G Oertel, H Holtschmidt, BRD P. 1 127 583
136. H Holtschmidt, F Spulak, E Müller, O Bayer, BRD P. 1 131 001
137. G Oertel, H Holtschmidt, M Dollhausen, E Bock, BRD P. 1 812 965
138. V I Nikolaev, A V Kostochko, R A Lazarev, USSR P. 304 260; *Byull. Izobret.*, 1971, (17) 86; *Ref. Zh. Khim.*, 1972, 10F306
139. Y Nakano, K Nakao, T Haneda, et al., Japanese P. 53-33632; *Ref. Zh. Khim.*, 1979, 19T295
140. G V Protopopova, L I Reidalova, B N Kozhushko, et al. *Fiziologicheski Aktivnye Veshchestva. Vypusk 5* (Physiologically Active Compounds. No. 5) (Edited by P S Pel'kis et al.), Izd. Naukova Dumka, Kiev, 1973, p. 8
141. G V Protopopova, L A Reidalova, E S Gubnitskaya, et al. *Fiziologicheski Aktivnye Veshchestva. Vypusk 10* (Physiologically Active Compounds. No. 10) (Edited by P S Pel'kis et al.), Izd. Naukova Dumka, Kiev, 1978, p. 13
142. G T Pis'ko, O V Gudz', V A Shokol *Fiziologicheski Aktivnye Veshchesta. Vypusk 17* (Physiologically Active Compounds. No. 17) (Edited by P S Pel'kis et al.), Izd. Naukova Dumka, Kiev, 1985, p. 39
143. V P Kukhar', V A Solodenko *Usp. Khim.*, 1987, **56**(9) 1504 [English translation in *Russ. Chem. Rev.*, 1987(9)]

Translated from *Uspekhi Khimii* **58** 1896–1937 (1989) U.D.C. 577.15.086.83:577.21

Genetic engineering and modern enzymology

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ABSTRACT. The role of genetic engineering in the solution of problems involving enzymology is demonstrated. The method for the cloning and mutagenesis of protein and enzyme genes and the possibilities of genetic engineering for the study of the structure and functions of enzymes and their active centres and for the determination of the relation between the structure and stability of protein molecules are examined. The role of directed site-specific mutagenesis in the study of the structure and mechanism of the action of enzymes as well as their stability is indicated. The investigation of the mechanism and factors determining the stability of enzymes with the aid of aminoacid substitutions has led to prospects for protein design — the creation of proteins with new specified properties and improved stability.

The bibliography includes 301 references.

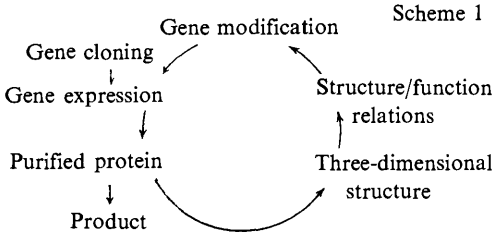
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I. Introduction

The extensive development of the recombinant DNA technique has led to its penetration into the protein chemistry and enzymology and to the appearance of a new discipline – protein engineering. The 1980s have been called the "era of the second coming" of protein chemistry and have been associated with a new boom in biotechnology — protein engineering. Protein engineering is a "marriage" between the fundamental science of the structure and functions of protein macromolecules, providing a basis for the deliberate alteration of their properties, and genetic engineering methods which make it possible to achieve this. The complete cycle of protein engineering is described by the following scheme:[1]

Scheme 1



Genetic engineering provides modern enzymology with unlimited possibilities for the investigation of the properties of enzymes: (1) the possibility of the rapid determination of the primary structure of protein molecules and their genes; (2) the discovery of the principles governing the coiling of the polypeptide chain and prospects for the prediction of the secondary and tertiary structures of the protein or the protein domain; (3) the study of the structure and of the mechanism of the functioning of enzymes *in vitro* and *in vivo*; the solution of fundamental problems in enzyme catalysis: the structure of the active centres of enzymes, the mechanism of enzyme–substrate interactions, the types and strengths of the interactions, process energetics, etc.; (4) the determination of the relation between the structure and stability of protein molecules. The solution of these problems leads to splendid prospects for protein design (the synthesis of enzymes with specified properties). The following features can be altered deliberately by genetic engineering methods: catalytic parameters (k_{cat} and K_M); thermal stability and the optimum temperature for activity; stability in organic solvents; substrate specificity; the need for cofactors; the pH optima for activity and stability; resistance to proteolysis; allosteric regulation; molecular weight and subunit composition.

Finally, it has become possible to create completely new proteins by means of the *de novo* synthesis of genes and their subsequent expression.

All these possibilities in genetic engineering for the solution of problems in modern enzymology are in fact considered in the present review.

II. General principles of the biosynthesis and structural organisation of protein and its gene

Protein is a polypeptide sequence made up of 20 aminoacid residues. A definite gene in DNA is responsible for the synthesis of each polypeptide chain.[2,3] The theoretical aspects and mathematical models of protein synthesis have been examined, for example, by Heijne et al.[4] A newly synthesised polypeptide chain in the cell undergoes post-translational modification and compartmentalisation.

The modification of various aminoacid residues (phosphorylation, methylation, hydroxylation, iodination, carboxylation, glycosylation, and substitution of lipids) in the protein chain can occur both during the period when the chain synthesised is linked to a ribosome and after the end of the synthesis.[5] The specific residues undergoing modification are determined in some proteins by the aminoacid sequence and in others by the conformation. For example, the carbohydrate binding sites in proteins are Asn in the Asn–X–Ser/Thr sequence, where X is any residue other than Pro. At this stage, there is a possibility of the binding of the protein synthesised to cofactors and M^{n+} ions, of the covalent and non-covalent assembly of subunits, and of the formation of disulphide linkages between polypeptide chains and within them. In certain cases, these processes take place cotranslationally. Intramolecular disulphide linkages are not encountered in molecules of intracellular cytoplasmic proteins. They are characteristic of extracellular proteins, for which the physiological environment and physicochemical conditions can be varied greatly and can induce the uncoiling of the protein.[6]

For proteins and enzymes functioning outside the cell, a signal sequence (presequence) is split off during passage through the cytoplasmic membrane by membrane signal proteases and the protein is simultaneously glycosylated.

The properties of the side groups in the aminoacid residues constituting the protein, which interact both with one another and with the molecules of the surrounding medium, exert the main influence on the steric structure of the protein molecule. All the aminoacid residues are divided into hydrophobic, hydrophilic, and neutral (Fig. 1). The assignment of a residue to a particular group as a function of criteria varies somewhat (cf. Kutuzova et al.[7] and Dolittle[8]). The hydrophobic residues (Gly), Ala, Cys, Val, Ile, Leu, Met, Phe, and Trp are fully immersed after the coiling of the protein, while the moderately polar residues (Gly), Ser, Thr, His, and Tyr and the highly polar residues (Gly), Pro, Asp, Asn, Glu, Gln, Arg, and Lys are immersed to a lesser extent: 76 and 63% respectively.[9] The structural organisation of the protein and the mechanism of the coiling and assembly of the polypeptide chain have been described in detail in a review.[10]

In the three-dimensional steric structure of a typical globular protein, the inner region is made up mainly of β-layers, while the surface consists of α-helices. Each third or fourth position in these outer α-helices is occupied by aminoacids with non-polar side groups directed into the interior of the globule, while the side groups of the remaining aminoacids are as a rule polar and are directed towards the aqueous medium.

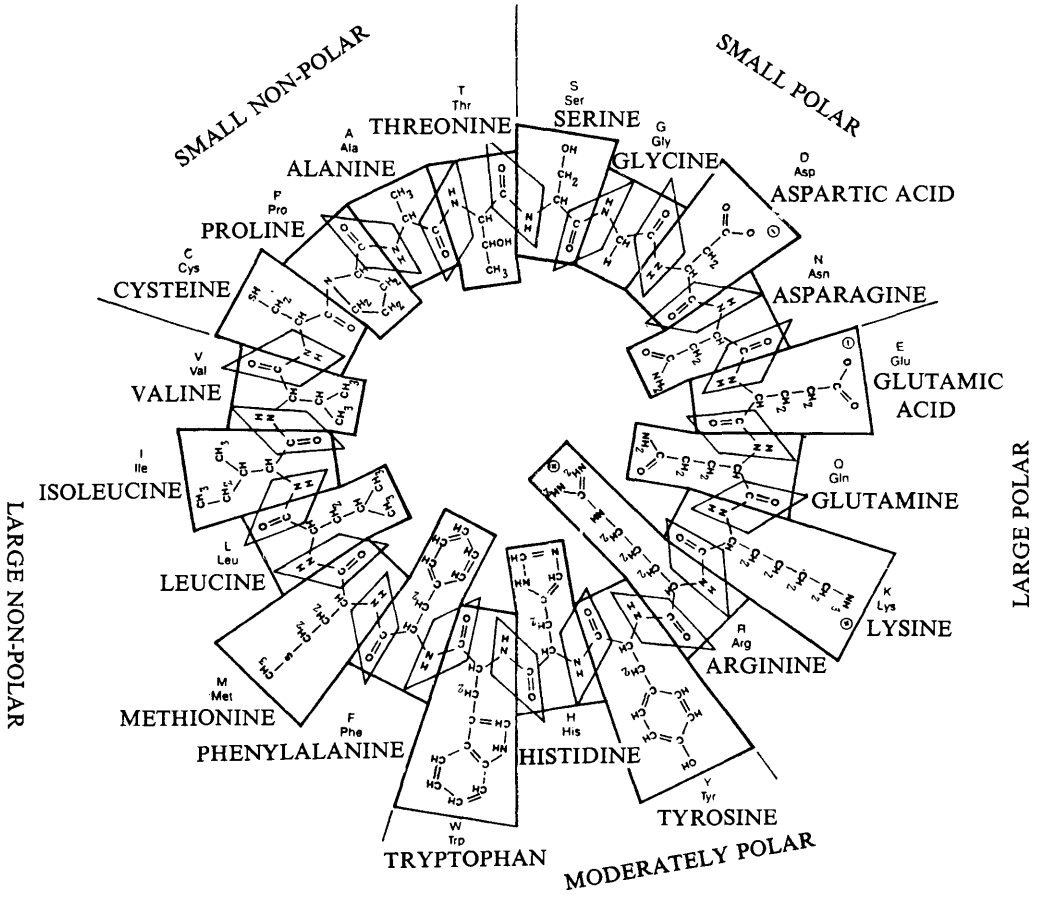


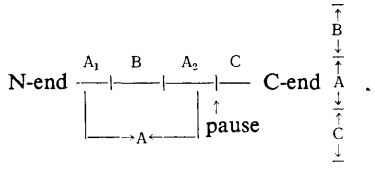
Figure 1. Classes of aminoacids based on the size and degree of polarisation of their side groups.[8]

The native protein molecule consists of several cooperative domains, each of which breaks down on denaturation as a single whole.[11] The protein consists as a rule of combinations of α- and β-structural elements, includes between 50 and 200 aminoacid residues, and is characterised by a minimal surface to volume ratio (S/V). Small proteins can contain only one domain, while larger ones contain up to tens of domains. Subdivision into domains, which is a general principle of the construction of protein molecules, ensures the necessary rigidity and relative mobility of specific groups in the protein and apparently reflects its evolution, which took place via the combination of previously independent small preproteins.[12] The existence of an independent unit of protein structure even smaller than the domain, namely the module,[13] has been postulated at the present time. The module consists of a polypeptide segment whose size is 2–5 kD (30–50 aminoacid residues) and which has a stable coiled conformation and performs a definite function in the highly specific binding of the ligand (substrate, allosteric effector, and cell components: lipids, carbohydrates, nucleic acids, etc.).[14] Thus the size of the protein may be determined by the number of different ligand-binding sections necessary for functioning *in vivo*. Knowing the size of the enzyme subunit, it is possible to estimate the number of ligand-binding sections: the size of the subunit, given by the ratio of the molecular weight to the average size of the module, is ~5.2 kD. The moduli and domains can also be visualised with the aid of crystallographic studies and microcalorimetric investigation of denaturation processes. Proteolysis usually occurs in the interdomain region and makes it possible to divide domains with partial retention of their function, as in the subdivision of DNA-polymerase into a large and a small domain, each of which is functionally active.[15]

Many proteins consist of several polypeptide chains—subunits, having both identical and different compositions and combined into a single entity via non-covalent interactions or disulphide linkages. The size of the subunit of a eukaryotic protein varies from 10 to 480 kD (the average size is 32 kD, while that of a prokaryotic protein is 24 kD).[16] For 90% of proteins, the size of the subunit is less than 60 kD. Thus the protein consists of subunits, each of which contains domains made up of moduli.

The problem of the coiling of the polypeptide chain synthesised with formation of the three-dimensional steric structure of the protein is one of the most complex and intriguing in protein chemistry. According to modern ideas about the mechanism of the coiling of the protein, the conformational information is distributed along the polypeptide sequence non-uniformly, certain aminoacids being of fundamental importance for the correct conformation. At the beginning of the coiling process, local reversible structures (nucleation centres) are produced. These are short sections of the secondary structure of the type of α-helices or β-layers. The structure is subsequently stabilised as a result of the interaction of neighbouring sections. Coiling begins independently and more or less simultaneously in several regions of the polypeptide chain (autonomous coiling domains).[17] The problem of coiling has now acquired especially great importance in connection with the preparation of hybrid proteins in the cloning of eukaryotic genes in bacteria, where the *N*-terminal section of the required protein has been fused with part of the prokaryotic protein, which can influence the coiling process, destabilising the kinetically important intermediate states of the eukaryotic protein. Furthermore, its *N*- or *C*-terminal component can be within the globule, while the fused hybrid protein will not have the required native conformation, giving rise to insoluble derivatives.[17]

The fact that the aminoacid residues in the polypeptide chain are separated not only in space but also in time during synthesis is very important for the protein coiling process. The importance of the separation in space and time of the aminoacid residues for the structure of the whole depends on the relative rates of synthesis of the protein and of its coiling. At the beginning of the synthesis, the coiling of the segment of the polypeptide chain synthesised takes place in microseconds, since it involves the interaction of only the nearest aminoacid residues. On average, the time required for the complete translation of a protein of average size is 2 min. The coiling of the polypeptide chain to a three-dimensional structure takes place before the completion of its total synthesis and there is a possibility of the formation of disulphide linkages, which did not exist in the completed protein. The subsequent isomerisation of disulphide linkages leads to the correct conformation, which has been demonstrated for the pancreatic trypsin inhibitor.[18] Direct evidence has been obtained for the existence of breaks during the synthesis of the protein, which results in the accumulation of specific polypeptides.[19,20] In terms of the mechanism of the coiling of the polypeptide chain *in vivo*, proteins can be divided into two groups:[21] (1) proteins the correct coiling of which is unaffected by the rate of translation; in such proteins the aminoacid sequence does indeed contain all the information necessary for the correct coiling of the chain (even *in vitro* after denaturation); (2) proteins incapable of coiling effectively into the native conformation *in vitro*. These are polypeptides with alternative kinetically easy coiling pathways, which can form distorted but stable conformations. The coiling of such proteins *in vivo* is greatly influenced by the translation process itself, which takes place at different rates and with translational pauses. The presence of the pauses is determined by the accumulation in the DNA chain of rarely used codons and hence by the presence of small amounts of the corresponding tRNA, which retards significantly the supply of the corresponding aminoacids. The presence of a secondary structure in mRNA also reduces the rate of translation.[21] The above features have been discovered, for example, for yeast pyruvate kinase.[22] Each of the four subunits of pyruvate kinase consists of a short N-terminal segment and three different domains: A, B, and C:



The translational pause before the start of the synthesis of the domain C enables the two sections A_1 and A_2 to form the central domain A, containing the catalytic centre, before the synthesis of the domain C containing the allosteric centre of pyruvate kinase. This prevents anomalous interactions between the still uncoiled regions of the domains A and C. Translational pauses, which enable functionally important domains to be formed, have also been observed for the Arom-protein catalysing the biosynthesis of aromatic acids.[23] The inability of certain proteins to return to the native conformation after denaturation *in vitro* may indicate the importance of the separation in time of the processes involving the synthesis and coiling of different sections of the polypeptide chain *in vivo*.

As a result of the employment of genetic engineering methods, it has now been possible to investigate in detail the mechanism of the coiling of proteins. The construction of mutant polypeptide

segments elucidates the role of individual aminoacid residues in the coiling and assembly of enzyme subunits.[24,25] It has been shown for the heterodimer (αβ) of *bacterial luciferase* that the scission of 10–15 residues from the C-terminal section of the β-subunit does not alter the activity and stability of the enzyme, but the mutant enzyme is incapable of recoiling after treatment with urea. The αβ complex of the subunits is formed initially between incompletely coiled α and β subunits and their final coiling takes place in the heterodimeric form. If the α and β subunits have been coiled *in vivo* separately, then the formation of the complex αβ is impossible without a preliminary treatment with urea. The coiling process is unaffected by the nature of the residues in the C-terminal section, but deletions in this region reduce the ability of the β-subunit to form a dimeric structure *in vitro* and *in vivo*.[26] Even one aminoacid residue can play a key role in the formation of the structure of the active enzyme. The introduction of an additional Met group at the N-end reduced significantly the rate of coiling of chick lysozyme, while the replacement of Ala-31 even by the structurally similar Val prevented the correct coiling of the protein.[27] In the pancreatic trypsin inhibitor, the Cys residues forming one of the three S–S bonds were replaced by Ala or Thr, whereupon the rate of coiling diminished by a factor of 3 but the correctly coiled protein was obtained.[28] Thus the formation of S–S bonds reduces the activation barrier to the polypeptide chain coiling process.

For enzymes with a known three-dimensional steric structure and gene structure, important conclusions have been reached by comparing these structures.[29] It is known that the genes of eukaryotic proteins are not continuous but are made up of coding sections (exons) and non-coding sections (introns). It has been suggested that the position of the introns in the gene corresponds to the boundary of the domain in the protein. For example, the subunits of NAD-dependent dehydrogenases contain two structurally and functionally different domains. One of them binds the coenzyme, while on the other there are substrate-binding and catalytic sections. The NAD^+-binding domains of alcohol dehydrogenase (ADH), glyceraldehyde-3-phosphate dehydrogenase (GAPD), and lactate dehydrogenase (LDH) have similar structures and bind the coenzyme in a similar way, while there is no homology as regards the catalytic domains and the latter have completely different structures.[30] The structure of the domain-containing subunits and the positions of the introns for these enzymes are presented in Fig. 2. The introns 6 and 9 for ADH, 5 and 6 for GAPD, and 3 and 7 for pyruvate kinase (PK) divide the catalytic and nucleotide-binding domains. Each nucleotide-binding domain can be roughly divided into two identical units, which refer to the mononucleotide-binding region and are separated by introns. This confirms the hypothesis that[31] the mononucleotide-binding domain is the principal unit for the generation of enzymes whose function is determined by the ability to bind nucleotides.

However, it has been shown for haemoglobin,[32] carboxypeptidase,[33] and antitrypsin[34] that the positions of the introns in the genes of eukaryotic proteins do not always correspond to the boundaries between the known domains. Furthermore, introns have not been observed in the genes of prokaryotes. It has been suggested that they have been eliminated in order to economise the genetic material.[8] On the other hand, several introns can be encountered within one domain (Fig. 2). Analysis of the genes of 80 proteins[35] has shown that for 70% of them the size of the exons

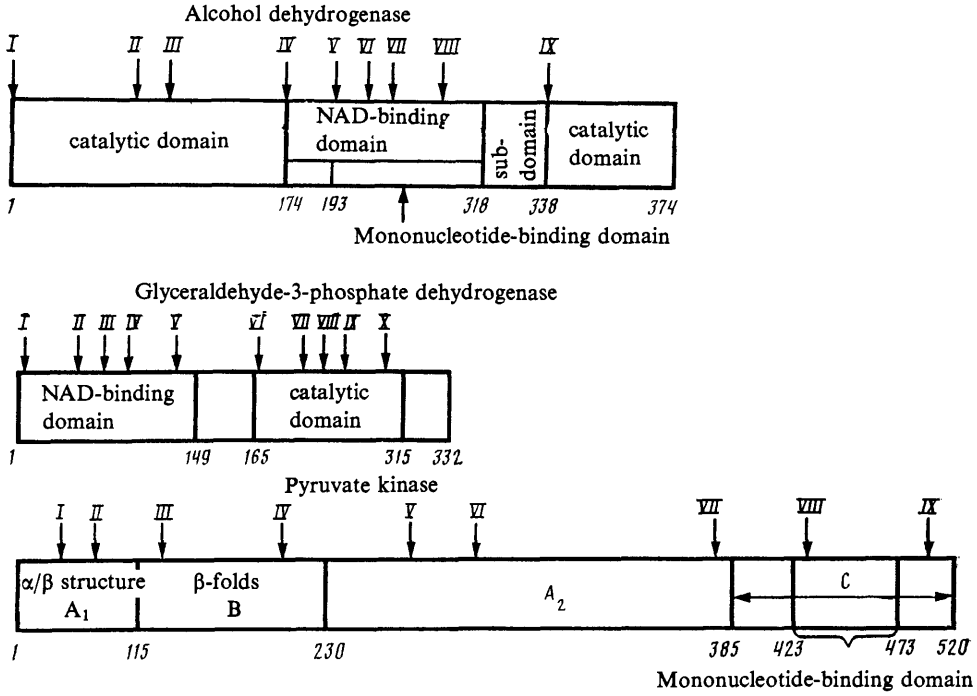


Figure 2. Diagram illustrating the positions of introns (roman numerals) and the limits of the domains along the polypeptide chains of enzyme subunits;[29] the arabic numerals indicate the positions of the residues in the aminoacid sequence.

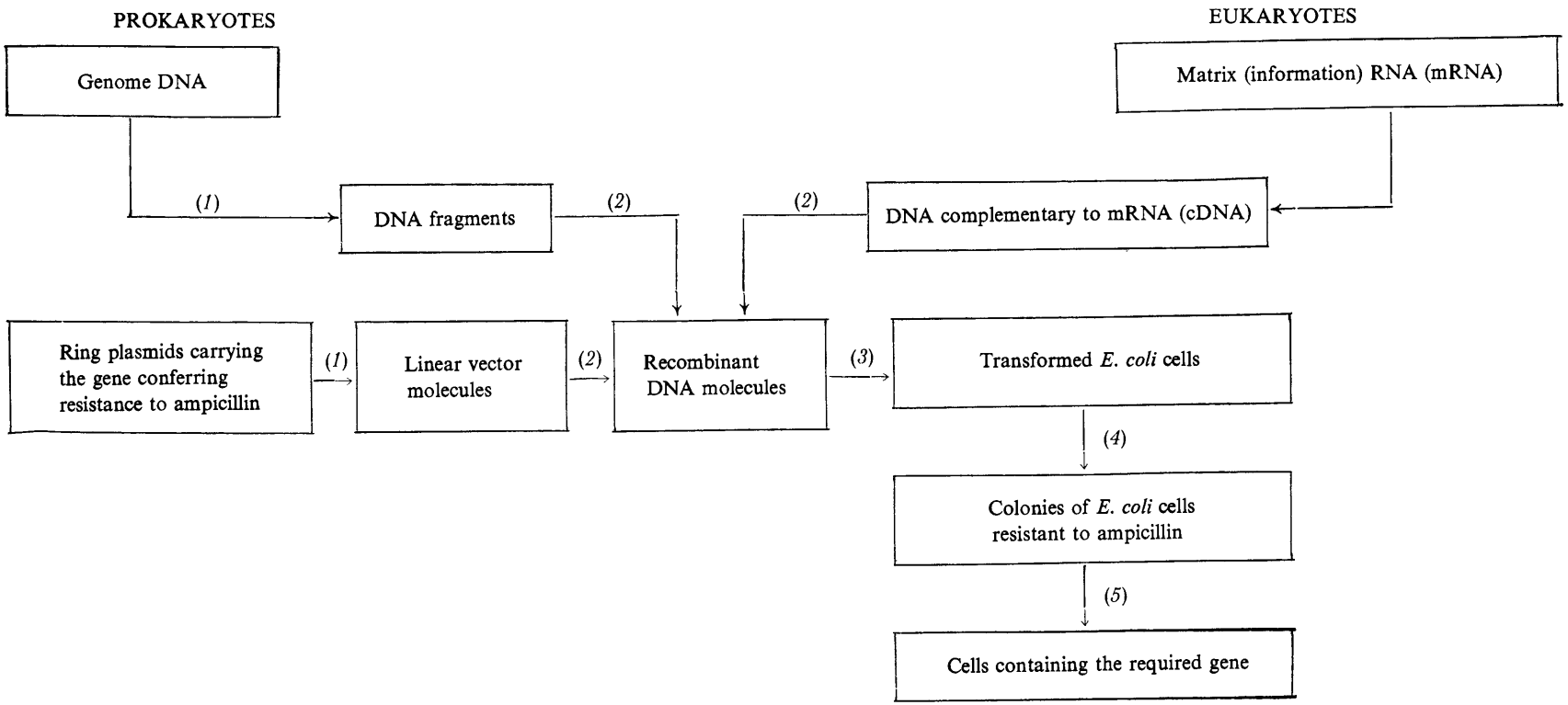


Figure 3. The principal stages in the cloning of the prokaryotic and eukaryotic DNA in the cells of *E. coli*:[3,37,38] (1) cleavage of DNA with the aid of restrictase; (2) cross-linking of DNA molecules with the aid of DNA ligase; (3) transformation of the cells of *E. coli* by the recombinant plasmids; (4) selection of *E. coli* colonies containing the recombinant plasmids on the basis of resistance to ampicillin; (5) screening of the library of clones with the aid of a radioactive probe.

varies from 52 to 223 pairs of nucleotides, which corresponds to the sizes of the moduli in the protein.[13] Introns apparently divide not only domains but also the protein moduli with definite ligand-binding functions. An algorithm has been proposed for the determination of the boundaries of the moduli and domains.[36] Many experimental facts confirm this hypothesis.

III. Methods for the cloning and mutagenesis of the genes of prokaryotic and eukaryotic proteins and enzymes

The methods for the cloning of the genes of proteins and enzymes from different sources, for the expression of genes in different host systems, have been described in detail in many textbooks and manuals.[3,37–39] The cloning of the DNA of the genes of prokaryotic proteins differs fundamentally from the cloning of the genes of the proteins from eukaryotic organisms. The DNA of the simplest organism consists of a set of genes coding for proteins and enzymes and arranged in a sequence. The first stage in its cloning is the isolation of the genome DNA, its splitting into fragments, and their incorporation into DNA vectors. The overall stages in the cloning of DNA in the plasmid vector of *E. coli* are presented in Fig. 3. The cells of *E. coli* are transformed by annular recombinant DNA molecules. The cells are then sewn in such a way that one colony, containing a population of identical daughter molecules (clones), grows from each cell. Among several thousand clones (the library), it is possible to find one or several clones containing the required incorporated DNA fragment. The colonies are screened by means of a specific radioactive probe, which makes it possible to inspect the library of clones. The probe can be pure or partly purified mRNA or a chemically synthesised oligonucleotide, which are hybridised with the corresponding gene sequence in the genome library. Antibodies to proteins, whose genes have to be detected, are also used frequently to identify the colonies.

Since the genes of the proteins of eukaryotes include non-coding sections (introns), one uses for the cloning of eukaryotic proteins cDNA — a DNA complementary to the matrix (information) RNA — or a chemically synthesised gene without introns. The first stage in the cloning of the proteins of eukaryotes is the isolation of mRNA on the basis of which the double-stranded cDNA is synthesised. Next it is incorporated in the cloning vector and is used to transform the host cells (Fig. 3).

The genetic engineering methods used for mutagenesis can be divided into two large classes. The first class includes the formation of random point mutations in the required gene. The classical method of mutagenesis with selection of mutant forms on the basis of a preselected property has been widely used hitherto for the formation of mutant enzymes differing from the wild enzymes in their catalytic activity, substrate specificity, or stability. A mutant gene is also obtained when the DNA in the form of an isolated fragment or as a component of a single-stranded or double-stranded DNA-vector is modified with the aid of chemical reagents or enzymes. In the second stage, the modified DNA is used to transform bacterial cells and individual clones are isolated. Next the mutant recombinant DNA is isolated from the set of clones and the nucleotide sequence in the mutant gene is determined. The characterised mutant gene is used to transform the host cells (bacteria, yeasts, and more rarely animal or plant cells), in which it is transcribed and translated, giving rise to the mutant protein.[40,41] The second class includes all the methods which make it possible to achieve specific preselected mutations. The modern methods for mutagenesis are classified in Table 1.

The most accurate and convenient method for the introduction of mutations into cloned DNA fragments is site-specific mutagenesis using synthetic oligonucleotides. A large number of studies have been devoted to the improvement of this method,[50–58] in particular to the increase of the yield of the mutant forms.[55,59–63] Site-specific mutagenesis has been used widely in the study of the relation between the structure and functions of proteins and their enzymes and for the creation of proteins with new properties.

Table 1. Classification of the methods for mutagenesis.

Name	Essential features of method	Remarks	Refs.
	Random mutations		
Chemical methods	Treatment of the gene by chemical mutagenic reagents (sodium bisulphite, hydrazine, nitrous acid, etc.)		[40–46]
Enzymic methods	Preparation of single-stranded DNA, construction of the second DNA chain with the aid of DNA polymerase in the presence of 4 deoxynucleotides, one of which has been replaced by its analogue	The bases of the nucleotides are modified, which leads to mutation	
	Specific preselected mutations		
Gene synthesis. Total synthesis of the gene	Construction of the gene from a set of segments of chemically synthesised oligonucleotides	The frequency of mutations approaches 100%, but the method is laborious and is nowadays rarely used	[42, 47, 48]
Partial (cassette) gene synthesis	Isolation of the gene, excision of a DNA segment at the restriction sites, and its replacement by the synthetic oligonucleotide containing the mutation	—	[40, 42, 49]
Deletion and insertion on cleavage of double-stranded DNA	Preparation of a linear DNA molecule, the removal of fragments located between restriction sites (deletions), the construction of an additional nucleotide chain (insertions)	—	[38, 42]
Site-specific oligonucleotide-directed mutagenesis	The synthetic oligonucleotide (10–20 bases) containing the mutation is hybridised with single-stranded DNA and is used as a primer for the synthesis of the second DNA chain. The additional chain is closed with the aid of DNA ligase and the resulting DNA is used to transform the *E. coli* cells, where DNA replicates with formation of two forms of the cloned gene: the wild and mutant types (Fig. 4)	The mutant form can be readily identified using the same nucleotide labelled with ^{32}P	[40–42, 47, 50–55]

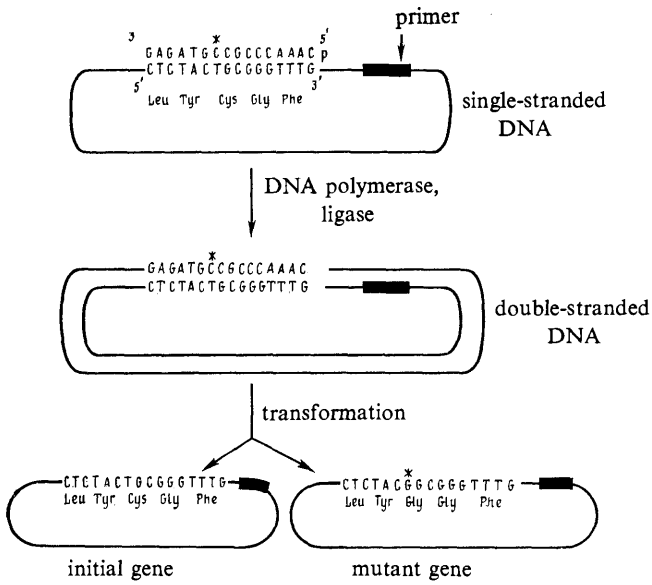


Figure 4. Schematic representation of the nucleotide-directed mutagenesis;[55] the asterisk designates the mutant nucleotide.

IV. The study of the structures and functions of proteins by genetic engineering methods

1. The primary protein structure and its evolution

The primary protein structure was determined previously solely by the sequence determination method with the aid of automatic aminoacid analysers. It was then necessary to have at ones disposal a large amount of the very pure protein, which was not always possible. With the aid of genetic engineering methods, it has become possible to isolate DNA and to determine the total nucleotide sequence in the gene coding for the given protein. The methods for the determination of the DNA sequence (the Maxan–Gilbert and Sanger methods)[3,37,38,64,65] made it possible to determine relatively simply and rapidly the sequence of nucleotide bases in the gene. With the aid of the genetic code, it is easy to establish subsequently the aminoacid sequence in the protein. The difficulty is the necessity for the error-free identification of a sequence of an enormous number of bases (a protein consisting of a thousand aminoacids is coded by 3000 bases) and also for a correct determination of the starting point of the reading of the code. The deletion of one base can lead to a shift of the reading framework and hence to an incorrect determination of the entire aminoacid sequence. In order to avoid such errors, one can, for example, determine the aminoacid sequences in short sections at the N- and C-ends of the protein by another method and to compare them with the sequence obtained from the nucleotide sequence of the gene. In order to check the correctness of the reading of the DNA base sequence, the molecular weights, measured mass-spectrometrically, of the tryptic peptides obtained from the test protein were also compared with the structures of these peptides derived from the DNA sequence.[66]

At the present time, the primary structures of more than 3700 proteins determined by different methods are known.[67] As genetic engineering methods have developed, the number of proteins and enzymes whose primary structures have been established has increased greatly (Fig. 5). In relation to certain enzymes, we shall consider what information about the structure of the enzyme itself and its active centre can be obtained solely from the analysis of the nucleotide sequence in the gene and by comparing it with the aminoacid sequence of the test protein.

The cloning and sequence determination for genes have made it possible to establish the presence of signal peptides in the proteins secreted: cytochrome c_3 from *Desulfovibrio vulgaris*,[68] protease III[69] and penicillin G-acylase[70] from *E. coli*, and chloroperoxidase.[71] The signal peptides promote the transmembrane protein transfer from the periplasm of bacteria and yeast and they split off immediately after secretion, so that the determination of nucleotide sequence in genes is a good method for the detection of signal peptides and for the investigation of their structure. Comparison of the aminoacid sequence of the protein and the nucleotide sequence of the gene shows whether the given protein undergoes post-translation modification. For example, aquarin is synthesised in the form of a precursor. During translation, seven *N*-terminal residues are split off.[72] The *N*-terminal residue in human creatine kinase M is lysine and the methionine residue is split off after translation.[73]

The determination of the aminoacid sequence makes it possible to reach certain conclusions concerning the presence of domains and the structure of the substrate-binding sections. Analysis of the structure of the penicillin acylase gene revealed the presence of four structural domains on the basis of the positions of introns: nucleotides 1–78 code for the signal peptide, nucleotides 79–705 code for the α-subunit, nucleotides 708–867 code for the peptide binding covalently two subunits, and nucleotides 868–2538 code for the β-subunit.[70] A multidomain structure has also been established for the heavy chain of calpactin (the substrate of viral protein-tyrosine kinase)[74] and calpastatin (inhibitor of the Ca^{2+}-dependent calpain).[75] The study of the structures of the genes of diglyceride synthetase and diglyceride hydrolase from *E. coli* showed that the former enzyme is an extremely hydrophobic membrane protein.[76] The latter enzyme is less hydrophobic, but

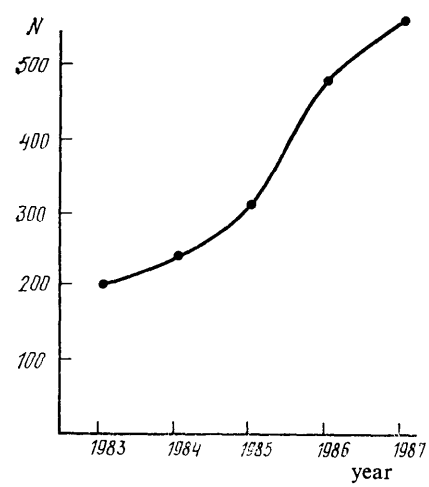


Figure 5. Number of publications (annually) on the determination of the aminoacid sequences of enzymes by genetic engineering methods (counted by the authors).

there is a very hydrophobic domain at its *N*-end, which binds the hydrolase to the membrane.[77] The composition of the bioluminescent Ca^{2+}-dependent protein aequorin incorporates three hydrophobic sections, which may be responsible for the binding of its functional chromophore, i.e. coelenterazine (luciferin), and three sections responsible for the binding of Ca^{2+} ions.[72] Analysis of the primary structure of Na^+, K^+-ATPase led to a hypothesis about the character of the disposition of this enzyme on the membrane.[78]

Comparison of the primary structure of the test enzyme with that of proteins having similar functions makes it possible to discover common structural sections. Analysis of the aminoacid sequences of aequorin and other Ca^{2+}-binding proteins (calmodulin, parvalbumin, and troponin C) revealed three Ca^{2+}-binding sections in the polypeptide chain of aequorin.[72] Important information about the structure of the active centre of bacterial luciferase has been obtained by comparing the primary structures of luciferases from different sources: *Vibrio fischeri*, *Vibrio harveyi*, *Photobacterium leiognathi*, and *P. phosphoreum*.[79] Data for the modification of the SH group of cysteine-106 in the luciferase from *V. harveyi* led to the hypothesis that this group participates in catalysis. However, the luciferases from other sources contain valine in the position 106. Thus the SH group of Cys-106 is not important for the manifestation of the activity of bacterial luciferase. The sections 115–117 and 280–282 of the α-subunit, which are the same in all the bacterial luciferases examined and are located close to one another in three-dimensional space, apparently constitute an appreciable proportion of the active centre.[39] Comparison of the primary structures of lipases from various sources (bacteria and pig pancreas) showed that Ser-83 is incorporated in the active centre.[80]

Similar aminoacid sequences have been noted for glutathione S-transferases from human and rat livers (50% homology),[81] catalase T from the yeast *S. cerevisiae*, the bacterium *Penicillinum vitale*, and ox liver (52.2% homology),[82] aromatic aminoacid hydroxylases — tryptophan, phenyl, and tyrosine hydroxylases (60% homology),[83] valyl-tRNA synthetase from *B. stearothermophilus* and isoleucyl tRNA synthetase from *E. coli*,[84] and for five adenylate kinases from various sources.[85] This means that the data for the steric structure and mechanism of action of one enzyme can be used in the study of an enzyme with a homologous sequence. The structure of the biopterin-dependent aromatic acid hydroxylases is homologous for approximately 2/3 of the molecule, starting from the C-end whereas at the N-end no homology has been observed. This confirms the hypothesis that the C-terminal domains in hydroxylases determine their catalytic properties (similar mechanism of catalysis), while 1/3 of the molecule, starting from the N-end, is made up of domains determining the substrate specificity.[83] The relation between the structure and function of human M creatine kinase,[73] Na^+, K^+-ATPase,[86] the heavy chain of calpactin,[74] glycogen phosphorylase,[87] glutathione S-transferase,[81] yeast catalase T,[82] and tryptophan hydroxylase[88] has been discussed on the basis of the homology established with other proteins.

It has become possible in recent years to investigate the evolution of protein in connection with the development of the recombinant DNA technique, the establishment of the primary structures of an enormous number of proteins, and advances in crystallography. Common domains have been discovered for a series of proteins with known crystal structures. Consequently, if any one structural element proves useful for the performance of a particular function, it is invariably used in different proteins. For example, Rossman[30] observed in a series of enzymes an invariant domain consisting of approximately 70 aminoacid residues. These enzymes had markedly different functions but had a property in common: they bound coenzymes of the type of NAD, FMN, or AMP, which had a common component — a mononucleotide. This domain is apparently a proprotein for a large number of nucleotide-binding enzymes, because its function proved to be vitally important. The first proteins capable of performing functions of any kind were small in size and had the property of being able to bind specifically other molecules. When two such proteins were combined, a primitive catalytic system might have arisen improving and developing in the course of evolution. From Gilbert's point of view,[89] exons are genome equivalents of protein domains which have been used to assemble the first proteins and which have been maintained throughout evolution in a genetically isolated state in the course of several billion years. The non-intersecting processes involving the transposition and reorganisation of domains into new combinations generated new proteins which included also useful constructions. The essential feature of the hypothesis is that the evolution of proteins was based on the sorting of exons coding for the domains.[8]

The principal mechanism of the evolution of proteins is the duplication of genes, which consists in the fact that two or more copies of the same gene arise in the cell genome. One of the copies retains the previous function, so that no changes take place in the organism, while the other copy can undergo mutations. The duplication of genes has been demonstrated by the existence of subunit enzymes with non-identical but homologous subunits (homologous proteins), containing one polypeptide chain, as in proteases of the serine–histidine–asparagine type with different substrate specificities.

Another example of gene duplication is provided by trypsin, chymotrypsin A, and elastase. Their sequences are approximately 40% homologous. They have a similar function, namely the hydrolysis of proteins, but there are differences in the type of bond hydrolysed. The residues in the active centre were different: Asp in trypsin and Ser in chymotrypsin. Analysis of the three-dimensional structures of these enzymes showed that serine proteases consist of two similarly coiled domains arranged symmetrically around a twofold axis.[90] In each case introns separate the codons of the catalytic triads (Asp, Ser, and His), but the main part of the exons is the same within this class of enzymes.

In the cAMP-, cGMP-, and Ca^{2+}-calmodulin-dependent protein kinases and phosphoryl azokinase, the domains fulfilling a similar function are homologous: for example, the cAMP- and cGMP-binding regions in the regulatory subunits are in homologous domains. The catalytic (ATP-binding) regions in all protein kinases are also encountered in homologous domains.[91] These proteins arose as a result of the duplication and fusion of the genetic elements of two related families, which determined the allosteric nature of these enzymes.[92] It may be that allosteric regulation arose initially from the random interaction of the active centre with inhibitor and the association was weakened by the covalent modification of the complex, for example, by phosphorylation, adenylation, etc.[88]

A model involving triple duplication of a precursor gene with formation of the gene of the prototype of modern calmodulin and the addition of non-coding segments to both ends of the gene has been proposed for the evolution of the calmodulin gene.[93] The last stage occurred relatively recently, since the size and nucleotide sequences of the segments of the 3′- and 5′-ends differ greatly for genes of different calmodulins.

Apart from the duplication of the genes, the latter can also fuse, as a result of which the protein becomes twice as long. The immunoglobulins, which arose from a common precursor—a polypeptide consisting of 110 aminoacid residues—may serve as an example. After duplication and merging, the different sections of the immunoglobulin chains acquired different biological functions.[2]

The evolution of proteins can be studied in terms of two aspects.

(1) Analysis of the changes in the structure of the same protein in different organisms during evolution. For example, comparison of the structures of cytochrome *c* derived from organisms ranging from yeast to man (more than 80 species) shows that closely related cytochromes hardly differ or differ in a small number of residues. The greatest differences in the aminoacid composition are characteristic of cytochromes *c* from the lowest and highest organisms. Conservative substitutions in which an aminoacid in the sequence is replaced by another aminoacid with similar properties and structure, so that the steric structure of the protein is not affected and there is no substitution in the region of the active centre and no substitution inducing pronounced conformational changes in the protein which can lead to the loss of activity, are characteristic of proteins from closely related species. There is an appreciable tolerance as regards substitutions, deletions, and insertions of aminoacids in many sections of the polypeptide chain in different proteins.[2] A homology has been observed near Cys residues among tryptophan, phenyl, and tyrosine hydroxylases from different sources. It has been suggested that they have arisen from a single gene as a result of the accumulation of point mutations.[83] On passing from the lowest to the highest organisms, the protein becomes more complex. Bacterial phosphofructokinase has a single regulatory section, while the human enzyme is larger and contains three regulatory sections and can bind in addition three different types of regulatory proteins.[13] In the limiting case, it may turn out that the aminoacid sequences of two proteins having similar steric structures differ so much that it is difficult to establish their evolutionary relation.

(2) Comparison of different proteins within the framework of a single species. A homology of the primary structure is frequently characteristic of enzymes catalysing similar reactions. For example, the homology reaches 40% for glutathione reductase and lipoamide reductase. On comparing the aminoacid sequences of any proteins, one may expect the coincidence to the extent of at least 5% on statistical grounds.

In comparing primary structures, it is essential to take into account the possibility of deletion and insertion. Cases where between 15 and 25% of coincidences are observed when account is taken of such deletions and insertions are of greatest interest. The roots of the family tree of proteins should be sought in this "intermediate" zone. For example, five proteins with different biological functions have been found to be related: antithrombin III (a protein present in blood plasma and neutralising the effect of thrombin), α_1-antitrypsin (a proteinase inhibitor), ovalbumin (a component of egg protein), angiotensin—(a precursor of the peptide hormone involved in the regulation of arterial pressure), and a barley grain protein with an unknown function.[8]

Structural similarity in the absence of homology in the sequence is exhibited by the chicken protein lysozyme and the bacteriophage T4 lysozyme, which suggests the presence of a common precursor.[94]

Studies of the evolution of proteins have given a powerful stimulus to the development of protein engineering at the level of DNA, because rearrangements, deletions, or insertions of exons can give rise to new combinations of domains and moduli, i.e. to proteins with completely new properties.

2. Prediction of the steric structure and functions of protein molecules

Comparison of the aminoacid sequences constitutes the basis for the modelling of protein at all the levels of the protein structure—the secondary structure, the structure of domains, the quaternary structure, the interaction with ligands, and the prediction of biological functions of the protein.[95–110] The approaches used to predict the protein structure on the basis of data for its primary structure can be represented schematically (Table 2).

The methods and criteria for the comparison of different proteins and for the modelling of the protein structure have been examined in a number of studies.[96,98–106]

The sequences in proteins are compared in order to discover homologous sections by means of standard programs for the analysis of aminoacid sequences and computer graphics. Special data banks of primary aminoacid sequences, for example, the data bank of The National Biomedical Research Foundation (NBRF) in the USA, have been created.

Table 2. Prediction of the structure of the protein on the basis of data for its primary structure.

Protein structure	Set of prediction methods
Aminoacid sequence	Prediction of the structures of individual section of proteins, determination of "structural motifs" (α- or β-helices, random coil, etc.)
↓ Secondary structure	The search for "structural" matrices, modelling of the disposition of structural motifs in space
↓ "Supersecondary" structure	Simplified energy calculations, minimisation of the energy, and molecular dynamics
↓ Domain	More detailed energy calculations, modelling of the disposition of the domains and subunits in space with the aid of computer graphics
↓ Set of domains, set of subunits	

There are several ways of predicting the secondary and tertiary protein structures. The first, simplest and most widely used method involves the finding of homologous proteins with a known steric structure. In order to construct a three-dimensional model of the test protein on the basis of structural homology with known proteins, special programs have been developed, for example the Frodo program[107] created by Jones as early as 1978 and the Composer program.[103] The latter is based on the simultaneous superposition of the structures of different proteins homologous with the modelled protein and on the derivation of an average structure or templet.

The following criteria serve as a basis for the comparison of the aminoacid sequences and the discovery of analogies between them: the identity of the aminoacid sequences, the identity of the nucleotide sequences, a minimal difference between the bases in the codon, the ratio of the number of modified aminoacids to the total number, and certain characteristics of the aminoacid residues, for example, their polarity, hydrophobicity, etc. Argos[100] developed a method for discovering weak analogies in protein sequences and established two sensitive criteria for their comparison: (1) the

relative molecular weight of the aminoacids replaced (the Dayhoff criterion); (2) comparison of five physical characteristics of aminoacid residues such as hydrophobicity, volume, refractive index, the location of the residue on sections corresponding to the rotation of the chain or sections anti-parallel to the chain. The author examined 30 classes of proteins, including haemoglobins, chymotrypsins, lysozymes, cytochromes *b* and *c*, triosephosphate isomerase, lactate dehydrogenase, the domains of different proteins fulfilling the same function — Ca-binding, arabinose-binding, etc. All these proteins have similar tertiary structures. If homologies with other proteins are not observed for the protein investigated, then some information about its secondary and tertiary structure can be obtained by analysing the structure of proteins close to it on the evolutionary scale. In the absence of a homology, a series of other methods are also used to establish secondary and tertiary structures. For example, the construction of a hydrophobicity profile and its comparison with the hydrophobicity profiles of other proteins permit the identification of sections forming the secondary structure. The structural profiles have been investigated for a series of proteins with different degrees of homology of the primary structures and it has been shown that identical structural profiles can imply identical three-dimensional structures even in the absence of a homology in the aminoacid sequences.[108,109] In the absence of homology, there are also other methods for predicting the tertiary structure of proteins, for example, calculations of the energy states of the protein molecule and the search for the conformation having the minimum free energy in the protein–solvent system, and also with the aid of templets: in proteins with different primary structures there is a possibility of the existence of regions which are structurally similar; thus the nucleotide-binding domain in certain proteins consists of parallel β-folds bounded by α-helices.[106]

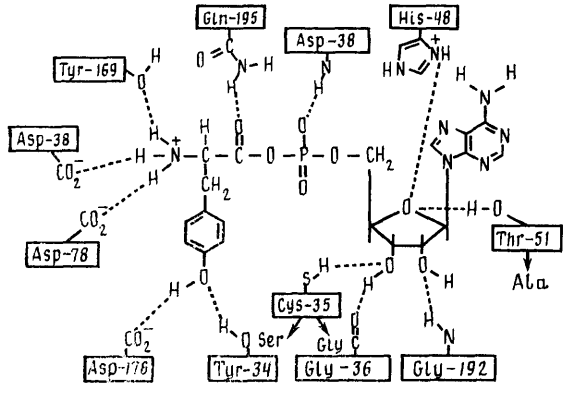


Figure 6. Schematic illustration of the active centre of tyrosyl-tRNA synthetase.[55]

Finally the primary structure permits the assignment of the protein to a particular functional class.[110] Klein analysed 2145 aminoacid sequences in the NBRF data bank and divided them into 26 functional classes. Physicochemical characteristics of the protein such as average hydrophobicity, maximum hydrophobicity, variation of the hydrophobicity of individual segments, charge, the probability of the formation of the α- or β-helix, and the periodicity in the appearance of glycine, phenylalanine, and the pentapeptide Phe-His-Phe-His-Trp were used in the analysis. It was found that 3–5 characteristics of this kind are sufficient to assign the protein with a high degree of probability to one of the 26 classes. These classes include collagen, nitrogenases, cytochromes (*b*, c_3, c^1, and *c* separately), carboanhydrases, ribonucleases, ATPases, ceratins, phospholipases, hormones, dehydrogenases, the class of prolactin and somatotropin, ferredoxins, toxins, histones, globins, the variable sections of antibodies, and the permanent sections of antibodies. A periodicity in the appearance of glycine in the primary structure is characteristic of the class of collagens, a periodicity in the hydrophobic regions is characteristic of globins, while the characteristic feature of ATPases is a low tendency towards the formation of β-folds. A characteristic feature of the variable sections of antibodies is a marked difference between the hydrophobicities of individual segments of the polypeptide chain. The knowledge of the primary and steric structures of the protein or its modelling by comparison with previously investigated proteins and data for the chemical modification of proteins and enzymes and for the activity of the enzyme centres, obtained by different methods, make it possible to proceed to a new level in the study of the active centres of enzymes with the aid of genetic engineering methods — site-specific mutagenesis.

3. The study of the active centres of enzymes with the aid of site-specific mutagenesis

Studies on proteins by the method of site-specific mutagenesis can be divided arbitrarily into two groups: the site-specific mutagenesis of enzymes with a known crystal structure and the site-specific mutagenesis of enzymes whose steric structure has not been determined. In the first case, the steric model of the enzyme serves as a basis for the specific alteration of the structure of the protein molecule and for the prediction of the results of mutation-induced changes with the aid of computer graphics. If the crystal structure of the protein is unknown, chemical modification data and comparison of the structures and properties of homologous species and species close on the evolutionary scale are used as a basis for the assessment of the mutation. In this case, the results of mutations are usually random and it is much more difficult to achieve the required alteration of the catalytic properties or stability of the test protein.

(a) Site-specific mutagenesis of enzymes with a known steric structure

Tyrosyl-tRNA synthetase[55,111–128] (from *Bacillus stearothermophilus*) catalyses the two-stage $tRNA^{Tyr}$ aminoacylation reaction:

Scheme 2

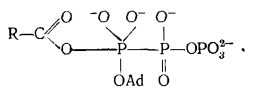
$$E + Tyr + ATP = E \cdot Tyr—AMP + PP_i \ (a),$$

$$E.Tyr - AMP = tPHK^{Tyr} = Tyr - tPHK + AMP + E \ (b)$$

Analysis of the steric structure of the complex E.Tyr–AMP showed that a hydrogen bond may exist between the SH group of Cys-35 and the 3′-OH group of the ribose ring of Tyr-AMP (Fig. 6). The replacement of Cys-35 by Ser and Gly by the method of site-specific mutagenesis led to the impairment of the binding to the ATP and a decrease in k_{cat}. This shows that the strengthening of the hydrogen bond impairs the affinity of the enzyme for the substrate and that its elimination can improve the binding of ATP.[55,111,112] The Thr-51 residue is capable of forming a weak hydrogen bond with adenylate. The removal of the hydrogen bond by means of

the replacement Thr-51 → Ala and the change in the structure of the side chain (the replacement Thr-51 → Pro) increased k_{cat} and reduced $K_{M,ATP}$ for the tyrosine activation reaction [stage (*a*), Scheme 2], while in the aminoacylation reaction the binding to ATP improved but k_{cat} fell somewhat. Overall, a single-point mutation led to an appreciable improvement in catalytic activity: in the mutation Thr-51 → Pro, the ratio $k_{cat}/K_{M,ATP}$ increased from 8400 to 208 000 litre mol^{-1} s^{-1} for stage (*a*) and from 1860 to 95 800 litre mol^{-1} s^{-1} for stage (*b*).[55,112]

Catalysis by tyrosyl-tRNA synthethase leads to the formation of a pentacoordinate intermediate compound when ATP is subjected to nucleophilic attack by tyrosine:



The γ-phosphate group of the intermediate compound can interact with Thr-40 and His-45 side chains. The site-specific mutagenesis (the replacement Thr-40 → Ala, His-45 → Gly) provided an answer to the question concerning the mechanism of the catalysis. The mutations of the γ-phosphate-binding region of the enzyme increase the energy of the complex in the transition state, while the energy levels of the enzyme–substrate complexes do not change.[113,114] The main groups participating in catalysis are Thr-40 and His-45, but certain other groups, not included in the active centre, are also important for catalysis: Tyr-34, Cys-35, His-48, Thr-51, and Tyr-169.[114–118] Comparison of the free energy profiles for the mutant and initial enzymes has shown that the change in binding energy influences the rate constant and equilibrium constants. The principal conclusion derived from the study of the kinetic properties of the mutant and from the comparison of the free energy profiles is as follows: tyrosyl-tRNA synthetase uses in catalysis the mechanisms involving the stabilisation of the transition complex (in contrast to covalent, nucleophilic, and acid–base catalysis), stabilisation occurring via hydrogen bonds and electrostatic interactions.[114–122] By substituting the Lys and Arg residues located on either side of the substrate-binding pocket, it has been shown that the structure of the enzyme changes during catalysis: the positively charged side chains neutralise the negative environment of the pyrophosphate in the transition state on formation of tyrosyladenylate.[123,124]

The method of site-specific mutagenesis has also been applied to the study of the subunit interactions in this enzyme.[125–128] It has been shown that tRNA interacts with the N-terminal (catalytic) domain of one subunit and with the C-terminal section of another. The mutation of the residue located on the subunit interaction section (Phe-164 → Asp) led to the appearance of a negative charge on the binding section and induced a pH-dependent dissociation of the dimer, while the replacement Phe-164 → Lys led to the appearance of a positive charge. The introduction of mutations into the subunit interaction zone made it possible to control the subunit interactions in tyrosyl-tRNA synthethase by controlling the subunit interactions.

Cytochromes[129–138] and cytochrome *c* peroxidase.[139,140] The cytochromes are series of structurally similar haem-containing proteins involved in electron transport over large distances (10–20 Å). The role of residues which are present in all the cytochromes in electron transport has been elucidated with the aid of site-specific mutagenesis. According to X-ray diffraction data, the Phe-87 residue is located on the surface of the globule at a distance of 5 Å from haem. This residue in yeast iso-1-cytochrome *c* has been replaced by Ser, Gly, and Tyr[129–131] and also by Leu.[132] The mutants retained 20–70% of the activity compared with the native protein but the reduction potential fell by 50 mV. Thus Phe-87 does not participate directly in electron transport but ensures a hydrophobic environment for haem and determines the high reduction potential of cytochrome *c*. The mutations of Phe-87 induced conformational changes in the protein globule or cytochrome *c*, which is indicated by changes in the CD spectra in the region of the Soret band (385–445 nm). The mutations of the conservative Glu-66 in horse mitochondrial cytochrome *c* led to the conclusion that (1) it contributes to the stabilisation of the active conformation of the protein, possibly via the formation of a salt bridge, and (2) it participates in the binding of ATP.[133] Substitutions of the Cys-102 residue on the surface of iso-1-cytochrome *c*, which is rarely encountered in other cytochromes, did not alter the properties of the protein.[135,136] The sections retained in the course of evolution are not always involved in the mechanism of electron transfer. For example, the replacement of the conservative Lys-77 by Arg in iso-1-cytochrome *c* from yeast did not influence its interaction with cytochrome b_2, cytochrome *c* peroxidase, and cytochrome *c* oxidase.[134]

In order to elucidate the role of the sections of the polypeptide chain in the functioning of cytochrome P450, chimeral proteins were obtained from cytochrome P450c by replacing the central section, or the C-terminal section, or both sections by the corresponding sections of cytochrome P450d.[137] Cytochrome P450ccd had a higher monoxygenase activity than the initial cytochrome P450c, while the P450cdd mutant had a lower activity. The substrate specificity of the mutants did not change. Hence it was concluded that the central section in cytochromes P450c and P450d participate in the binding of substrates, while the C-terminal sections play an important role in electron transport.[137] However, other workers,[138] who obtained 13 mutants with substitutions at the C-terminal section of cytochrome P450d, discovered aminoacid residues on the C-end important for the binding of the apoprotein.

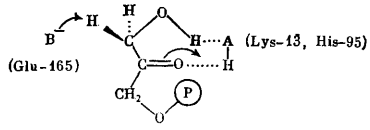
The method of site-specific mutagenesis helped to elucidate the role of Met-172 and Trp-51 in the catalytic function of **cytochrome c peroxidase**.[139,140] The interaction of the enzyme with hydroperoxide results in the formation of the intermediate (I), which contains [Fe^{IV}=O] and a free radical located on a certain hitherto unidentified group of the enzyme. It has been suggested that this group is either the indole ring of Trp-51, located 3.3 Å above and almost parallel to the plane of haem, or Met-172. However, the replacement of the indole ring by the phenylalanine ring, which is much more difficult to oxidise, did not entail a loss of activity. The Met-172 → Ser mutations also did not prevent the formation of compound (I). Thus the Trp-51 and Met-172 residues are not obligatory for the formation of compound (I) and the question of the location of the free radical remains open.

The serine proteases (trypsin[141–143] and subtilisin[144–151]) have been a satisfactory model for the construction of proteins by genetic engineering methods, since detailed information is available about their structure and kinetic and spectroscopic properties. Data on the structure of a protease from one source can be used to investigate the enzyme from another source. Although, for example, the crystal structure of trypsin from rat liver is unknown, the known structure of bovine trypsin was employed for experiments on site-specific mutagenesis having made sure that the aminoacid compositions of these enzymes are 74% identical. When Gly-166

in the substrate-binding region of the enzyme was replaced by the negatively charged Asp and Glu residues, the catalytic effectiveness (k_{cat}/K_M) of native subtilisin increased in relation to poor substrates and diminished in relation to good substrates. On replacement of Gly-166 by non-ionic residues (Ala, Leu), the catalytic activity increased for substrates containing hydrophobic groups. The change in specificity is associated mainly with the change in K_M and not in k_{cat}.[144-147]

Analysis of the crystal structures of the complexes of subtisilin with inhibitors demonstrated the presence of a hydrogen bond between the amide group of Asn-155 and the oxygen of the tetrahedral anion. Point changes in the position 155, leading to a change in the steric configuration (Asn-155 → Thr, Gln) or charge (Asn-155 → His, Asp) and in the hydrogen bond donor, diminished k_{cat} by a factor of 200–4000 and K_M by a factor of 7, which can be explained by a decrease in the stabilisation energy of the transition state by 9.2–20 kJ mol^{-1}.[148,149]

Triosephosphate isomerase.[152-155] The basic group (carboxylate ion) of Glu-165 is involved in the mechanism of catalysis by this enzyme:



Following the substitution Glu-165 → Asp, i.e. after the removal of one methylene group which shifts the basic group by 1 Å, k_{cat} diminished by a factor of 10^3 (from 4300 to 2.8 s^{-1}) with a slight alteration of K_M. Free energy calculations demonstrated that the mutation influences the free energy of the transition state in the enolisation stage.

Aspartate carbamoyltransferase[156-162] contains 12 polypeptide chains of two types: six catalytic and six regulatory. With the aid of point substitution in these chains and also on sections between them, the regions of the enzymes responsible for the regulatory properties were discovered: the loops formed by the residues 230–245 of the catalytic chains;[157] the Trp-209 residue on the section corresponding to the interaction of subunits.[156,158] The substitution Lys-83 → Gln in the catalytic chain diminishes the capacity of the enzyme for cooperation, while the substitution Gln-138 → Ala increases it, i.e. the aminoacid residues apparently determine many interchain and intrachain interactions.[159-162] Crystallographic studies on the complexes of the enzyme with substrate analogues showed that the active centre of aspartate carbamoyltransferase consists of several sections located on different catalytic subunits. A method has been proposed for the detection of the catalytic sites on oligomeric enzymes involving the construction of hybrids containing mutant monomers, for example, hybrids made up of monomers containing the Lys-84 → Glu, His-134 → Ala, and Ser-52 → His mutations or hybrids made up of trimers of the wild type and the Glu-84, Ala-134 binary mutant. The results of the mutation showed that the active species are formed only after the association of the chains with formation of an oligomer.

Staphylococcal nuclease.[163-167] Although the structure of staphylococcal nuclease has been determined by X-ray diffraction with a high resolution (1.5 Å), the detailed mechanism of the action of this enzyme has not been established. In order to elucidate the mechanism of the binding of Ca^{2+} ions, one of the residues surrounding Ca^{2+} in the protein was mutated (Asp-40 → Glu). The removal of one of the three *cis*-ligands diminished the affinity for Ca^{2+} by a factor of five and the maximum rate by a factor of 31. The mutation did not affect the binding of DNA, which agrees with the structural X-ray diffraction data, according to which Asp-40 interacts with the metal and not with the nucleotide chain.[163,164] The replacement of various Tyr residues in the substrate-binding cavity of the enzyme showed that the OH group in the Tyr residues does not play an appreciable role in catalysis. However, the mutations weakened the binding to the substrate (single-stranded DNA and RNA).[165] The mutations of Glu-43 in the active centre induce conformational changes in the protein at a distance of 15–30 Å from the residue 43.[166,167]

α-Antitrypsin[168-171]—an inhibitor of serine proteases. It has been shown by the method of site-specific mutagenesis that its inactivation is associated with the modification of Met-358 by oxidants. The Ile-356 and Pro-357 residues play an important role in the functioning of the inhibitor. The Met-358 residue in the active centre determines the specificity of the binding of antitrypsin to proteins. Native α-antitrypsin containing Met-358 recognises the Pro-Met sequence of elastase. The Ala-358, Ile-358, and Val-358 mutants proved to be effective inhibitors of neutrophilic and pancreatic elastases but not of cathepsin G; the Leu-358 and Phe-358 mutants inhibited cathepsin G preferentially.

Yeast 3-phosphoglycerate kinase[172-174] consists of two globular domains separated by a polypeptide chain loop. It has been suggested that the conformational change leading to the "merging" of the domains takes place during catalysis under the influence of the substrate. The Glu-190 and His-388 residues may interact with one another in the region between the domains (the formation of a hydrogen bond or of a salt bridge) and regulate the transition from the closed to the open form of the enzyme. The Glu-190 → Gln, Asp and His-388 → Glu mutations led to some decrease in catalytic activity and resulted in a change in the K_M with respect to both substrates. Thus the results of mutagenesis have shown that the model of the transition from the closed to the open form in catalysis requires further study.[172,173] The construction of a chimeral protein, one of the domains of which was isolated from human 3-phosphoglycerate kinase and the other from the corresponding yeast enzyme, was an interesting experiment. The hybrid retained the properties of the native proteins.[174]

Carboxypeptidases.[175-178] The three-dimensional structure of carboxypeptidase A has already been known for about 20 years, but certain details of the mechanism of its action are still not understood, for example, the role of Tyr-248 located at a distance of 3 Å from the substrate peptide bond undergoing cleavage. The results of site-specific mutagenesis have shown that this group participates in the binding of substrates and not in hydrolysis.[175,176] The OH group of Tyr-198 participates in the catalysis, stabilising the complex in the transition state.[177] The substitution Met-398 → Leu for yeast carboxypeptidase *y* altered the enzyme specificity. The mutation made the substrate-binding section more hydrophobic and the mutant therefore had an increased affinity, compared with the initial enzyme, for substrates with bulky and hydrophobic substituents.[178]

Other enzymes. The method of site-specific mutagenesis has also been used to investigate the influence of structure on the activity of dihydrofolate reductase from *E. coli* (DHFR).[179,180] The mutations of the Asp-27 residue in the enzyme active centre showed that it participates in the protonation of the substrate but not in the stabilisation of the transition state as had been postulated earlier. The dihydrofolate may be protonated directly by the asparagine group or with participation of water molecules. It has been shown for human DHFR that the Cys-6 residue partipates in the binding to NADPH and *p*-hydroxymercuriobenzoate.[181] Mutants with substitutions of aminoacids in the active centre have been obtained for human *lysozyme*.[182,183] Their analysis showed that the Asp-53 residue participates in the electrostatic stabilisation of the intermediate state in the hydrolysis of the glycosidic linkage. The existence of an aromatic residue in the position 63 and of Trp-64 is essential for the effective hydrolysis of chitin substrates but not for the lysis of bacterial substrates. The influence of insertions and deletions on the activity of ribonuclease P has been studied in detail[184] and it has been shown that, for the normal functioning of the RNA subunit of ribonuclease P from *E. coli*, a section of the secondary structure coded by the nucleotides 275–295 is essential.

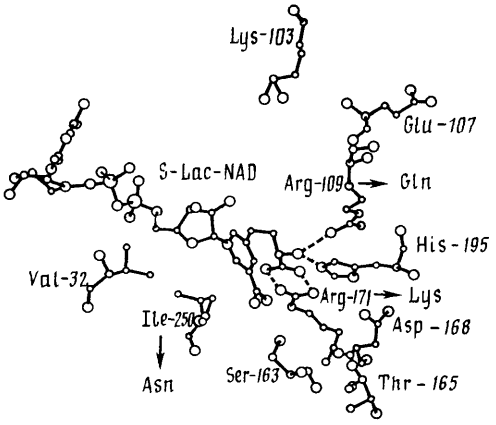


Figure 7. The active centre of native lactate dehydrogenase bound to the substrate.[188]

The sections at which the enzyme is bound to DNA have been discovered with the aid of mutagenesis for the **restriction endonuclease (restrictase)** EcoRI. The initial information about these sections was obtained from the X-ray diffraction structure of the complex EcoRI with a synthetic oligonucleotide. Point mutants (the Glu-111, Glu-144, and Arg-145 residues) hardly differed in their specificity from the initial enzyme, but their specific activity was reduced by a factor greater than 100 mainly as a result of the decrease in V.[185] Analysis of the crystal structures, especially of the geometry of the active centres, made it possible to alter with the aid of mutations the substrate specificity of *aspartate aminotransferase*,[186] *lactate dehydrogenase*,[187,188] and *alcohol dehydrogenase* [189] (see Section VI). The mutations of the Arg-109 residue in *lactate dehydrogenase* from *B. stearothermophilus*—a component of the mobile polypeptide group exposed to the solution—showed that it increases the polarisation of the carbonyl group of pyruvate and thus stabilises the transition state. The Ile-250 → Asn mutation impairs the catalytic properties of the enzyme (Fig. 7). The substitution of the catalytically important Ser-102 residue in *alkaline phosphatase*[190] by Cys altered the rate-limiting stage in the hydrolysis of esters: in contrast to the native alkaline phosphatase, the kinetics of the action of the mutant with the SH group instead of the OH group depend on the leaving group of the ester, a high catalytic constant being retained. Studies on *ATP synthetase* by the method of site-specific mutagenesis have been initiated.[191] Four residues capable of ionisation and important for the manifestation of activity have been found on the α- and β-subunits of the enzyme: Lys-175 and Asp-261 on the α-subunit and Lys-164 and Asp-252 on the β–subunit of the enzyme.

(b) The site-specific mutagenesis of enzymes with an unknown crystal structure

β-Lactamase[192–198] catalyses the opening of the β-lactam ring in penicillins and cephalosporins, ensuring the resistance of the cells to antibiotics. The class A β-lactamases contain the conservative catalytic triad (Ser-70) – (Thr-71) – (...) – (Lys-73). Point substitutions of Ser-70 permitted the conclusion that only mutants containing a nucleophilic group, for example, Cys, in the position 70 are catalytically active, although their activity is appreciably lower than that of the native β-lactamase.[192–196] Analysis of 19 mutants containing all the possible variants of the aminoacid residues in the position 71 showed that the Thr-71 residue does not participate in the binding of substrates and in catalysis but is important for the stabilisation of the protein and influences in some ways the specificity of the catalysis, determining the configuration of the β-lactam ring binding section.[197] The mutation Lys-73 → Arg led to an appreciable loss of activity. The role of the Lys-73 residue in catalysis has been discussed: the orientation of the proton moving away from the carboxy-group of the Ser-70 residue; the presence of a salt bridge with the Glu-166 residue participating in the hydrolysis of the acylenzyme.[198]

Ribulose diphosphate carboxylase.[199–202] Mutants with substitutions in the sections for the binding of CO_2, Mg^{2+} ions, and ribulose diphosphate have been obtained for the enzyme from *Rhodospirillum rubrum*. The ε-NH_2 group of the Lys-201 residue participates in the formation of the carbamate ion in the interaction with CO_2 and Mg^{2+}. The Asp-198 → Glu mutation showed that the carboxy-group of the Asp-198 residues also plays a role in the binding of the divalent metal.[199] It has been suggested that two residues (Lys-166 and His-291) participate in the enolisation of ribulose diphosphate, but the mutant in which the His-291 → Ala substitution has taken place showed a high catalytic activity. Thus the His-291 residue does not play a central role in catalysis.[200] The replacement of Lys-166 by seven different residues led to an appreciable loss of activity, but the mechanism of the participation of this group in catalysis has not been finally elucidated. The lack of crystallographic data precludes an answer to the question of the involvement of this group also in the binding of substrates.[201] The role of the small non-catalytic subunit S, point substitutions in which affected the catalytic activity but not the specificity, has been investigated by the method of site-specific mutagenesis in the enzyme from *Anacystis nidulans*. Hence it was concluded that the subunit participates in the activation of substrates but not in regulation.[202]

Lactose permease[203–212] is a hydrophobic enzyme controlling the transport of β-galactoside and of protons across a membrane. In order to investigate the role of the SH group of the active centre in catalysis, the Cys-148 → Gly[203,204] and Cys-148 → Ser mutants were obtained.[205,206] The results showed that Cys-148 is important for protecting the enzyme against inactivation (with the aid of the substrate) but is not obligatory for the transport of lactose. The mutations of other cysteine residues showed that, out of the eight residues, only Cys-154 is essential for the manifestation of activity.[207–209] According to preliminary data, the histidine residue also participates in the transport of the substrate. Each of the four histidine residues was replaced by Arg,[210] Gln, or Asp.[211] It was found that the His-322 residue is involved in the H^+ transport across the membrane via the protonation of the imidazole ring. The His-205 residue forms a hydrogen bond either with the substrate or within the protein. The Glu-325 and His-322 residues are located on the α-helix intersecting the membrane, form an ion pair, and act as components of the charge transfer system. The polarity of the residues and the distance between the imidazole and carboxy-groups therefore play an important role. The Glu-325 → Ala, Val mutations and the double mutation Glu-325 → His, His-322 → Glu lead to a partial or complete loss of activity.[212] Preliminary experiments with another membrane enzyme, melibiose permease, also demonstrated the presence of the His/Glu pair, which is important for catalysis.[212]

Other proteins and enzymes. The mutation-induced substitution of the Cys and His residues on three Ca^{2+} binding sections in the postulated active centre of the bioluminescent Ca^{2+}-dependent protein aequorin[213] showed that the binding of molecular oxygen does not proceed solely via the SH group. The His-58 residue and at least two of the four SH groups are necessary for the manifestation of activity. For another Ca^{2+}-binding protein, namely *calmodulin*,[214] a study has been made with the aid of mutagenesis of the influence of structure on the interaction with related proteins—myosin kinase, phosphodiesterase, and NAD kinase. The removal of the anionic α-helical section, which is complementary to the positively charged region of the binding protein, altered the binding specificity.

An unexpected result was obtained on substitution of the Thr–190 residue by Ile on the section close to the active centre of *malate dehydrogenase*: the catalytic activity increased mainly as a result of the increase in k_{cat}. It had been postulated earlier that the residues surrounding Asp-152, His-180, and His-187 in the active centre play a role in the binding of substrates and cofactors, but it has been found that the Thr-190 residue influences significantly also the activity.[215] The site-mutagenesis of the viral *neuraminidase*[216,217] suggested a model of the catalytic action of the enzyme involving the Glu-276 residue as a proton donor. Mainly conservative residues were used for the mutagenesis (12 residues identical for different types of viruses in 14 mutations). A series of mutants of the *RNA ligase* of the phage T4 have also been obtained.[218–220] The removal of 20% of the polypeptide chain from the C-end does not affect the RNA ligase activity. Mutations on the ATP-binding sections showed that the Lys-99 residue participates in the formation of the enzyme–adenylate complex, while the residues 100–101 do not affect this reaction. In order to elucidate the structure of the active centre of the *thiolopenicillin-binding protein* from *E. coli*, the Ser-307 and Ser-445 residues were substituted. It was found that the Ser-445 residue does not form part of the active centre, while the Ser-307 residue is responsible for the binding of penicillin in the penicillin-binding Ser–X–X–Lys section discovered in functionally similar proteins.[221] The Glu-49 residue, which is important for the manifestation of the activation of the α-subunit of *tryptophan synthetase*,[222] and the SH group important for the manifestation of the activity of *anthranylate synthetase*[223] have been identified. It has been shown for *isopenicillin N-synthetase* that the Cys-106 residue participates in the binding of the substrate but is not obligatory for catalysis.[224] The His-228 residue has been found next to the functionally important Lys-229 residue in the active centre of serine *hydroxymethyl transferase*.[225] The His-228 residue in enzymes of this type from various sources forms a hydrogen bond or a salt bridge with an aminoacid or pyridoxal phosphate. The results of mutation-induced substitutions in (or near) the phosphorylation centre of the *cAMP-dependent protein kinase* showed that the phosphorylation of the regulator subunit does not play a significant role in the regulation of the activity,[226] while the Tyr-371 residue makes a significant contribution to the manifestation of the positive cooperation between the two cAMP-binding centres of this subunit.[227]

V. Determination of the relation between the structure and stability of protein macromolecules (by genetic engineering methods)

1. Factors determining the structural stability of the protein

The difference between the Gibbs free energies of the native (N) and denatured (D) states of the cooperative domain or of a single-domain protein is a measure of the stability of its structure.[11,228]

Scheme 3

$$H \rightleftarrows D$$

$$\Delta G_{den} = G_{den} - G_{nat}.$$

For the majority of single-domain proteins, the temperature dependence of ΔG_{den} is described by a curve (Fig. 8) passing through a maximum at the temperature of the maximum stability of the protein (T_{max}) and having upper ($T_{den\,1} = T_m$) and lower ($T_{den\,2}$) temperature limits of the stability of the protein (for $\Delta G_{den} = 0$), i.e. proteins are inactivated in the cold as well as at an elevated temperature.[229] [T_m = melting point]. The temperatures T_{max} for many globular proteins are in the range from −3 to +15 °C and their ΔG_{den} in the physiological temperature range vary from 20 to 60 J mol^{-1}.[230]

The stability of the protein is characterised by the average temperature of the transition to the denatured state T_{den} (or T_m) at which 50% of the protein is denatured and $\Delta G_{den} = 0$, or by the temperature of the maximum stability of the protein T_{max} at which ΔG_{den} is a maximum (Fig. 8), or by the average concentration of the denaturing agent, etc. In the case of irreversible denaturation, the kinetic stability of proteins ($\Delta G^{\neq}_{den}$) is usually characterised by the rate constant k_{in} for the change in some kind of property of the protein (the CD or UV spectra, fluorescence, and, in the case of enzymes, their activity). The kinetic and thermodynamic parameters of the denaturation of proteins frequently vary in parallel with the variation of the denaturation conditions, i.e. the intramolecular interaction conditions, which govern the thermodynamic stability (ΔG_{den}), apparently determine their kinetic stability ($\Delta G^{\neq}_{den}$). In the general case, thermal denaturation is described by the scheme

Scheme 4

$$H \rightleftarrows D \rightarrow I,$$

where I is the irreversibly denaturing agent. When $K_{den} \geqslant 1$, the greater the stability of the enzyme in relation to reversible thermal denaturation, the greater its stability also in relation to the irreversible denaturation, but it has been assumed (without proof) that there is no such correlation for $K_{den} \ll 1$.[231] In the general case, the retention of the activity of enzymes may not in fact be identical with the stability of the entire protein globule.[232] The stability of enzymes is as a rule determined by the stability of the domains (or domain) forming the active centre and is in fact determined by the stability of the most labile domain.

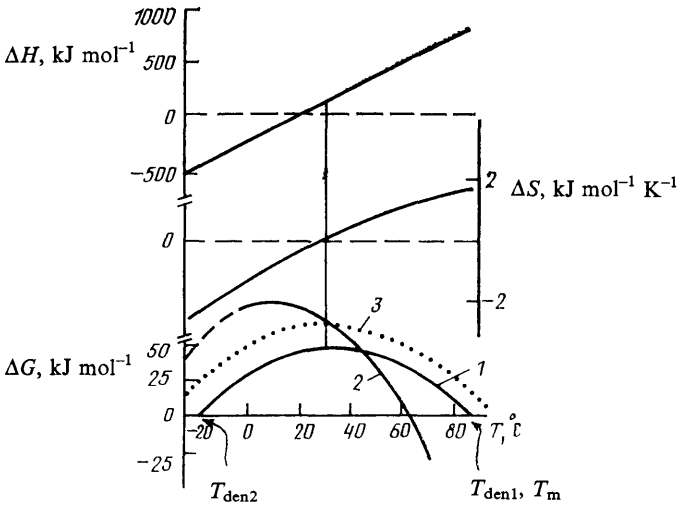


Figure 8. Temperature dependences of the enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) of the transition of proteins from the native to the denatured state: (1) myoglobin;[11] (2) α-chymotrypsin;[229] (3) hypothetical curve for the stabilised protein.

The factors responsible for the stability of the native conformation of the protein have been examined in detail in a review.[232] The main ones are as follows: (1) hydrogen bonds. (2) Increase in conformational entropy when the protein structure is uncoiled. (3) Long-range electrostatic interactions. If the charge distribution on the surface of the macromolecule is asymmetric in relation to composition and geometry, then the surface electrostatic potential in the absence of steric hindrance generates specific ion-binding regions whose saturation by the corresponding ions entails an increase in the stability of the protein.[233] (4) Hydrophobic interactions of the non-polar aminoacid residues resulting mainly from the van der Waals interactions between the molecules. The contributions of the hydrophobic interactions and hydrogen bonds to the stability of the protein structure are comparable.[228] (5) Intramolecular salt bonds (the energy of one bond is 1–3 kcal mol^{-1}) forming either single salt bridges or clusters. (6) Intramolecular –S–S– cross-links (1.8 kcal mol^{-1} per disulphide bond). (7) Formation of complexes by the protein with prosthetic groups and M^{n+} ions. The overall stability of the protein molecule is determined by the balance between the stabilising and destabilising contributions of the above interactions. The effective concentration of the interacting groups in the coiled and uncoiled states of the molecule makes a decisive contribution to the stability of the protein.[234]

The thermal stability of the protein is described by a complex relation between ΔG_{den} and temperature (Fig. 8).[11,229] The thermal stabilities of different enzymes must therefore be investigated and compared over a wide range of temperatures and not at a single temperature (cf. Lale and Klibanov[231] and Torchilin et al.[235]). The ratio of the ΔG_{den} for enzymes at a fixed temperature cannot be extrapolated to other temperatures. The formula for the calculation of small changes in ΔG_{den} from changes in T_{den} has been found for the case where the structure of one protein is altered, for example, by means of mutations.[229]

2. General relations for the specific alteration of the stability of proteins and enzymes *in vitro* and *in vivo*

(a) **Stability** *in vitro*. In order to elucidate the causes of the different stabilities of proteins, the first attempts have been made to find a correlation between the aminoacid composition of the proteins and their stability (T_{den}) and to compare the primary structures of proteins with identical functions and aminoacid sequences but having different stabilities (isolated from thermophilic and mesophilic microorganisms). These questions have been described in detail.[236] Correlations have been proposed between T_{den} and the hydrophobicity index of the residues and their average volume,[237] between T_{den} and the ratio of the areas of the surface of the protein accessible to the solvent in the native and denatured states,[238] between T_{den} and the percentage content of the stabilising and destabilising residues in the protein,[239] and between T_{den} and the aliphatic index of the protein.[240] These correlations suffer from the following disadvantages: (1) they are valid only within a limited group of proteins of a definite class; (2) T_{den}, which, as already stated above, does not characterise the stability of the protein as a whole, was adopted as a measure of stability. It is most likely that, in view of the large variety of factors responsible for the stability of the native conformation of the protein, the existence of a simple correlation is hardly possible and interest in studies of this kind has therefore diminished. When thermophilic (*t*-) and mesophilic (*m*-) proteins with known primary and three-dimensional crystal structures were compared, the structural factors responsible for the increased thermal stability of *t*-enzymes were discovered:[7,236,241,242] (1) the thermodynamically more favourable disposition of a large number of polar and charged residues on the surface and of hydrophobic residues on the inside, which is characteristic of *t*-enzymes;[241] (2) additional one–two salt and hydrogen as well as hydrophobic linkages in *t*-enzymes; (3) the most frequent occurrence of the Ser → Gly, Thr, Ala, Gly → Ala, Lys → Arg, Ala, Val → Ala, Ile, and Asp → Asn, Glu substitutions on transitions from *m*- to *t*-enzymes; an increased content of the Arg residues and a reduced content of Lys residues are characteristic of *t*-enzymes;[243] (4) *t*-enzymes have a larger number of S–S bonds, α-helices, and β-structures.[7]

Knowledge of the principal factors determining the stability of the native conformation of the protein in solution and of the characteristic features of the structures of *t*-proteins makes it possible to formulate the general principles enabling one to obtain proteins and enzymes with an increased stability: (1) the introduction of additional intramolecular and intersubunit bonds (salt and hydrogen bonds) and the enhancement of hydrophobic interactions increase ΔG_{den} for the protein, as shown in Fig. 8 (the upward shift of curve *1*). Calculation shows that a decrease in k_{in} by a factor of

10 at 70 °C requires an increase in ΔG_{den} by only 1.56 kcal mol^{-1}, while an increase in T_{den} from 35 to 45 °C for a polypeptide chain with M = 35 kD requires an increase in the number of hydrogen bonds by only 3%.[244] Therefore even one additional bond with an energy of 1–3 kcal mol^{-1}, achieved as a result of the replacement of 1–2 aminoacid residues, can increase significantly the stability of the protein. (2) The decrease in the conformational mobility of the fragments of the polypeptide chain as a result of the formation of additional intermolecular covalent or non-covalent "cross-links" in the globule; substitutions by residues with a lower conformational flexibility diminish the conformational entropy ΔS_{conf} and hence increase ΔG_{den} (and T_{den}).

The practical application of these principles to a specific protein makes it necessary to establish the position in the three-dimensional structure where the aminoacid residues are to be substituted (or modified), which particular aminoacid residues are to be replaced, what aminoacids are to replace them, and what method must be used to achieve these aims.

Up to the beginning of the 1980s, the only method for the specific alteration of the structure of aminoacid residues was the chemical modification of functional side groups in the protein. However, this method suffers from important disadvantages and limitations: it is possible to modify only residues having functional groups and accessible to the solvent under the given conditions, the volume of the residues increases after modification, and the number of modifying agents is small.[245] Site-specific mutagenesis makes it possible to replace one aminoacid residue at any position in the polypeptide chain by another, even one with a smaller bulk. It is possible to substitute only one aminoacid residue.

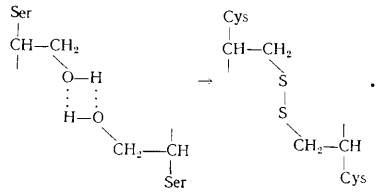
The general characteristics of the changes in the stability of proteins and enzymes as a result of chemical modification have been formulated.[236] In a coiled protein globule, there are three types of functional groups accessible to modification. *The functional residues of type I* are distributed on the surface of the globule. These are effectively hydrated, polar, or charged groups, which do not interact with one another under the given conditions, interacting only with the solvent or ions in solution; their modification does not affect the structure and stability of the protein. *The functional residues of type II* are distributed on or near the surface of the protein. In the native enzyme, they have an unfavourable environment (charged groups in a hydrophobic environment or in an environment comprising groups bearing like charges) and destabilise the protein globule. The number of groups of this type in the protein is usually small. Their modification accompanied by a change in the destabilising factor increases the stability of the protein as a function of the degree of modification and the nature of the modifying agent. *The functional residues of type III* are remote from the surface of the globule and form intramolecular salt and hydrogen bonds stabilising the enzyme. These groups are inaccessible to modification under the usual conditions and are modified for a loosened protein conformation (at an elevated temperature, at extreme pH values, or in the presence of organic solvents). The modification of type III groups diminishes the thermal stability as a result of the rupture of intramolecular bonds stabilising the native conformation of the protein. The structure of the enzyme approaches the denatured structure after such modification.

If the three-dimensional steric structure of the protein is known, it is easy to determine the aminoacid residues located on the surface of the molecule (type I groups) and within it (type III groups). The type II groups can be identified by studying the immediate environment of the given aminoacid residue. Comparison of the crystal structures of proteins of different classes (homologous proteins and their evolutionary precursors and *t*- and *m*-proteins) and data for the influence of site-specific mutagenesis on the stability of the enzymes suggest that the rules governing the influence of the chemical modification of different functional groups of the protein on its stability are on the whole valid also in cases where the stability is changed by site-specific mutagenesis. The aminoacid substitutions in homologous proteins are encountered most often on the surface of the molecule, so that the conformation of the molecule hardly changes. More radical insertions and deletions tend to be encountered in surface loops between units of the surface structure. For proteins which are more than 50% homologous, their inner region contains more than 90% common aminoacid residues.[101]

The mechanism and strategy used in altering the stability of proteins and enzymes with the aid of aminoacid substitutions. In selecting the residues in the proteins to be replaced, it is essential to take into account the following factors: (1) the replacement of type I residues by any others will hardly alter the stability of the protein, since their average environments in the coiled and uncoiled states differ little. (2) The replacement of type II residues (non-polar Leu, Ile, Val, Phe, Tyr, Trp, Met, and Pro residues), which are in contact with water, and of residues in an unfavourable electrostatic environment by small polar and charged residues can increase the stability of the protein.[246] So far, this has been confirmed only in nature. Cytochrome *c* from ox heart is more stable than the protein from horse heart by 1.1 kcal mol^{-1}, which is due, according to the authors, to the fact that the first protein contains the Gly residue, while the second contains the Lys residue exposed to water (the energy of the destabilisation of the Lys residue on contact with water is 1.5 kcal mol^{-1}). In principle, the presence of unfavourably solvated Lys, Tyr, Met, and Trp residues can be established by chemical modification under non-denaturing conditions. The replacement of exposed Lys residues by the His residues (or Arg as in *t*-enzymes) on the whole takes place with retention of the overall charge of the molecule, but the protein destabilisation energy is diminished.[246] (3) The internal region of the proteins is packed to the optimum extent and all the polar atoms form hydrogen bonds.[247] An arbitrary alteration of the size, shape, or polarity of the inner residues (type III residues) destabilises the molecule. Experiments designed to investigate proteins from temperature-sensitive strains (and their chemical modification) showed that mutations in the inner nucleus of the molecule are critical for stability, while any mutations on the surface of the globule do not alter the stability of the protein. However, it is possible to increase the thermal stability of the protein by accurate substitutions of these residues in order to form additional S–S, hydrogen, and salt bonds and by improving the hydrophobic packing, as happens in nature. The aminoacid residues to be replaced are selected with the aid of computer modelling in such a way that the steric disposition of neighbouring residues is not altered and the shortest-range intramolecular interactions are unaffected.[248]

One of the energetic approaches to the stabilisation of the globular structure of the protein involves the decrease in its *conformational entropy* ΔS_{conf} in the uncoiled state. This can be achieved, for example, by forming *intramolecular disulphide bonds* by replacing type III residues. Disulphide bonds have been formed in proteins during evolution in order to increase their stability

during functioning under altered extracellular conditions (the intracellular proteins do not have S–S bonds). The S–S bonds increase the thermodynamic stability of the protein and its resistance to irreversible thermal inactivation, diminishing its capacity for aggregation or adsorption and restricting the exposure of the inner hydrophobic regions to the solution.[249] The strategy used in introducing additional S–S bonds into proteins is as follows.
(a) The Ser or Thr residues, resembling most closely the Cys residue, are selected. For example, the Ser–Ser pair, forming hydrogen bonds, can be replaced by Cys–Cys:



If the Ser–Thr pair is replaced by Cys–Cys, then an empty space is inserted in place of the methyl group, which can be compensated by the replacement of the nearest Val residue by a Leu or Ile residue.[250] (b) For proteins with a known crystal structure, residues are selected by computer analysis in which the carbon atoms are in the same geometrical position as in the residues between which a disulphide bond exists. There are steric limitations to the introduction of an additional disulphide bond. The distance between the carbon atoms of the residues forming a S–S bond should be 4.5–6.5 Å, while the angles formed by the S–S bond should fit within the range of values established.[251] (c) The energy of the strain in the S–S bonds in native proteins varies from 0.5 to 4.7 kcal mol^{-1}. If the S–S bond produced has a strain energy >4.7 kcal mol^{-1}, then the stabilising effect of this cross-link in proteins will be abolished.[249] For this purpose, hypothetical S atoms are introduced into the model structure and candidates with unsuitable steric interactions are rejected. The selected model structures must meet yet another requirement. The cysteine mutations must be in the positions for which certain changes are observed in the course of evolution.[252]

A decrease in ΔS_{conf} is achieved also by replacing aminoacid residues having a conformational flexibility, for example, Gly, by residues containing a β-carbon atom and therefore having a smaller flexibility (Ala, Pro),[250] since

$$\Delta S_{conf/residue} = R \ln Z,$$

where Z is the number of conformations accessible to the residue in the uncoiled protein. The residues to be replaced are chosen so that steric hindrance should not arise after the substitution and the functional properties of the protein should not be altered.

The contribution of the Ala residue to ΔS_{conf} relative to the Gly residue is 2.4 e.u., while that of the Pro residue relative to Ala is 4 e.u. For example, the substitution Ala → Pro for the phage T4 lysozyme at pH 6.5 corresponds to an increase in ΔG_{den} by 1.4 kcal and to an increase in T_m by 3.5 °C.

There exist also several special approaches to increasing the stability of proteins. A higher structural stability of the α-helix in proteins can be attained following the substitution Val → Ala, while the substitution Ala → Val stabilises the β-layered protein structure. Overall, it is essential to use for the substitutions not unduly hydrophobic and bulky residues in order to preserve their structure.[253] The Ala residue is an interesting candidate for the substitution of other residues and proteins. On the one hand, its introduction frequently increases the thermal stability of proteins (see above) and its increased content is characteristic of *t*-enzymes. On the other hand, the "antifreeze" proteins (proteins preventing the freezing of cells in organisms living at temperatures below 0 °C) contain up to 60 mol. % Ala.[254] The site-specific enrichment of the proteins in Ala residues apparently increases their resistance to denaturation by the cold. The site-specific substitutions of charged residues at the ends of the α-helix (a change in the charge on the N-terminal component from +2 to –1, as in the *S*-peptide of ribonuclease) can increase the stability of the protein.[255] Somewhat different approaches to the stabilisation of proteins have been proposed in relation to tyrosinase: (1) the replacements should involve exposed residues or residues in β-coils, while the residues in the α-helix or in β-layers should not be altered; (2) the hydrophobicity of the molecule must not change; (3) the Asp → Glu, Lys → Gly, Val → Thr, Ser → Asn, Ile → Thr, Asn → Asp, and Lys → Arg substitutions are preferable (on the basis of a comparison of the structures of *t*- and *m*-enzymes).[256]

The stability of proteins in relation to oxidation and heavy metal ions can be increased by the following substitutions: Cys → Ala or Ser; Met → Glu, Val, Ile, Leu; Trp → Phe or Tyr. The bulk of the residues after the substitution hardly changes and steric hindrance does not arise, but groups sensitive to oxidation and complex formation with metal ions are substituted.[257] An increase in stability can be achieved by increasing the number of metal-binding sections in proteins by introducing additional negative charges.[1]

It has been suggested in certain studies that mutations stabilising the protein act additively, i.e. the stability of the protein can be increased significantly by accumulating a large number of stabilising mutations. An increase in the stability of the protein can also be achieved by removing (or saturating) certain uncompensated groups capable of forming hydrogen bonds and also by filling the inner cavities in the three-dimensional structure.[258] On the other hand, the substitutions of many residues can hardly act additively.[259]

Thus, although the overall theory of the prediction of the stability of a protein on the basis of its primary structure is far from completion, with the aid of graphical modelling in the presence of a three-dimensional structure it is possible to reveal the presence in the protein of residues of types I, II, and III, to select *a priori* the residues to be replaced and the substituting aminoacid residues, and to obtain the expected result.

(b) **The stability of proteins** *in vivo* in the cell is determined primarily by their resistance to intracellular proteolysis. The degradation of intramembrane proteins and long-lived cytoplasmic proteins takes place in lysosomes and in cytosol (the latter is the most selective). The rates of turnover of different proteins in the cell differ by factors up to 1000 (from 2 min to more than 200 h). The question arises what determines the half-life of the intercellular proteins ($\tau_{1/2}$). When 35 proteins with unknown crystal structure were introduced into a culture of Hela cells, it was found that their $\tau_{1/2}$ varied from 16 to 220 h and was not correlated with the size, charge, and content of hydrophobic aminoacids, the acylation of the N-terminal aminoacid, or the ratio of the α-helical and β-layered conformations.[260] Calorimetric data obtained for 22 of these proteins showed that their thermal stability *in vitro* is also not correlated with $\tau_{1/2}$. The hypothesis that intracellular proteases "recognise" more readily the inner part of proteins rather than the outer part (i.e. proteins with a greater mobility and flexibility should

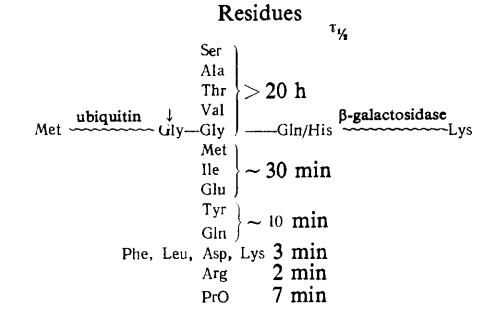
be degraded faster) has also not been confirmed, although it is known that proteins with a conformation distorted as a result of mutations are rapidly degraded.[261]

After denaturation, proteins become more accessible to proteolysis *in vitro*. However, comparison of the values of $\tau_{1/2}$ for native and denatured bovine serum albumin in cytosol and of β-lactoglobulin and cytochrome *c* in a culture of rat haepatoma cells showed that the denatured proteins are sometimes degraded several times more slowly than the native proteins (or at the same rate).[262]

Thus none of the global structural properties of the protein macromolecule which were examined above can serve as a criterion of its stability in the cell. Nevertheless, the latest data on protein sequences indicate the existence of definite signals in the sequence responsible for the degradation of the molecule. Thus proteins with $\tau_{1/2} < 2$ h contain one or more regions enriched in Pro, Glu, Ser, and Thr.[263] These regions have between 12 and 60 residues and are protected by clusters of positively charged aminoacids, which has been confirmed for a large number of intracellular proteins. There exists yet another type of signal for increased proteolysis: the S-peptide of ribonuclease — 20 N-terminal aminoacids in which (Lys-7)-Phe-Glu-Arg(Gln-11) are critical. The S-peptide "grafted" to lysozyme and insulin increased by a factor of 2 the rate of their degradation in fibroblasts.[264]

In the case of the ubiquitin-dependent non-lysosomal selective proteolysis, the state of the α-NH_2 group in the protein plays a fundamental role. The ubiquitinisation of the N-end of the protein is critical. The "N-end rule", establishing the dependence of the stability of the protein *in vivo* ($\tau_{1/2}$) on the nature of the N-terminal aminoacid, has been established.[265] With the aid of site-specific mutagenesis involving the cross-linking of β-galactosidase to the ubiquitin proteins, proteins with different aminoacids at the N-end of the molecule were obtained after the removal of the ubiquitin protein (Scheme 5). Depending on the aminoacid, $\tau_{1/2}$ varied as follows:

Scheme 5



If a Met group is placed at the ubiquitin binding site ahead of the residues destabilising β-galactosidase, then the $\tau_{1/2}$ for the enzyme increases (> 20 h). The authors suggest that, after the N-terminal peptidases have split off the N-end of the polypeptide chain synthesised, the "N-end reading" enzymes recognise specific residues at the N-end, which in fact determines their $\tau_{1/2}$. Long-lived proteins in the cell do indeed have Met, Ser, Ala, Gly, Thr, and Val residues at the end. On the other hand, eukaryotic toxins contain the destabilising Arg, Lys, Leu, Phe, and Asp residues at the N-end. Thus the rule established not only explains the metabolic stability of the protein but also suggests possible ways of regulating it. However, other workers[260] believe that this is a contranslation rule and holds immediately after translation for proteins which have still not coiled up, since $\tau_{1/2} = 1-3$ min is comparable to the protein translation time.

The oxidation of the His, Cys, and Met residues in the protein as well as the deamidation of Asn lead to its rapid degradation. The oxidised proteins are apparently recognised by special enzymes.[266] The stability of the intracellular proteins depends also on the site where they are located. The proteins forming part of multienzyme complexes and bound to membrane structures are more stable.

Thus the stability of proteins *in vitro* in solution is determined by specific intramolecular interactions. The stability of proteins *in vivo* is a more complex quantity and depends not only on the structure of the protein but also on its function — on the interaction of the protein with other proteins and cell components. The presence of specific signals in the aminoacid sequence, recognised by specific proteinases, and not the stability of the inner structure and the capacity for uncoiling when acted upon by various factors is of fundamental importance for the stability of the protein *in vivo* (in contrast to its stability *in vitro*).

3. The study of the stability of proteins with the aid of aminoacid replacements

The first studies of the influence of random aminoacid replacements on the stability of proteins were published at the end of the 1970s and concern the lysozyme of the T4 phage and the α-subunits of tryptophan synthetase (for a review of the first investigations, see Kutuzova et al.[236]). Since the proteins were isolated from mutant strains obtained in different ways, the influence of random aminoacid replacements on the stability of the proteins was also unpredictable. As the crystallographic technique and genetic engineering methods developed, it became possible to carry out specific replacements with prediction of a definite result. Examples of the study of the stability of different proteins with the aid of mutations (random and directed), which in many respects confirm and illustrate the features described above, are described below.

The presence of the type I, II, and III residues in proteins has been clearly demonstrated in a study of the lysozyme from the temperature-sensitive strains of the T4 phage, a convenient model monodomain protein, which has no S—S bond and prosthetic groups. Comparison of the crystal structures of the mutant lysozymes showed that the majority of the mutations destabilising lysozyme and encountered among residues which are inaccessible to the solvent have a rigid conformation, and are most static in the molecule. These aminoacid residues, located in the "hard" part of the molecule, form stabilising intermolecular bonds (type III residues). Mutant lysozymes, in which the inner Thr-157 residue, forming hydrogen bonds, has been replaced by the Ile, Ala, Ser, Leu, Asp, etc. residues, had T_{den} smaller than T_{den} for the native lysozyme by 9 — 13 °C (pH 2.0). This is caused by a dissociated and uncompensated hydrogen bond.[267—269]

Temperature-sensitive mutations are scarcely encountered among aminoacid residues which are exposed to the solvent and are mobile. For example, the replacement of the Cys-54, Glu-128, and Pro-86 residues by any others does not affect the stability of lysozyme.[270] Similar results were obtained for the staphylococcal nuclease[271] and kanamycin-nucleotidyl transferase.[272] Six mutants with one aminoacid substitution in the C-terminal region by the method of segment-directed mutagenesis were obtained for the last enzyme. The stability of all the Gly-242 → Arg, Gly-242 → Glu, Gly-204 → Asp, Phe-230 → Ser, and Pro-252 → Leu (except only Glu-210 → His) mutants diminishes in the above sequence and is smaller than the stability of the native enzyme. According to the authors, this can be explained by replacements among the residues

immersed into the hydrophobic nucleus of the molecule and depends on the nature of the substituted residue.[272] For the *protein* of the λ-phage repressor, which consists of an N-terminal DNA-binding domain (92 residues) and a C-terminal domain (144 residues), 11 single-point mutants were obtained in the region of the N-terminal domain. Analysis of the CD spectra showed that the mutations of the aminoacid residues exposed to the solvent do not alter the stability of the λ-repressor, while the mutations of the inner aminoacid residues diminish it. Just one surface mutation Gln-33 → Tyr increases the thermal stability of the λ-repressor (type II residue). It has been suggested that the Tyr-33 residue introduced interacts with the Tyr-22 residue over a distance of 25 Å, which stabilises the structure.[273]

A rare proved example of mutations of type II residues is of interest. All the mutations in subtilisin (Met-50 → Phe/Ile-107 → Val/Lys-113 → Arg), which increase its stability in the region of alkaline pH, are located near the surface of the molecule, which has been demonstrated for the three-dimensionai structure of the protein. The modelling of the Met-50 substitutions showed that the introduction of the Phe residue makes the hydrophobic interaction with the Trp-113 residue more favourable, which has in fact been observed in the crystal structure of the protein.[274]

Examples involving the introduction of additional S—S bonds. A patent has been recently obtained for the preparation of stable proteins with additional S—S bonds.[275] For this purpose, X-ray diffraction data for a specific protein are read into a computer and the sites for the introduction of Cys residues are found taking into account the necessary conditions indicated above.[39] The gene coding for the given protein with nucleotide replacements giving rise to the Cys residue is modified by the method of site-specific mutagenesis and is incorporated into the plasmid and expressed in the required culture.

A stable mutant of the T4 phage lysozyme was obtained in this way. The native enzyme has two Cys residues (54 and 97), but contains no S—S bonds. Analysis of the X-ray diffraction structure of lysozyme led to the selection of positions 3 and 97 for the formation of the disulphide bond and the Ile-3 → Cys mutant was constructed (with retention of 77% of activity) (Fig. 9). Oxidation of lysozyme *in vitro* leads to the formation of the (Cys-3)—(Cys-97) S—S bond. The stability then increases approximately by a factor of 30 (at 67 °C). Thermal inactivation in the presence of dithiothreitol (DTT) showed that the stabilisation is caused precisely by the formation of the S—S bond and not by the Ile → Cys substitution. At the same time, at an elevated temperature the Cys-54 residue is involved in the thiol—disulphide exchange, which inactivates the lysozyme as a result of the formation of intermolecular S—S bonds. Mutants were therefore obtained in which the Cys-54 residue was replaced by other residues with retention of the S—S bond in positions 3 and 97, which increased the stability several times more (the replacements of only the Cys-54 residue by Thr and Val do not alter the stability of lysozyme).[276] For a detailed study of the role of the Cys-54 and Cys-97 residues in the oxidative inactivation of the T4 phage lysozyme, the Cys-54/Cys-97 → Val/Ser double mutant was constructed. Its stability proved to be higher than that of native lysozyme. The use of such mutations made it possible to discover the mechanism of the thermal inactivation of lysozyme. The reversible uncoiling of the molecule at elevated temperatures is complicated by secondary processes, the main ones of which are oxidative inactivation with

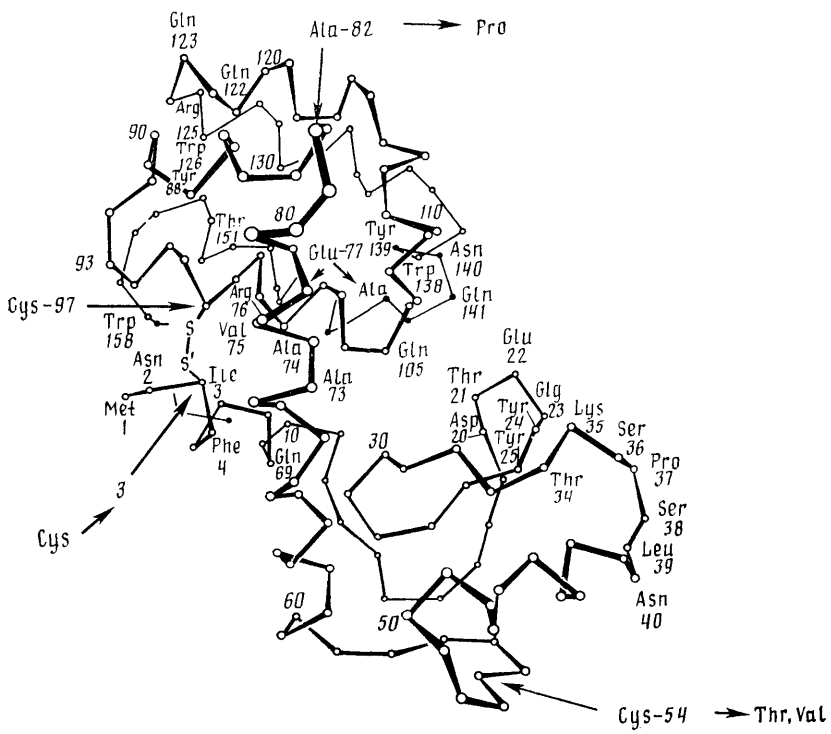


Figure 9. Steric structure of the T4 phage lysozyme.[277]

formation of oligomers linked by S—S bonds (this has been demonstrated electrophoretically). The removal of the Cys residue from lysozyme prevents the oxidative inactivation. On heating, this mutant uncoils reversibly with regeneration of the activity after treatment with guanidine hydrochloride (Gu.HCl). On the other hand, although the mutant with the 3—97 S—S bond, in which the Cys-54 → Val substitution has been carried out, does exhibit a higher stability, nevertheless the percentage regeneration of the activity after uncoiling in the presence of Gu.HCl and coiling up again is close to zero. Other proteins containing free Cys residues probably also undergo thermo-oxidative inactivation and can therefore be stabilised by similar aminoacid replacements.[277]

Dihydrofolate reductase (DFR) contains one polypeptide chain (159 residues). The Pro-39 residue is located opposite the Cys-85 residue. The distance between the α-carbon atoms is 6 Å, which is the same as in the S—S bond, and both residues are remote from the active centres. For this reason, the Pro-39 → Cys mutation leads to the formation of the 39—85 S—S bond after oxidation with dinitrobenzoate without a change in enzyme activity.[278] The DFR mutant obtained is more stable in relation to denaturation by urea and Gu.HCl to the extent of 1.8 kcal mol^{-1} and its coiling—uncoiling mechanism is altered.[279] Comparison of the crystal structures of the mutant and the native enzyme demonstrated their identity. The thermal stability of the mutant is approximately the same as that of the native DFR (T_m = 44 and 41 °C respectively).

Computer analysis for the λ-phage repressor protein[280] demonstrated the usefulness of the introduction of the (Cys-88)—(Cys-88′) S—S bond between the repressor subunits after the replacement of Thr-88 by the Cys residue.[281]

For the Thr-88 → Cys mutant, the S—S bond forms spontaneously; the mutant was more resistant to denaturation by urea than the native protein and T_m increased from 49 to 56—60 °C. On the other hand, the Tyr-85 → Cys mutant does not form a covalently bound dimer. Its chain structure is damaged and its stability is therefore lower than that of the native λ-repressor.[280]

For the subtilisin from *B.amyloliquefaciens*, which contains no S—S bonds, the Thr-22 and Ser-87 positions were selected for the production of such a bond. The Cys residues were introduced into these positions by the method of site-specific mutagenesis. They then formed spontaneously an S—S bond (either during the synthesis of the protein or during its secretion). These mutations did not affect the catalytic properties of subtilisin, while T_m increased from 58.9 to 62 °C. On the other hand, in the presence of DTT,† whereupon the S—S bond is ruptured, T_m = 56.2 °C. The rate of thermal inactivation of the Cys-22 → Cys-87 mutant is 1.5— 2 times lower, while $\tau_{1/2}$ in 8 M urea is higher by a factor of 2.[252]

Stabilisation of proteins by the replacement of residues with a high flexibility (Gly) in the uncoiled state of the protein by residues with a limited conformational freedom (Ala, Thr, Val, Ile, Pro). The replacement sites such that neither the tertiary structure of the protein nor the interactions with neighbouring residues were altered were selected for the T4 phage lysozyme by computer modelling. The selected candidates for replacement by the Ala residue were Gly-77 and Gly-113, while the Ala-82 residue was chosen for replacement by the Pro residue. Comparison of the crystal structures of the native and the Gly-77 → Ala and Ala-82 → Pro mutant lysozymes showed that they are virtually identical with the exception that the carbonyl carbon atom of the Glu-108 residue, closest to the Ala-77 residue, is displaced by 1.3 Å. Nevertheless the hydrogen bonds between the residues are unaffected. In the Ala-82 → Pro mutant, the H_2O molecule bound to the peptide nitrogen atom of the Ala-82 residue in the native protein is displaced. However, these are minor changes and do not influence the stability of lysozyme. For the Ala-77 and Pro-82 mutants, the T_m at pH 6.5 increase from 64.7 to 65.6 and 66.8 °C respectively, while the stabilisation energies are 0.4 and 0.8 kcal mol^{-1} respectively as a result of the decrease in the entropy of the uncoiling of the protein.[258] Similarly the Gly → Ala substitutions increase the stability of the *λ-repressor*[282] and of the *neutral protease from B. stearothermophilus* following the replacement Gly-144 → Ala.[283] This replacement was discovered on comparing the *t*- and *m*-enzymes. Admittedly, in such cases the increase in stability was explained by the replacement in the α-helix of the weakly helix-forming Gly residue by the effective helix-forming Ala residue.

The linear *correlation between the hydrophobicity of the substituted residues and the increase in* ΔG_{den} after point mutations was demonstrated for the α-subunit of tryptophan synthetase.[273,284] This correlation can be accounted for by the fact that the dielectric constant within the protein diminishes with increase in the hydrophobicity of the inner aminoacid residues, which intensifies the hydrophobic and electrostatic interactions. The point mutants of the α-subunit of tryptophan synthetase, isolated from mutant strains, are twice as stable as the native enzyme after the Glu-49 → Met, Gly-211 → Glu, and Gly-234 → Asp replacements and are less stable after the Phe-22 → Leu, Glu-49 → Gln, Leu-177 → Arg, Gly-211 → Arg, and Gly-213 → Val replacements. However, the tertiary structures of the mutants were not compared in these cases, which renders the results not altogether unambiguous.

Individual independent mutations can act additively on the stability of the protein and the accumulation of several such mutations with a stabilisation energy of 1 kcal mol^{-1} can give rise to a radical increase in ΔG_{den}. For example, the mutants of kanamycin-nucleotidyl transferase with the Asp-80 → Tyr and Thr-130 → Lys replacements and the Tyr-80/Lys-130 double mutant had maximum activities at 56, 60, and 62 °C respectively, while the native enzyme had a maximum activity at 52 °C. The resistance of the double mutant to proteolysis is greater than that of the point mutants and of the native enzyme.[285] The stabilisation is caused by additional hydrogen bonds and electrostatic interactions.

One of the causes of the instability of proteins is their oxidation with subsequent inactivation and denaturation. This refers particularly to proteins containing the Met, Cys, or Trp residues near the active centre. In subtilisin, the Met-50 and Met-222 residues are on the surface of the molecule, the Met-222 residue being close to the Ser-221 residue in the active centre. Following the replacement of Met-222 by the Cys-residue, the mutant had 138% of the original activity, while the replacements by the Ala and Ser residues resulted in mutants with 53% and 35% activities respectively. All other replacements led to a greater fall of the activity of subtilisin. Native subtilisin in 0.1 M H_2O_2 has $\tau_{1/2}$ = 2.5 min. The Met-222 → Ser, Ala, or Leu mutants are stable under these conditions for more than 1 h, while the

† Dithiothreitol (Translator).

Met-222 → Cys mutant is not oxidised by 0.1 M H_2O_2 at all. Thus the replacement of the Met-222 residue by residues resistant to oxidation increases the stability of subtilisin.[286]

The stability of proteins can be increased by reducing the surface area of the hydrophobic component in contact with the solvent, as shown for lactate dehydrogenase from *B. stearothermophilus*. The hydrophobic Ile-250 residue, located on the surface of the NAD binding pocket, was replaced by the hydrophilic Asn residue, whereupon k_{in} for the mutant diminished by a factor of 4.5 (at 90 °C), possibly as a result of the formation of the additional (Thr-246–(Asn-250) hydrogen bond.[287]

Examples confirming the general features of the variation of the stability of protein molecules and also examples where desirable results were achieved in the stabilisation of proteins on the basis of these features were considered above. However, many investigations showed that the influence of the aminoacid replacements on the stability is specific to each protein. As a rule, this applies to proteins with an unknown three-dimensional structure for which computer modelling of replacements and a reliable prediction of the effect are impossible.

In the monomeric form of iso-1-cytochrome *c* (the Cys-102 residue is blocked), the Pro-71 residue (the conservative residue as regards evolution) is important for the coiling of the protein and separates two short α-helical regions, defining the end of one and the beginning of the other helix. Its replacements by the Val, Thr, and Ile residues do not alter the functional properties of the structure but do alter the stability of the protein. Thus the stability of the mutants in relation to guanidine hydrochloride (ΔG_{den}, kcal mol^{-1}) diminishes in the following sequence: native; Val-71; Thr-71; Ile-71 (3.6, 2.6, 1.9, and 1.9 respectively).[288] The study of the denaturation kinetics showed that the location of the mutation in the primary structure determines the stage whose rate will change, while the nature of the substituent influences the change in the rate of the stage.[289]

The Pro-87 → Ser mutant of *adenylate kinase* from the temperature-sensitive strain of *E. coli* had k_{cat}/K_M smaller by a factor of 17 (at 27 °C) than the native enzyme and its thermal stability was lower. In the mutant adenylate kinase, the α-helix content diminished by 11%. Analysis of the CD spectra showed that the mutation broadens the structure of the enzyme. As a result, the sensitivity of the mutant to proteolysis increased. It has been suggested that the Pro-87 residue is located within the globule in the region of intensely interacting Asp-84, Phe-86, and Arg-88 residues and that its replacement by the more flexible and polar Ser residue disrupts these interactions and destabilises the structure of adenylate kinase.[290] The single point replacements in the α-subunit of *tryptophan synthetase*[291,292] and in dihydrofolate reductase[293] made it possible to discover the role of the individual aminoacid residues at each stage of the reversible denaturation of these enzymes by urea.

All the studies examined above were devoted to the stabilisation of enzymes in relation to reversible denaturation. The transition of the protein molecule to the irreversibly uncoiled state is caused by the aggregation of the protein molecules—the chemical modification of the functional groups more accessible to the solvent in the denatured state, as a result of which the molecule cannot coil up into the native conformation.

An attempt has been made to prevent the irreversible denaturation process with the aid of site-specific mutagenesis for *triose phosphate isomerase* (TPI)—an enzyme consisting of two identical subunits without S–S bonds and non-protein components. Analysis of the crystal structure established that the Asn residues located on the surface of the molecule between the subunits are deaminated in the thermal inactivation process with formation of charged Asp residues, which leads to the dissociation of the dimer into inactive monomers. The Asn-78 → Thr, Ile and Asn-14/Asn-78 → Thr/Ile mutants were obtained. Their half-lives at 100 °C increased from 13 to 17, 16, and 25 min respectively, and at the same time they had lower T_m (by 2–3 °C) than the native TPI, i.e. these mutations destabilise the enzyme in relation to reversible thermal inactivation.[294,295] This approach of the authors does not appear to be altogether correct, because the irreversible thermal inactivation of proteins involves not only (and not so much) the chemical modification of the functional groups but also physical processes leading to the aggregation of the denatured molecules after uncoiling. The stabilisation of the native conformation of the protein using the strategy described above appears more promising.

VI. Protein design

The construction of proteins with specified properties, structure, and stability, i.e. protein design, is a higher stage of development of genetic engineering. For a specific alteration of catalytic properties and substrate specificity, it is essential to investigate in detail the mechanism of the enzymic reaction and the structure of the substrate-binding section and of the active centre in order to alter the resistance to the effect of temperature or chemical reagents—factors which determine the stability of the protein, as well as the disposition of the groups, which are functionally important for catalysis, in order that the changes made in the structure to increase stability should not entail the loss of catalytic function. Protein design becomes possible provided that the X-ray diffraction structure of the protein has been obtained with a high degree of resolution. Such a structure serves as a basis for computer analysis and graphics.

For example, analysis of the steric disposition of the Met-222 group in subtilisin showed that its replacement by residues with small side chains (Glu, Ala, Ser, Cys, etc.) would not alter the conformation of the catalytic region and a high activity would be retained, while replacement by residues with long side chains would lower the activity of the enzyme. The results of mutagenesis confirmed the validity of the model. One of the mutants involving the replacement Met-222 → Cys showed a higher activity than the native subtilisin.[296]

Allowance for electrostatic effects in the active centre of subtilisin yielded mutants with an altered pH activity profile. Rules have been formulated for the construction of proteins with an altered pH dependence:[297] (1) the increase in the negative charge in the region of the active centre increases the pK_a for the acid groups, while an increase in the positive charge reduces the pK_a; (2) the change in the pH dependence is manifested at a low ionic strength; (3) the mutations should be carried out in such a way that the counterions do not concentrate in the region of the active centre. The change in the surface charge in the active centre of subtilisin (as a result of the replacement Asp-99 → Ser) (Fig. 10) led to an appreciable shift of the activity pH-profile to the acid region.[150,151,297]

The specific alteration of the substrate specificity of enzymes is achieved by altering the conformation of the substrate-binding region. The Gly-216 → Ala replacement in trypsin increased the catalytic activity in relation to arginine substrates, while the

Gly-226 → Ala replacement increased it in relation to lysine substrates.[141] In the case of lactate dehydrogenase, the active centre was reconstructed in the following way: Thr-246 → Gly (increase in the volume of the active centre), Asp-197 → Asn (neutralisation of the acid), and Glu-102 → Arg (introduction of a base to ensure the binding of a carboxylate). The ternary mutant oxidised malate 23 times more effectively than lactate and reduced oxaloacetate 500 times more effectively than pyruvate, while the native enzyme had a catalytic activity in relation to pyruvate 1000 times greater than in relation to oxaloacetate. Thus the mutant enzyme acquired the properties of malate dehydrogenase.[179]

In alcohol dehydrogenase, the long side chains of the Trp-93 and Thr-48 residues diminish the size of the substrate-binding pocket and the enzyme therefore catalyses most effectively the oxidation of alcohols with a short side chain (ethanol, 1-propanol). The replacement of these residues by residues of smaller size (Trp-93 → Phe and Thr-48 → Ser) increased the effectiveness of the oxidation of long-chain alcohols (1-octanol, 1-heptanol) compared with ethanol.[182]

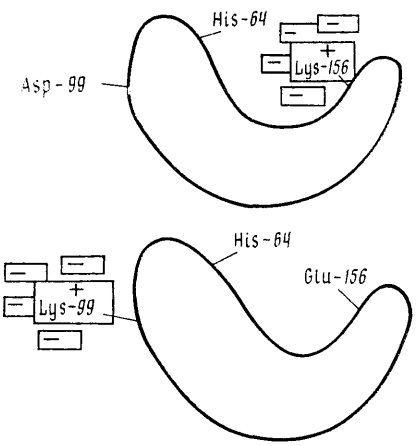


Figure 10. Schematic representation of the ionic atmosphere, made up of the Lys-99 and Lys-156 residues, of the active centre of subtilisin.[297]

The site-specific mutagenesis of haem ligands in cytochrome b_5 is an interesting example of the formation of a protein with new improved properties.[298]

The His-39 → Met replacement of the axial haem ligand greatly reduced the oxidation-reduction potential. The peroxidase activity in the reaction of the mutant protein with *o*-dianisidine increased by a factor of 30. In addition, the mutant acquired a new property—it catalysed the intermolecular oxidative demethylation of *NN*-dimethylaniline by H_2O_2. The native cytochrome b_5 is completely inactive in this reaction.

The C-terminal hydrophobic segment of penicillin-binding protein 5 from *E. coli*, which binds this protein to a membrane, was replaced by a shorter segment containing hydrophilic aminoacids, which led to the formation of a water-soluble protein with complete retention of its activity.[299]

The construction of proteins with a much higher stability by employing the general approaches and features examined in Section 5 is a brilliant example of protein design. The introduction of intramolecular disulphide bonds stabilised the T4 phage lysozyme,[276] subtilisin,[252] the N-terminal domain of the λ-repressor,[280] and dihydrofolate reductase.[180] The replacement of Met-222 in subtilisin by residues resistant to oxidation (Ser, Ala) greatly increased the stability of this enzyme.[286] The replacements of unbranched residues by branched β-carbon chains (Thr, Val, Ile) restricted the conformation of the protein and hence greatly increased the stability of the T4 lysozyme.[258]

Studies designed *to create protein-hybrids* possessing the set of properties of their constituent proteins are of interest. Thus the *E. coli* protein possessing adenylate cyclase and β-galactosidase activities has been constructed.[300] It consists of the first 556 (out of 848) aminoacid residues of adenylate cyclase (the enzyme responsible for the synthesis of cAMP), linked via the synthetic pentapeptide Val-Gly-Asp-Pro-Val to the eighth residue of β-galactosidase (M = 175 kD). The resulting chimeral protein is a tetramer. The pH optimum of the adenylate cyclase activity in the hybrid protein has been displaced to the alkaline region (from 8.5 to 9.5) and an excess of ATP does not inhibit the adenylate cyclase activity of the hybrid in contrast to the native enzyme, which can apparently be accounted for by the absence of a regulatory domain from the hybrid. The kinetic properties of the hybrid protein are close to those of both constituent proteins, but the hybrid is less stable than β-galactosidase. The hybrid of the human growth hormone and the signal peptide of the extramembrane *E. coli* protein OmpA has also been obtained by the genetic engineering method. The recombinant DNA was expressed in the cells of *E. coli* and the growth hormone synthesised was secreted into the periplasm of *E. coli*. It had the correct secondary structure and formed the required S–S bonds. Thus the addition of the signal peptide ensured the passage of the hybrid protein through the cell membrane of *E. coli* and the correct coiling of the protein synthesised with formation of the required disulphide bonds.[301]

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The analysis of the literature described shows that the protein engineering technique is a revolutionary experimental instrument for the solution of fundamental problems in modern enzymology: the determination of the structure–function–stability of protein macromolecules relation. The study of numerous mutant proteins with the aid of computer graphics has provided an algorithm for the preparation of enzymes with properties specified beforehand in order to use them in biotechnology. The need for the employment of genetic engineering methods in modern protein chemistry is not only evident but is genuinely essential for the solution of both theoretical and applied problems.

References

1. P N Bryan *Biotechnol. Adv.*, 1987, **5** 221
2. A White, P Handler, E L Smith *Principles of Biochemistry*, McGraw Hill, New York, 1968 (Translated into Russian), Izd. Mir, Moscow, 1981, Vol. 2, Chapters 25, 26
3. J D Watson, J Tooze, D J Kurtz *Recombinant DNA: A Short Course*, Scientific American Books, New York, 1983 (Translated into Russian), Izd. Mir, Moscow, 1986

4. G Heijne, C Blomberg, H Liljenström *J. Theor. Biol.*, 1987, **125** 1
5. C Ghelis, J Yons *Protein Folding*, Acad. Press, New York, 1983
6. M T McLaman, W H Andrews, J G Files *J. Biotechnol.*, 1985, **2** 117
7. G D Kutuzova, N N Ugarova, I V Berezin *Bioorg. Khim.*, 1982, **8** 1445
8. R F Dolittle, V Mire *Nauki*, 1985, (12) 40
9. G D Rose, A R Geselonitz, G J Lesser, et al. *Science*, 1986, **229** 834
10. R Yaenicke *Prog. Biophys. Molec. Biol.*, 1987, **49** 117
11. P L Privalov *Vestn. Akad. Nauk SSSR*, 1986, (2) 72
12. P L Privalov *Biofizika*, 1985, **30** 722
13. T W Traut *Mol. Cell. Biochem.*, 1986, **70** 3
14. D B Wetlaufer *Adv. Protein Chem.*, 1981, **34** 61
15. D Ollis, P Brick, R Hamlin, et al. *Nature*, 1985, **313** 762
16. E D Kiehn, J J Holland *Nature*, 1970, **226** 544
17. E Querol, A Parrilla *Experientia*, 1987, **43** 920
18. T E Creighton, D P Goldenberg *J. Mol. Biol.*, 1984, **179** 497
19. A Protzel, A J Morris *J. Biol. Chem.*, 1974, **249** 4594
20. L L Randell, L G Josefsson, S J Hardy *Eur. J. Biochem.*, 1980, **107** 375
21. I J Purvis, A J E Bettany, T Ch Santiago, et al. *J. Mol. Biol.*, 1987, **193** 413
22. R L Burke, P Tekamp-Olson, R Najarian *J. Biol. Chem.*, 1983, **258** 2193
23. J R Coggins, D G Hardie *Multidomain Proteins*, Elsevier, Amsterdam, 1986, p. 1
24. C R Matthews, M K Hurle *Bio Essay*, 1987, **6** 254
25. C R Matthews *Methods Enzym.*, 1987, **154** 498
26. J Sugihara, T O Baldwin *Biochemistry*, 1988, **27** 2872
27. T Imoto, H Yamada, T Yasukochi, et al. *Prot. Eng.*, 1987, **1** 333
28. C B Marks, H Naderi, Ph A Kosen, et al. *Science*, 1987, **235** 1370
29. C-I Brändeu *Chem. Scr. B*, 1986, **26** 247
30. M G Rossman *Phil. Trans. Soc. London*, 1981, **293** 191
31. S T Rao, M G Rossman *J. Mol. Biol.*, 1973, **76** 241
32. S J Wodak, J Janin *Biochemistry*, 1981, **20** 6544
33. C Quinto, M Quirago, W F Swain, et al. *Proc. Natl. Acad. Sci. USA*, 1982, **79** 31
34. M Leicht, C L Long, T Chandra, et al. *Nature*, 1982, **297** 655
35. H Naora, N J Deacon *Proc. Natl. Acad. Sci. USA*, 1982, **70** 6196
36. Go H, M Nosaka *Evolution of Catalytic Function, Cold Spring Harbor Lab.*, 1987, Vol. 52, p. 915
37. T Maniatis, E F Fritsch, J Sembruk *Methods for Genetic Engineering: Molecular Cloning* (Translated into Russian), Izd. Mir, Moscow, 1984, 480 pp
38. D H Glover *Gene Cloning. Mechanics of DNA Manipulation*, Chapman and Hall, London–New York, 1984, 222 p
39. B D Hames, S J Higgins (Editors) *Transcription and Translation: A Practical Approach* (Translated into Russian), Izd. Mir, Moscow, 1987, 399 pp
40. M Smith *Philos. Trans. R. Soc. London, A*, 1986, **317**(1540) 295
41. G Dalbadie-McFarland, J H Richards *Ann. Rev. Med. Chem.*, 1983, **18** 237
42. M Smith *Ann. Rev. Genet.*, 1985, **19** 423
43. D Shortle, D Botstein *Methods Enzym.*, 1983, **100** 457
44. L A Loel *Cell.*, 1985, **40** 483
45. R Pine, P C Huang *Methods Enzym.*, 1987, **154** 415
46. R M Myers, L S Lerman, T Maniatic *Science*, 1985, **229** 242
47. K Itakura, J J Rossi, R B Wallace *Ann. Rev. Biochem.*, 1984, **53** 323
48. J Blöcker, R Frank *Biotechnology: Potentials and Limitations* (Edited by S Silver), Dahlem Konferenzen, Springer-Verlag, Berlin–Heidelberg–New York–Tokyo, 1986, p. 41
49. J A Wells, M Vasser, D B Powers *Gene*, 1985, **34** 315
50. D Botstein, D Shortle *Science*, 1985, **229** 1193
51. G Winter, P Carter, H Bedouelle, et al. *Biotechnology: Potentials and Limitations* (Edited by S Silver), Dahlem Konferenzen, Springer-Verlag, Berlin–Heidelberg–New York–Tokyo, 1986, p. 55
52. P Carter *Biochem. J.*, 1986, **237** 1
53. M J Zoller, M Smith *Methods Enzym.*, 1983, **100** 468
54. M J Zoller, M Smith *DNA*, 1984, **3** 479
55. A R Fersht, G P Winter *Ciba. Found. Symp. 111*, Pitman, London, 1985, p. 204
56. M J Zoller, M Smith *Methods Enzym.*, 1987, **154** 329
57. W Kramer, H J Fritz *Methods Enzym.*, 1987, **154** 350
58. W Mandecki *Proc. Natl. Acad. Sci. USA*, 1986, **83** 7177
59. V A Efimov, O V Mirskikh, O G Chakhmakhcheva, Yu A Ovchinnikov *Bioorg. Khim.*, 1985, **11** 621
60. V A Efimov, O V Mirshkikh, O G Chakhmakhcheva, Yu A Ovchinnikov *FEBS Lett.*, 1985, **181** 407
61. V A Petrenko, N N Pozdnyakov, S M Kipriyanov, et al. *Bioorg. Khim.*, 1986, **12** 1088
62. V A Petrenko, L N Semenova, S M Kupriyanov, et al. *Bioorg. Khim.*, 1987, **12** 1612
63. V A Petrenko, S M Kipriyanov, L N Semenova, A N Boldyrev *Bioorg. Khim.*, 1987, **13** 344
64. W J Martin, R W Davies *Biotechnology*, 1986, **4** 890
65. J C Moores *Anal. Biochem.*, 1987, **163** 1
66. B W Gilson, K Beiman *Proc. Natl. Acad. Sci. USA*, 1984, **81** 1956
67. M J Zvelebil, G J Barton, W R Taylor, M J Stenberg *J. Mol. Biol.*, 1987, **195** 957
68. G Voordouw, S Brenner *Eur. J. Biochem.*, 1986, **159** 347
69. P W Finch, R E Wilson, K Beocon, et al. *Nucl. Acids. Res.*, 1986, **14** 7695
70. G Schumaster, D Sizmann, H Haug, et al. *Nucl. Acids. Res.*, 1986, **14** 5713
71. G-H Fang, P Kenigsberg, M J Axley, et al. *Nucl. Acids. Res.*, 1986, **14** 8061
72. S Inouye, M Noguchi, Y Sakaki, et al. *Proc. Natl. Acad. Sci. USA*, 1985, **82** 3154
73. B Perryman, S A Kerner, T J Bohlmeyer, R Toberts *Biochem. Biophys. Res. Commun.*, 1986, **140** 981
74. C J M Saris, B F Tack, T Kristensen, et al. *Cell*, 1986, **46** 201
75. E Takano, M Maki, M Hatanaka, et al. *FEBS Lett.*, 1986, **208** 199
76. T Icho, C P Sparrow, C B H Raetz *J. Biol. Chem.*, 1985, **260** 12078
77. T Icho, C E Bulawa, C B H Raetz *J. Biol. Chem.*, 1985, **260** 12091
78. Yu A Ovchinnikov, N E Broude, K E Petrukhin, et al. *Biokhimiya*, 1986, **51** 1491
79. T O Baldwin, J-W Lin, L H Chen, et al. *Bioluminescence and Chemiluminescence, New Perspectives. Proceedings of the IV International Biolum. and Chemilum. Symp., Freiburg, 1986*, John Wiley and Sons, New York, 1987, p. 351

80. W Kugimiya, Y Otani, Y Hashimoto, Y Takagi *Biochem. Biophys. Res. Commun.*, 1986, **141** 185
81. C-P D Tu, B Qian *Biochem. Biophys. Res. Commun.*, 1986, **141** 229
82. A Hartig, H Ruis *Eur. J. Biochem.*, 1986, **160** 487
83. H E Grennett, F D Ledley, L L Reed, S L Woo *Proc. Natl. Acad. Sci. USA* 1987, **84** 5530
84. T Y Borgford, N Y Beand *Biochemistry*, 1987, **26** 2480
85. G E Schulz, I Shulz, A G Tomaselli, et al. *Eur. J. Biochem.*, 1986, **161** 127
86. G E Sheell, L K Lanett, J B Lingrel *Nature*, 1986, **321** 429
87. C B Newgard, K Nakano, P K Hwoeng, R J Fletterick *Proc. Natl. Acad. Sci. USA*, 1986, **83** 8132
88. E H Fischer *Bull. Inst. Pasteur*, 1983, **87** 7
89. W Gilbert *Nature*, 1978, **271** 501
90. H Neurath *Chem. Scr. B*, 1968, **26** 221
91. T Hunter, J A Cooper *Adv. Cyclic Nucleotide Res.*, 1984, **17** 443
92. K Takio, R D Wade, S B Smith, et al. *Biochemistry*, 1984, **23** 4207
93. H Nojima *FEBS Lett.*, 1987, **217** 187
94. R G Brennan, L H Weaver, B W Mattheus *Chem. Scr. B*, 1986, **26** 251
95. R Jaenicke *Progr. in Biophys. and Mol. Biol.*, 1987, **49**(2–3) 117
96. G J Barton, J E Sternberg *Prot. Eng.*, 1987, **1** 89
97. L Kelly, L A Halladay *Prot. Eng.*, 1987, **1** 137
98. P Argos, Y K Mohanakao *Methods Enzym.*, 1986, **130** 185
99. P Argos, A D Tucher, L Phillipson *Virology*, 1986, **149** 208
100. P Argos *J. Mol. Biol.*, 1987, **193** 385
101. T L Blundell, B L Sibanda, M Y E Sternberg, Y M Thornton *Nature*, 1987, **326** 347
102. T J Hubbard, T L Blundell *Prot. Eng.*, 1987, **1** 159
103. M J Sutcliffe, I Haneef, D Carney, T L Blundell *Prot. Eng.*, 1987, **1** 377
104. M J Sutcliffe, F R F Hayes, T L Blundell *Prot. Eng.*, 1987, **1** 385
105. S H Bryant, M J E Sternberg *J. Mol. Graphics*, 1987, **5** 4
106. M J E Sternberg *NATO ASI Ser, Ser. A*, 1987, **126** 141
107. T A Jones *J. Appl. Crystallogr.*, 1978, **11** 268
108. J Novotny, C Auffray *Nucl. Acids Res.*, 1984, **12** 243
109. J Novotny, C Auffray *Proc. Natl. Acad. Sci. USA*, 1986, **83** 742
110. P Klein, J A Jancquez, C Delisi *Math. Biosci.*, 1986, **81** 177
111. A J Wilkinson, A R Fersht, D M Blow, G Winter *Biochemistry*, 1983, **22** 3581
112. A R Fersht, J P Shi, A J Wilkinson, et al. *Angew. Chem.*, 1984, **96** 455
113. A J Wilkinson, A R Fersht, D M Blow, et al. *Nature*, 1984, **307** 187
114. R J Leatherbarrow, A R Fersht, G Winter *Proc. Natl. Acad. Sci. USA*, 1985, **82** 7840
115. A R Fersht, R J Leatherbarrow, T N G Wells *Nature*, 1986, **322** 284
116. T N C Wells, A R Fersht *Biochemistry*, 1986, **25** 1881
117. T N C Wells, C K Ho, A R Fersht *Biochemistry*, 1986, **25** 6603
118. K A Brown, P Brick, D M Blow *Nature*, 1987, **326** 416
119. A R Fersht, R J Leatherbarrow, T N C Wells *Philos. Trans. Soc. London, A*, 1986, **317** 305
120. H Bedouelle, P Carter, G Winter *Philos. Trans. Soc. London, A*, 1986, **317** 433
121. C K Ho, A R Fersht *Biochemistry*, 1986, **25** 1891
122. A R Fersht *Biochemistry*, 1987, **26** 8031
123. A R Fersht *Biochemistry*, 1988, **27** 1577
124. A R Fersht, J W Knill-Jones, H Bedouelle, G Winter *Biochemistry*, 1988, **27** 1581
125. D H Johnes, A J McMillan, A R Fersht *Biochemistry*, 1985, **24**(2) 5852
126. W H J Ward, D H Jones, A R Fersht *J. Biol. Chem.*, 1986, **261** 9576
127. P Carter, H Bedouelle, G Winter *Proc. Natl. Acad. Sci. USA*, 1986, **83** 1189
128. H Bedouelle, G Winter *Nature*, 1986, **320** 371
129. G J Pielak, A G Mauk, M Smith *Nature*, 1986, **313** 152
130. G J Pielak, K Oikawa, A G Mauk, et al. *J. Am. Chem. Soc.*, 1986, **108** 2724
131. G J Pielak, D W Concar, G R Moore, J P Williams *Prot. Eng.*, 1987, **1** 83
132. P B W ten Kortenaar, P J M H Adams, G I Tesser *Proc. Natl. Acad. Sci. USA*, 1985, **82** 8279
133. C J A Wallace, B E Corthesy *Prot. Eng.*, 1986, **1** 23
134. D Holzche, L Puncipio, K T Conklin, et al. *J. Biol. Chem.*, 1987, **262** 7125
135. R L Culler, G J Pielak, A G Mauk, M Smith *Prot. Eng.*, 1987, **1** 95
136. S L Mayo, W R Ellis, R J Crutchley, H B Gray *Science*, 1986, **233** 948
137. T Sakaki, M Shibata, Y Yubusaki, H Ohkawa *DNA*, 1987, **6** 31
138. T Shimizu, K Hiramo, M Takahashi, et al. *Biochemistry*, 1988, **27** 4138
139. D B Goodin, A G Mauk, M Smith *Proc. Natl. Acad. Sci. USA*, 1986, **83** 1295
140. L A Fishel, J E Villafranca, J M Mauro, J Kraut *Biochemistry*, 1987, **26** 351
141. C S Craik, C Loveqman, T Fletcher, et al. *Science*, 1985, **228** 291
142. C S Craik, S Roczniak, S Sprang, et al. *J. Cell. Biochem.*, 1987, **33** 199
143. L Craf, C S Craik, A Patthey, et al. *Biochemistry*, 1987, **26** 2616
144. D A Estell, J V Miller, T P Graycar, et al. *World Biotech. Rep.*, 1984, **2** 181
145. D A Estell, T P Graycar, J V Miller, et al. *Science*, 1986, **233** 659
146. R R Bott, M Ultsch, J Burnier *ACS Symp. Ser.*, 1987, **334** 139
147. J A Wells, D B Powers, R R Bott, et al. *Proc. Natl. Acad. Sci. USA*, 1987, **84** 31
148. J A Wells, D C Cunningham, T P Graycar, D A Estell *Philos. Trans. R. Soc. London, A*, 1986, **317** 415
149. J A Wells, D B Powers *J. Biol. Chem.*, 1986, **261** 6564
150. P G Thomas, A J Russel, A R Fersht *Nature*, 1985, **318** 375
151. A J Russel, P G Thomas, A R Fersht *J. Mol. Biol.*, 1987, **193** 803
152. D Straus, R T Raines, E Wawashima, et al. *Proc. Natl. Acad. Sci. USA*, 1985, **82** 2272
153. R T Raines, D R Straus, W Gilbert, J P Knowles *Philos. Soc. London, A*, 1986, **317** 371
154. R T Raines, E E Sutton, D R Straus, et al. *Biochemistry*, 1986, **25** 7142

155. G A Petsko, R C Davenport, D Frankel, V L Raybhandary *Biochem. Soc. Trans.*, 1984, **12** 229
156. K A Smith, S F Nowlan, S A Middleton, et al. *J. Mol. Biol.*, 1986, **189** 227
157. S A Middleton, E R Kantrowitz *Proc. Natl. Acad. Sci. USA*, 1986, **83** 5866
158. S F Nowlan, E R Kantrowitz *J. Biol. Chem.*, 1985, **260** 14712
159. E A Robey, H K Schachman *Proc. Natl. Acad. Sci. USA*, 1985, **82** 361
160. E A Robey, S R Wente, D W Markly, et al. *Proc. Natl. Acad. Sci. USA*, 1986, **83** 5934
161. H K Schachman *Biochem. Soc. Trans.*, 1987, **15** 772
162. S R Wente, H K Schachman *Proc. Natl. Acad. Sci. USA*, 1987, **84** 31
163. E H Serpersu, D Shortle, A S Mildvan *Biochemistry*, 1986, **25** 68
164. E H Serpersu, D Shortle, A S Mildvan *Biochemistry*, 1987, **26** 1289
165. E Uhlmann, J A Smith *Nucleosides Nucleotides*, 1987, **6** 331
166. D W Hibler, N J Stolowich, H A Reynolds, et al. *Biochemistry*, 1987, **26** 6278
167. J A Wilde, P H Bolton, M Dell'Acqua, et al. *Biochemistry*, 1988, **27** 4127
168. J Travis, M Owen, P George, et al. *J. Biol. Chem.*, 1985, **260** 4384
169. M Courtney, S Jallet, J-H Tissier, et al. *Nature*, 1985, **313** 149
170. S Jallet, D Carvallo, L H Tessier, et al. *Prot. Eng.*, 1986, **1** 29
171. M Courtney, S Jallet, J-H Ressier, et al. *Philos. Trans. R. Soc. London, A*, 1986, **317** 381
172. M T Mas, L E Resplandor, A D Riggs *Biochemistry*, 1987, **26** 5369
173. C A B Wilson, N Hardman, L A Fothergill-Gilmore, et al. *Biochem. J.*, 1987, **241** 609
174. M T Mas, C Y Chen, R A Helzeman, A D Riggs *Science*, 1986, **233** 788
175. S J Gardell, C S Craik, D Hilvert, et al. *Nature*, 1985, **317** 551
176. D Hilvert, S J Gardell, W R Rutter, E T Kaiser *J. Am. Chem. Soc.*, 1986, **108** 5298
177. S J Gardell, D Hilvert, J Barnett, et al. *J. Biol. Chem.*, 1987, **262** 576
178. J R Winther, M C Keilland-Brandt, K Breddam *Carlsberg Res. Commun.*, 1985, **50** 273
179. J Kraut *Science*, 1986, **231** 1123
180. J E Villafranca, E E Howell, S J Oatley, et al. *Philos. Trans. R. Soc. London, A*, 1986, **317** 405
181. N J Prendergas, T J Delcamp, P L Smith, J H Frusheim *Biochem.*, 1988, **27** 3664
182. M Michiro, Y Jigami, M Morikawa, H Tanaka *Biochem. Biophys. Acta*, 1987, **911** 376
183. M Muraki, M Morikawa, Y Jigami, H Tanaka *Biochem. Biophys. Acta*, 1987, **916** 66
184. N P Lawrence, S Altman *J. Mol. Biol.*, 1986, **191** 163
185. H Wolfes, J Alves, A Fliess, et al. *Nucl. Acids Res.*, 1986, **14** 9063
186. C N Cronin, B A Malcolm, J E Kirsch *J Am. Chem. Soc.*, 1987, **119** 2222
187. A R Clarke, D B Wigley, W N Chia, et al. *Nature*, 1986, **324** 699
188. A R Clarke, D B Wigley, D A Barstow, et al. *Biochem. Soc. Trans.*, 1987, **15** 152
189. C Murali, E H Creaser *Prot. Eng.*, 1986, **1** 45
190. S S Ghosh, S C Bock, S E Rokita, E T Kaiser *Science*, 1986, **231** 145
191. M Yohda, S Ohta, T Hisabori, Y Kagava *Biochem. Biophys. Acta*, 1988, **992** 156
192. G Dalbadie-McFarland, L W Cohen, A D Riggs, et al. *Proc. Natl. Acad. Sci. USA*, 1982, **79** 6409
193. I S Sigal, B G Harwood, R Arentzen *Proc. Natl. Acad. Sci. USA*, 1982, **79** 7157
194. I S Sigal, W F DeGrado, B J Thomas, S R Petteway *Biol. Chem.*, 1984, **259** 5327
195. G Dalbadie-McFarland, A D Riggs, J H Richards *Biochem. Soc. Trans.*, 1984, **12** 226
196. G Dalbadie-McFarland, J J Naitzel, J H Richards *Biochemistry*, 1986, **25** 332
197. P H Seeburg, W W Colly, D J Capon, et al. *Nature*, 1984, **312** 71
198. P J Madguvick, S G Waley *Biochem. J.*, 1987, **248** 657
199. S Gutteridge, I Sigal, B Thomas, et al. *EMBO J.*, 1984, **3** 2737
200. S K Niyagi, R S Foote, R J Murel, et al. *J. Biol. Chem.*, 1986, **261** 10087
201. F C Hartman, T S Soper, S K Miyogi, et al. *J. Biol. Chem.*, 1987, **262** 3496
202. G Voordouw, P A DeVries, W A M Van Den Berg, E P J De Clerk *Eur. J. Biochem.*, 1987, **163** 591
203. W R Tremble, P V Vitanen, H R Sarkar, et al. *Biochem. Biophys. Res. Commun.*, 1984, **119** 860
204. P V Vitanen, D R Menick, H R Sarkar, et al. *Biochemistry*, 1985, **24** 7628
205. J M Naehaus, J Soppa, J K Witgh, et al. *FEBS Lett.*, 1985, **185** 83
206. H R Sarhar, D R Menicj, P V Vitanen, et al. *J. Biol. Chem.*, 1986, **261** 8914
207. D R Menick, H R Sarkar, M S Poonian, H R Kaback *Biochem. Biophys. Res. Commun.*, 1985, **132** 162
208. R J Brooker, T H Wilson *J. Biol. Chem.*, 1986, **261** 11765
209. D R Menick, J A Lee, R J Brooker, et al. *Biochemistry*, 1987, **26** 1132
210. E Ragan, H R Sarkar, P V Vitanen, et al. *Proc. Natl. Acad. Sci. USA*, 1985, **82** 6765
211. I B Püttner, H R Sarkar, M S Poonian, H R Kaback *Biochemistry*, 1986, **25** 4483
212. H R Kaback *Biochemistry*, 1987, **26** 2071
213. F I Tsuji, S Inouye, T Goto, Y Sakaki *Proc. Natl. Acad. Sci. USA*, 1986, **83** 8107
214. T A Craig, D M Watterson, F G Prendergast, et al. *J. Biol. Chem.*, 1987, **262** 3278
215. M Nishiyama, V Matsubara, K Yamamoto, et al. *J. Biol. Chem.*, 1986, **261** 14178
216. M R Lentz, R G Webster, G M Air *Biochemistry*, 1987, **26** 5351
217. X Wli, M C Els, R G Webster, G M Air *Virology*, 1987, **156** 253
218. K N Rand, H Singhn, H C Thogersen, M J Gait *J. Biosci.*, 1985, (1) 89
219. M Singh, S Heapy, M J Gait *Prot. Eng.*, 1986, **1** 75
220. S Heapy, M Singh, M J Gait *Biochemistry*, 1987, **26** 1688
221. N Houla-Herin, H Hara, M Inouya, Y Hirota *Mol. Gen. Genet.*, 1985, **201** 499
222. K Yutani, K Ogasahara, T Tsujita, et al. *J. Biol. Chem.*, 1987, **262** 13429

223. J L Paluh, H Zalkin, D Belsch, H L Weith *J. Biol. Chem.*, 1985, **260** 1889
224. S M Samson, J L Chapman, R Belagaie, et al. *Proc. Natl. Acad. Sci. USA*, 1987, **84** 5705
225. S Hopkins, V Schirch *J. Biol. Chem.*, 1986, **261** 3363
226. S Yamano, K Tanaka, K Matsumoto, A Tohe *Mol. Gen. Genet.*, 1987, **210** 413
227. J Bulis, L D Saraswat, S S Taylor *Biochem.*, 1988, **27** 1570
228. P L Privalov *Biofizika*, 1987, **39** 742
229. W J Becktel, J A Shellman *Biopolymers*, 1987, **26** 1859
230. W Pfeil *Mol. Cell. Biochem.*, 1981, **40** 3
231. S E Lale, A M Klibanov *Biotechnol. Bioeng.*, 1983, **25** 2221
232. J F Brandts *Structure and Stability of Biological Macromolecules* (Edited by S H Timasheff, G D Fasman), Marcel Dekker, New York, 1969, (Translated into Russian), Izd. Mir, Moscow, 1973, p. 174
233. J B Matthew, R F N Gurd *Meth. Enzym.*, 1986, **130** 437
234. D P Goldenberg *J. Cell. Biochem.*, 1985, **29** 321
235. V P Torchilin, A V Maksimenko, V N Smirnov, et al. *Biochim. Biophys. Acta*, 1979, **567** 1
236. G D Kutuzova, N N Ugarova, I V Berezin *Usp. Khim.*, 1984, **53** 1852 [English translation in *Russ. Chem. Rev.*, 1984(11)]
237. H B Bull, R Breese *Arch. Biophys. Biochim.*, 1973, **158** 681
238. E Stellwagen, H Wilgus *Nature*, 1978, **275** 342
239. P K Ponnuswamy, R Muthusamy, P Manavalan *Int. J. Biol. Macromol.*, 1982, **4** 186
240. A Ikai *J. Biochem.*, 1980, **88** 1895
241. H Zuber *Structural and Functional Aspects of Enzyme Catalysis* (Edited by H Eggerer, R Huber), Springer Verlag, Berlin–Heidelberg–New York, 1981, p. 114
242. D P Ward, M Moo-Young *Biotech. Adv.*, 1988, **6** 39
243. D J Merkler, G K Farrington, F C Wedler *Int. J. Pep. Protein Res.*, 1981, **18** 430
244. A Atkinson *J. Appl. Chem. Biotechnol.*, 1976, **26** 577
245. G D Kutuzova, N N Ugarova, I V Berezin *Itogi Nauki i Tekhniki. Ser. Biotekhnologiya* (Advances in Science and Engineering. Biotechnology Series), Izd. VINITI, Moscow, 1986, Vol. 5, p. 5
246. E Stellwagen *Enzyme Eng.*, 1984, **234** 1
247. C Chotia *Nature*, 1975, **254** 304
248. P A Bash, U C Singh, R Langridge, P A Kollman *Science*, 1987, **236** 564
249. R Wetzel *Trends Biotechnol.*, 1987, **12** 478
250. B S Hartley *Philos. Trans. R. Soc. London, A*, 1986, **317** 321
251. J Richardson *Adv. Prot. Chem.*, 1981, **34** 154
252. M W Pantoliano, R C Ladner, P N Bryan, et al. *Biochemistry*, 1987, **26** 2077
253. P Argos *J. Mol. Biol.*, 1987, **197** 331
254. D S C Yang, M Sax, A Chakrabartty, C L Hew *Nature*, 1988, **333** 232
255. C Mitchison, R L Baldwin *Proteins: Struct. Funct. Genet.*, 1986, **1** 23
256. E Qucrol, A Parrilla *Enz. Microb. Technol.*, 1987, **9** 238
257. L J Perry, R Wetzel *Science*, 1984, **226** 555
258. B W Matthews *Biochemistry*, 1987, **26** 6885
259. K A Dill *Prot. Eng.*, 1987, **1** 369
260. M Rechsteiner, S Rogers, K Rote *TIBS*, 1987, 390
261. K V Rote, M Rechsteiner *J. Biol. Chem.*, 1986, **261** 15430
262. R Katznelson, R G Kulka *Eur. J. Biochem.*, 1985, **146** 437
263. S Rogers, R Wells, M Rechsteiner *Science*, 1986, **234** 364
264. J M Baker, J F Dice *Proc. Natl. Acad. Sci. USA*, 1986, **83** 5830
265. A Bachmair, D Finley, A Varshavsky *Science*, 1986, **234** 179
266. E E Stadman *Trends Biochem. Sci.*, 1986, **11** 11
267. M G Grütter, T M Grag, L H Weaver, et al. *J. Mol. Biol.*, 1987, **197** 349
268. T Alber, T M Gray, L H Weaver, et al. *NATO ASI Ser. A*, 1987, **126** 251
269. T Alber, M G Grütter, T M Gray, et al. *UCLA Symp. Mol. Cell. Biol. New Ser.*, 1985, **39** 307
270. T M Alber, Doo-pin Sun, J A Nye, et al. *Biochemistry*, 1987, **26**(13) 3754
271. D Shortle, B Lin *Genetics*, 1985, **110** 539
272. M Matsumura, Sh Rataoka, Sh Aiba *Mol. Gen. Genet.*, 1986, **204** 355
273. K Yutani, K Ogasahara, Y Sugino *Adv. Biophys.*, 1985, **20** 13
274. B C Cunningham, J A Wells *Prot. Eng.*, 1987, **1** 319
275. R B Wetzel *Eur. P. Appl.*, 1986, **155** 832
276. L J Perry, R Wetzel *Biochemistry*, 1986, **25** 733
277. L J Perry, R Wetzel *Prot. Eng.*, 1987, **1** 101
278. J E Villafranca, E E Howell, D H Voet, et al. *Science*, 1983, **222** 782
279. J E Villafranca, E E Howell, S J Oatley, et al. *Biochemistry*, 1987, **26** 2182
280. R T Sauer, K Hehir, R S Stearman, H A Weiss, et al. *Biochemistry*, 1986, **25** 5992
281. C O Pabo, E G Suchanek *Biochemistry*, 1986, **25** 5987
282. M H Heccht, J M Sturtevant, R T Snuer *Proteins: Struct. Funct. Genet.*, 1986, **1** 43
283. T Imanaka, M Shibazaki, M Takagi *Nature*, 1986, **324** 695
284. K Yutani, H Akutsu, K Ogasahara, et al. *Biochemistry*, 1987, **26** 5666
285. M Matsumura, S Yasumura, S Aiba *Nature*, 1986, **323** 356
286. D A Estell, T P Graycar, J A Wells *J. Biol. Chem.*, 1985, **260** 6518
287. D B Wigly, A R Clark, C R Dunn, et al. *Biochim. Biophys. Acta*, 1987, **916** 145
288. L Ramdas, F Sherman, D T Nall *Biochemistry*, 1986, **25** 6952
289. L Ramdas, B T Nall *Biochemistry*, 1986, **25** 6959
290. A Gilles, I Saint-Girons, M Monnot, et al. *Proc. Natl. Acad. Sci. USA*, 1986, **83** 5798
291. C R Matthews, M M Crisanti, J T Manz, G L Gepner *Biochemistry*, 1983, **22** 1445
292. A M Beasty, M R Hurle, J T Manz, et al. *Biochemistry*, 1986, **25** 2965
293. K M Perry, J J Onuffer, N A Touchette, et al. *Biochemistry*, 1987, **26** 2674
294. J I Casal, T J Ahern, R C Davenport, et al. *Biochemistry*, 1987, **26** 1258
295. T J Ahern, J I Casal, G A Petsko, A M Klibanov *Proc. Natl. Acad. Sci. USA*, 1987, **84** 675
296. R Bott *World Biotechnol. Rep.*, 1985, **2** 51
297. A J Russel, A R Fersht *Nature*, 1987, **328** 496
298. S G Sligar, K D Egeberg, Y T Sage, et al. *J. Am. Chem. Soc.*, 1987, **109** 7896
299. L C S Ferreira, V Schwarz, W Keck, et al *Eur. J. Biochem.*, 1988, **171** 11
300. I Crenn, D Ladant, N Guiso, et al. *Eur. J. Biochem.*, 1986, **159** 605
301. H M Hsiung, N G Mayne, G W Becker *Biotechnology*, 1986, **4** 991

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The development of the concept of the chemical bond from hydrogen to cluster compounds

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ABSTRACT. The principal types of chemical bond have been analysed, and their ranges of applicability noted. Fields in which the concept of a localised bond is inapplicable have been indicated, and, in particular, the electronic structure of Δ-polyhedral clusters has been examined. The principle of isolobal analogy has been discussed, and its unique importance for an understanding of the structure of organometallic compounds has been demonstrated.

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I. Introduction

The present-day theory of chemical structure is based on the apparatus of quantum chemistry and the generalisation of experimental data. The methods of quantum chemistry make it possible to obtain fairly reliable information on electronic structure and to predict the physicochemical properties of both existing specific molecules and hypothetical molecules. These characteristics are usually obtained by numerical experiments using computers, and are used either to interpret experimental data or to predict the properties of chemical compounds.[1] The solution of problems of this type has applications, however. It is of no less interest to develop the general principles of the classification of chemical compounds, to describe their structure, and to establish the relationships between structure and properties.[1,2]

Structural theories in chemistry are based on the concept of the chemical bond. This concept, which appeared long before the nature of chemical bonding became clear, arose as a result of the necessity, unavoidable in chemistry, to imagine the breakdown into parts of the integral objects of chemical studies, that is molecules. It was this breakdown of molecules into a set of known parts that made possible a clear description of their structure and the prediction of a number of their physicochemical properties.

The success of the classical theory of chemical structure and its subsequent development proves the appropriateness of the description of molecules by means of chemical bonds and structural formulae. Neither structural formulae nor chemical bonds are real objects. They are theoretical constructions, or ideal formulations.[3,4] The extremely fruitful nature of these abstract imaginary objects indicates, however, that they correctly reflect the most important features of chemical reality. The present review follows the devleopment of the concept of the chemical bond as it is applied to systems of increasing complexity, and indicates the ranges of applicability of this concept.

II. The hydrogen molecule and the chemical bond

The electron in the ground state of the hydrogen atom is in the single valence orbital of this atom, the 1*s*-atomic orbital (AO), which is a function of the spatial coordinates. In a pictorial interpretation, the square of this function defines the density of the electron cloud of the hydrogen atom at a given point in space.

In the hydrogen molecule, the electrons occupy not atomic orbitals but a molecular orbital (MO), encompassing both atoms. In the MO LCAO approximation, the molecular orbitals are constructed from the atomic orbitals. The two 1*s*-atomic orbitals φ_1 and φ_2 give two molecular orbitals: a bonding MO (BMO) $\psi_+ = (\varphi_1 + \varphi_2)/N_+$ which is favourable and whose energy is lower than that of the atomic orbitals, and an antibonding MO (AMO) $\psi_- = (\varphi_1 - \varphi_2)/N_-$ which is unfavourable and whose energy is higher than that of the atomic orbitals[5,6] (Fig. 1).

The density of the electron cloud in the molecule is proportional to the square of the molecular orbital $\psi_\pm^2 = (\varphi_1^2 + \varphi_2^2 \pm 2\varphi_1\varphi_2)/N_\pm^2$. In the expression obtained, the terms φ_1^2 and φ_2^2 correspond to the electron clouds of the atoms, but the most interesting term in it is the so-called interference term $2\varphi_1\varphi_2$. As a consequence of the existence of this term, the density of the electron cloud in the molecule is not equal to the sum of the densities of the atomic orbitals, that is the cloud is deformed.

In the case of the BMO, an excess of electron density arises between the atoms. The negative cloud attracts the positive nuclei. A two-electron two-centre chemical bond is formed.

In the case of the AMO, on the other hand, the interference term decreases the electron density between the atoms. The nuclei are as it were uncovered, their repulsion is not compensated by the attraction of the electrons, and in this state the molecule breaks apart.[7] This is of course a very crude description. Its value can be examined.

Progress in computer technology has provided extremely refined methods of calculation even for fairly complex systems. While they are of undoubted value in quantum chemistry, however, these studies provide comparatively little for its users. Fig. 2 helps to explain why this is so.[8] It gives the potential curves for the hydrogen molecular ion, characterising the change in energy with increase in the distance between the nuclei. Curve *1* was obtained in the approximation just described. The presence of the minimum on this curve reflects the fact that a bond is formed. The depth of this minimum correctly reflects the order of magnitude of the bond energy, and its position the bond length. The method of calculation can be improved. Thus if account is taken of the possible change in the effective charge of the atomic orbital, curve *2* is obtained for the optimum value of the effective charge. If account is also taken of the fact that in the field of a neighbouring nucleus the atomic orbital is polarised, losing its spherical symmetry, the result is curve *3*, part of which is shown in Fig. 2.

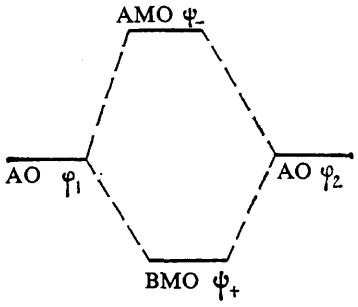


Figure 1. Correlation diagram for the H_2 molecule.

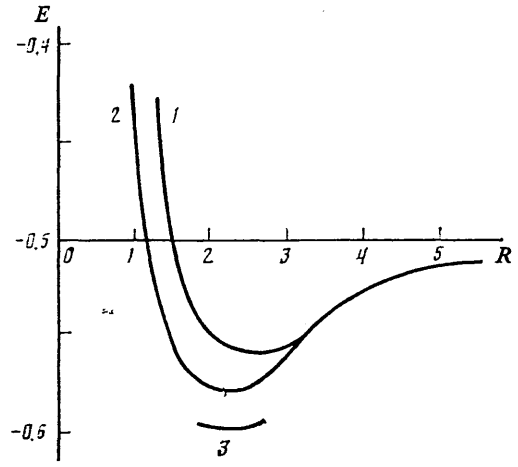


Figure 2. Potential curves for H_2^+ (in atomic units), obtained in different approximations of the MO method: *1*, molecular orbital constructed as a linear combination of the atomic orbitals of the hydrogen atoms; *2*, optimisation of the effective charge of the atomic orbitals carried out; *3*, a polarisation correction to the atomic orbitals introduced.

It is possible to improve the method of calculation even further, to expand the basis set, to abandon the MO LCAO approximation completely, and to proceed to an exact calculation. The results will be increasingly accurate, but this cannot be shown in Fig. 2, since the curves obtained coincide with curve *3*.

This situation is fairly general: the principal qualitative conclusions of greatest importance for chemistry are obtained even in the most approximate calculations. It is not accidental that Nobel Laureate R Hoffman, who has generated the most important theoretical concepts of the last quarter century, bases his work on the simplest quantum-chemical method, namely the extended Hückel method.[9]

Thus the chemical bonding in the two-electron diatomic system formed by the hydrogen molecule has been described by the two-electron two-centre bond. The description of polyatomic many-electron systems can now be considered.

III. The chemical bond and organic chemistry. The principle of isolobal analogy

A molecule is a single system bonded by forces of electrostatic interaction and consisting of relatively immobile nuclei and a cloud of rapidly moving electrons. In chemistry, however, the integral picture of chemical bonding is broken down, and replaced by a set of chemical bonds. It can be shown for the case of the methane molecule how the concept of the two-electron two-centre bond, which is strictly applicable to the hydrogen molecule and others, can be transferred to polyatomic molecules.

The carbon atom, like that of all the elements of the second period, has four valence orbitals. These are used to construct four equivalent tetrahedral hybride orbitals (HO),[10,11] each of which contains an electron. In the methane molecule, each of these HO is directed towards its own hydrogen atom. The hybrid orbital of the carbon atom and the atomic orbital of the corresponding hydrogen atom are used to construct localised molecular orbitals (exactly as in the case of the hydrogen molecule). The two atomic orbitals give two molecular orbitals: one bonding and one antibonding. The bonding orbital is occupied by two electrons. The four equivalent two-electron two-centre C—H bonds of methane are described in this way.[12]

The conceptual breakdown of a whole into parts is of course always arbitrary, so that the description of polyatomic molecules by means of two-centre bonds is also arbitrary, but the whole of chemical practice indicates that the concept of the chemical bond is extremely fruitful. The task is essentially to establish the fields of chemistry in which the concept of the two-centre bond reflects the principal features of chemical reality, and those in which it has to be replaced.

The electronic structure of the hydrides of the elements of period II following carbon can now be discussed, beginning with nitrogen. The nitrogen atom, like the carbon atom, has four valence orbitals; these can be used to obtain four tetrahedral orbitals, into which the valence electrons can be put. The nitrogen atom has five valence

electrons, however. If one of these is removed, then one electron remains in each hybrid orbital, so that it is possible, exactly as in the case of the methane molecule, to construct the four two-electron two-centre N–H bonds of the ammonium cation.

But what if the electron is not removed? One of the hybrid orbitals of nitrogen will then contain two electrons (Fig. 3). The bonding and antibonding molecular orbitals constructed from this orbital and the atomic orbital of hydrogen will then have to accommodate three electrons, and one electron enters the antibonding orbital. This is less favourable than remaining in the atomic orbital, and instead of a bond with the hydrogen atom, a lone pair of electrons appears on the nitrogen atom. Nitrogen forms only three N–H bonds. The oxygen atom has two lone pairs, the fluorine atom has three, and the neon atom has four lone pairs, and does not form any bonds.

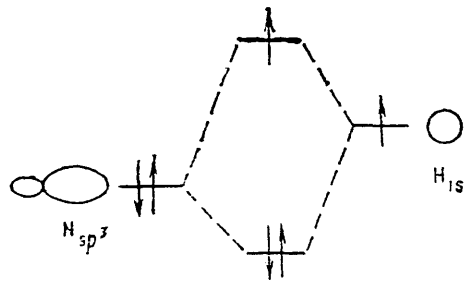


Figure 3. Correlation diagram of a three-electron system.

Thus when spare electrons appear, that is when the number of valence electrons becomes greater than the number of valence orbitals, lone pairs appear.[13] It will be seen that this is not the only way to distribute extra electrons, but it is the simplest and most widespread.

A number of simple groups can now be considered. Firstly, the fluorine atom, which is much more complex than the hydrogen atom. The only similarity between them is that the fluorine atom, like the hydrogen atom, has only one boundary orbital with an unpaired electron—one "working" boundary orbital.† The hydroxyl group also has only one boundary orbital with an unpaired electron, which coincides with one of the valence orbitals of the oxygen atom. Of the remaining three valence orbitals of oxygen, two are occupied by lone pairs and one is involved in the O–H bond. The NH_2 group also has only one orbital with an unpaired electron; of the remaining three valence orbitals of nitrogen, one is occupied by a lone pair, and the other two are involved in the formation of two N–H bonds.

The CH_3 group also has only one symmetrical boundary orbital containing an electron. The other three valence orbitals of the carbon atom are involved in C–H bonds.

† The boundary orbitals are the highest occupied and the lowest unoccupied orbitals.

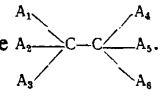
Thus the groups CH_3, NH_2, OH, F, and H have the same number of boundary orbitals containing unpaired electrons. These groups are called isolobal (from "lobe"), and this is represented as follows:

$$CH_3 \overset{0}{\longleftrightarrow} NH_2 \overset{0}{\longleftrightarrow} OH \overset{0}{\longleftrightarrow} F \overset{0}{\longleftrightarrow} H.$$

The well-known principle of isolobal analogy[14–17] can now be used.

According to this principle, isolobal groups can replace one another, so that as soon as methane is known to exist, it means that methyl fluoride may also exist, that the formation of methyl alcohol is probable, that the existence of methylamine is possible, and that ethane should be stable.

The statement that the replacement of a hydrogen atom in methane by a methyl group will give a stable molecule is based only on the fact that three valence orbitals of the carbon atom in the methyl group are involved in bond formation. The fact that they are involved in bonds with hydrogen atoms in particular is not important. Thus the principle of isolobal analogy suggests the existence of

molecules of the type  . The formula used the letter A,

to which no definite chemical significance is attached. This can be any group isolobal with hydrogen.

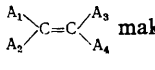
The ethylene molecule, which is made up of two methylene groups CH_2, can now be considered. Two of the sp^2 hybrid orbitals of the C atom of the methylene group are involved in C–H bonds. This leaves two boundary orbitals. The two-electron two-centre bonds of ethylene are constructed from these boundary orbitals: the σ-bond from the sp^2-orbitals and the π-bond from the *p*-orbitals orthogonal to them.[18–20]

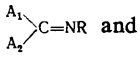
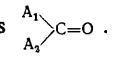
Groups isolobal with the methylene group CH_2 can now be considered.

In the NR group, one of the valence orbitals of the nitrogen atom is involved in the N–R bond, and a second contains a lone pair. This leaves two boundary orbitals, in which the two remaining valence electrons of nitrogen are placed, so that this group is isolobal with the methylene group. The oxygen atom is also isolobal with the methylene group. Thus two of its four valence orbitals are occupied by lone pairs, and the remaining two are boundary orbitals, each containing an unpaired electron. Thus

$$CH_2 \overset{0}{\longleftrightarrow} NR \overset{0}{\longleftrightarrow} O$$

and according to the principle of isolobal analogy the existence of

ethylenes  makes it possible to assume the existence of

imines  and carbonyl compounds  .

The acetylene molecule can now be considered. This molecule is made up of two methylidyne groups CH. One *sp*-hybrid orbital of the carbon atom of the CH group is involved in the C–H bond, leaving three orbitals: the symmetrical *sp*-orbital and two antisymmetric *p*-orbitals of the carbon atom perpendicular to it. Each of these boundary orbitals contains one electron. These orbitals are used to construct the three two-electron two-centre bonds of the acetylene molecule: one σ-bond and two π-bonds.[21] A group of any type, size, or structure, so long as it has three boundary orbitals with three electrons, will be isolobal with the CH group. In particular, the nitrogen atom is isolobal with the methylidyne group; one

valence orbital of the nitrogen atom is occupied by a lone pair, and the three remaining orbitals each contain one electron: CH ⟷ N. Thus hydrocyanic acid HCN and in general nitriles RCN exist.

The variety of isolobal groups and the infinite possibilities of their different combinations and superstructures indicates that by making use of the principle of isolobal analogy it is possible to "synthesise" on paper an unlimited number of molecules. And due credit must be given to chemists: very many of these compounds have also been obtained in flasks. Of course, when planning their syntheses, organic chemists did not know that they were using the principle of isolobal analogy.

The demonstration of the principle of isolobal analogy using the simplest examples was intended to emphasise its essential feature, namely the interchangeability of isolobal groups, which in turn is a consequence of the similarity in their ability to form chemical bonds. This ability is determined by the nature of the boundary orbitals.‡ A second, so to speak, technical aspect of the isolobal analogy is the establishment of the isolobal nature of groups. Groups are said to be isolobal if they have the same number of boundary orbitals with similar symmetry properties, similar three-dimensional structures, similar energy values, and the same number of electrons occupying these boundary orbitals.[16,17]

Organic chemistry has done extremely well without the isolobal analogy; more accurately, it has always used it, but only implicitly. the isolobal nature of the characteristic groups of organic chemistry was known to organic chemists, so to speak, historically, and was established empirically with no knowledge of the nature of boundary orbitals, long before the appearance of the concept of orbitals in general. To chemists, the isolobal nature of the above groups is obvious. The fruitfulness of the principle of isolobal analogy is revealed in non-traditional fields at the boundary between organic and inorganic chemistry, and in particular in organometallic chemistry.

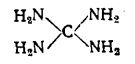
Hoffmann was able not only to express clearly an idea which was in the air but also to select an extremely successful term,[14,15] which spread rapidly. Hoffmann, however, did not simply propose the term and the concept; he used it extensively and demonstrated its value. For most organometallic fragments, which are often very complex, isolobal character is neither obvious nor trivial. Hoffmann had therefore to determine the nature of the boundary orbitals of many organometallic fragments, and this led to the unique library of isolobal groups.[16]

The isolobal analogy makes it possible to understand the structure of complex organometallic compounds and clusters, reveals in so-called monsters usual organic structures in the most remarkable forms, and prompts the choice of completely unexpected directions in the search for new types of compound by analogy with organic chemistry. According to Hoffmann,[16] the isolobal analogy "... brings together different sub-fields of our central science. We are separated, split asunder — organic, inorganic, physical, biological, analytical chemists — by the very largesse of our creation. The variety of molecules we create, and the methods we use to study them, breed jargon and specialisation. Yet underneath the seeming complexity there must be a deep unity ...".

‡ Different boundary orbitals of the same group may be "working" orbitals, depending on the specific chemical situation. This explains the complexity and ambiguity of isolobal relationships, particularly when lone pairs are present together with unpaired electrons in the boundary orbitals.[16]

Chemistry lives and develops by analogies. An analogy, however, is an analogy, and not a law. Hoffmann often pointed this out, and warned that the isolobal analogy suggests possibilities, but does not necessarily guarantee their realisation.[16]

An example is provided by a molecule which is faultless from the viewpoint of the isolobal analogy, but which it has not yet been possible to synthesise:



Thus by using the concept of the two-electron two-centre chemical bond and the isolobal analogy it is possible to construct and describe an unlimited number of saturated and unsaturated molecules. It cannot be said, however, that all organic compounds are described completely by two-centre chemical bonds.

The conceptual breakdown of a molecule into two-centre bonds is fruitful only when it corresponds to chemical reality, that is when it is possible to regard these bonds as more or less independent of one another. In fact, of course, they do influence one another, but these influences should be slight. This condition is usually satisfied for carbon σ-bonds. This is due to the strength of these bonds, and the fact that they are compact and localised in space. π-Bonds are weaker, and more easily polarised. Their three-dimensional structure is such that the interaction of conjugated π-bonds is considerable. In large planar conjugated systems, individual π-bonds are often changed until they are unrecognisable, and in cyclic aromatic systems it is no longer possible to speak of two-centre π-bonds.

The π-electron systems of aromatic molecules are indivisible; they represent a single whole, to which the concept of two-centre bond is inapplicable.

IV. The chemical bonds formed by non-transition elements

The atoms of the elements of period III, like those of period II, each have four valence orbitals, in which their valence electrons are situated. The single but very significant difference between them and the elements of period II is that their valence orbitals are much larger and more diffuse.[22–24] This follows both from the most general physical considerations and from the fact that in the hydrogen atom and one-electron cations the average radius R of an orbital increases with increase in the principal quantum number n according to the law $R \sim n^2/Z$.[22] In many-electron atoms the relationship is naturally more complex, but the general trend is preserved. It is reflected, for example, in Slater's rules, which define the form of the Slater atomic orbitals.[23] The differences in the sizes of the valence orbitals of the atoms of the elements of periods II and III are also reflected in the positions of the radial density maxima[24] and in other characteristics.

As a result of the larger size of the valence orbitals, the simple bonds formed by the atoms of the elements of period III are longer, weaker, and more easily polarised. As a result, the interaction of these bonds with one another, and more particularly with π-bonds and with lone pairs, that is their ability to take part in hyperconjugation, is much greater. These interactions are not too strong, however, and the concept of the two-electron two-centre chemical bond is still applicable to the chemistry of the elements of period III.

Since the features of interest are those relating to the development of the concept of the chemical bond, and not the explanation of the properties of the elements of period III (see for example the review

by Bochvar and co-workers[25]), only two characteristics of these elements will be considered.

The atoms of the elements of period III are larger than those of period II, it is possible to place five or six atoms round them, and they form hypervalent compounds such as sulphur hexafluoride SF_6 and phosphorus pentachloride PCl_5.

The structure of the phosphorus pentachloride molecule[25,26] can be considered.

Three of the chlorine atoms lie in the equatorial plane. Phosphorus is joined to them by ordinary two-electron two-centre bonds lying at an angle of 120° to one another. These bonds are formed by three sp^2-hybrid orbitals of phosphorus. Phosphorus still has one $3p_z$-orbital at right angles to them (Fig. 4), containing its lone pair. Above and below the phosphorus atom there are two axial chlorine atoms. Phosphorus has two electrons with which to form two P—Cl bonds, but does not have two orbitals, one for a bond with the upper chlorine atom and another for a bond with the lower atom, and has only one, which has to interact with the two orbitals of the axial chlorine atoms.

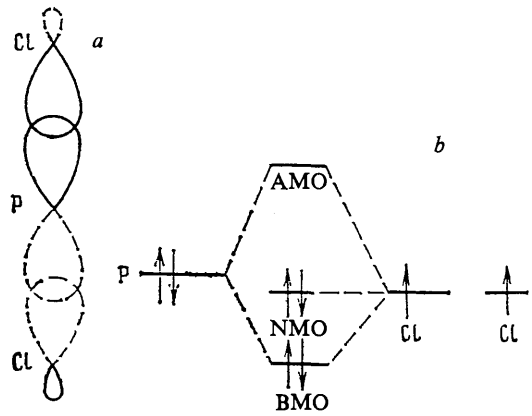


Figure 4. Three-centre bonds in hypervalent compounds: *a*, bonding molecular orbital of the three-centre bond; *b*, energy level diagram.

The three atomic orbitals give three molecular orbitals: one bonding (BMO), one non-bonding (NMO), and one antibonding (AMO). The four electrons are placed in these orbitals. Two enter the three-centre BMO. Three-centre BMO are much more favourable than two-centre BMO,[27] and the two electrons entering the three-centre BMO form the bond between phosphorus and the two axial chlorine atoms. The two remaining electrons enter the NMO; they are not involved in bonding, but do not hinder it.

This situation is characteristic of other hypervalent compounds. In hypervalent compounds a new type of bond appears — the two-electron three-centre chemical bond. The extra electrons not involved in bonding occupy non-bonding molecular orbitals.

The second characteristic of the atoms of the elements of period III is also related to their size. As a result of the greater size of the valence orbitals of the atoms of the elements of period III, these atoms form longer bonds. At these distances, π-overlap is ineffective, and the elements of period III form extremely weak π-bonds.[28–30]

Thus in the nitrogen molecule N_2 the atoms are joined by three strong bonds, one σ-bond and two π-bonds, whereas the P_2 molecule does not exist under ordinary conditions, but is dimerised. It is more favourable for the phosphorus atom to form three strong bonds with three other phosphorus atoms situated at the vertices of a tetrahedron than to form one strong bond and two weak π-bonds in the P_2 molecule.[25]

The silicon atom, like the carbon atom, is tetravalent. One of the electrons of the lone pair, which in the ground state of the Si atom occupies the *s*-orbital, is transferred to the unoccupied *p*-orbital ("is unpaired"), and the energy expended is fully recovered in the formation of two additional strong bonds. The situation is quite different if the additional bonds are π-bonds, whose formation does not compensate the expenditure of energy for the "unpairing" of the lone pair of *s*-electrons.

Thus for carbon,[31] the equilibrium between hydrocyanic acid and its isomer is displaced towards the isomer containing tetravalent carbon HC≡N. The silicon analogue, on the other hand, exists in the form HN=Si with divalent silicon. The silicon π-bonds are so weak that the unpairing of the lone pair of silicon is unfavourable. For the same reason, silicon forms not the analogue of acetylene but its isomer with divalent silicon $H_2C=Si$.

The elements of period III form multiple bonds only when special conditions are fulfilled, for example when there is spatial protection of the multiple bond by bulky substituents.[32,33] The difficulty of synthesising compounds of the elements of period III with multiple bonds is leading to a search for the factors stabilising molecules containing these bonds.[34]

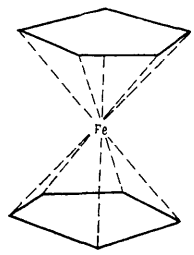
These examples have been considered in order to emphasise that because of the low strength of the π-bonds, the elements of period III do not form large planar conjugated molecules or more particularly aromatic compounds. Thus overall the concept of the two-centre bond plays an even greater role in the chemistry of the elements of period III than in organic chemistry.

V. The chemical bonds formed by transition metals

The situation is radically different for transition metals. Transition metals differ from non-transition elements in that, in addition to *s*- and *p*-valence orbitals, they also have five working *d*-orbitals,[35] that is they have a total of nine valence orbitals. They therefore obey not the octet rule but the effective atomic number (EAN) rule, that is their compounds are stable when the valence level of the transition metal atom contains 18 electrons.§ They can therefore form more bonds, and can have more lone pairs. The octahedral configuration with six bonds is most frequently encountered. The two-centre bonds formed by transition metals with other atoms and in particular with carbon do not differ essentially from the two-electron two-centre bonds formed by non-transition elements.[37] It is not these bonds, but the bonds in transition metal π-complexes, that are specific for transition metals.

§ For a modern substantiation of the Lewis—Sidgwick rule (the EAN rule), see the paper by Mingos and Hawes.[36]

The electronic structure of transition metal π-complexes cannot be described by two-centre bonds. It is possible to take as an example the molecule of ferrocene



In this molecule the iron atom is situated between two parallel cyclopentadienyl rings so that it is next to ten carbon atoms. The iron atom cannot form ten bonds with carbon atoms, however. It has neither the electrons nor the orbitals for this. Since it is not possible to represent the π-complex uniquely using two-centre bonds, and a large number of structures usually have to be considered, the description using resonance theory is too cumbersome, and is used by hardly anyone apart from Pauling himself.[38,39] The opinion has grown that π-complexes have to be described by the molecular orbital method. The MO method, however, considers the molecule as a whole. The results are generally not readily transferable from one molecule to another. Moreover, it is difficult to interpret this description in a manner familiar to chemists.[40]

It is not necessary, however, for transition metal π-complexes, to give up ordinary chemical ideas based on the need for the conceptual breakdown of the whole into parts. It is simply because it is not possible in this case to represent the molecule by two-centre bonds that its conceptual breakdown into larger parts is necessary. In π-complexes the transition metal atom is bonded not to individual atoms of the π-ligand but to its entire π-electron system as a whole.

The bonding molecular orbital of an ordinary bond is constructed from the atomic orbitals of two atoms. It contains two electrons. This describes the two-electron two-centre chemical bond. The bonding molecular orbital of a generalised bond is constructed from an atomic orbital of the transition metal atom and a molecular π-orbital (MO) with appropriate symmetry from the ligand, which in its entirety acts as the second partner in the bond. This bonding molecular orbital contains two electrons. This describes the two-electron multi-centre generalised chemical bond.[40] Fig. 5 shows generalised chemical bonds (GCB) for the case where the ligand is a ring. The lowest-energy π-orbital of the ring is symmetrical with respect to the metal–ring Z axis. It can interact with a metal hybrid orbital (HO) symmetrical with respect to this axis. A headlight-shaped multi-centre generalised σ-bond is formed.[41] The ring π-orbitals of next lowest energy have one nodal surface, containing the Z axis, and are π-orbitals. They can interact with metal π-orbitals. Two-lobed generalised chemical π-bonds are formed. There are two such bonds.[40]

Generalised chemical bonds are localised metal–ligand (given ligand) bonds, independent of the number and nature of other ligands.[40] It has already been emphasised that the concept of bonds is meaningful only if the interaction of the local bonds into which it is possible to mentally break down the molecule is slight and if these local bonds are more or less independent of one another. A familiar example will show clearly that this condition is fulfilled for generalised chemical bonds.[35]

The example to be considered is benzenetricarbonylchromium. Chromium is joined to the ring by three two-electron multi-centre generalised chemical bonds: one headlamp-shaped σ-bond and two two-lobed π-bonds. The six electrons for these bonds are supplied by the ring. Chromium is joined to each of the carbonyl groups by a two-electron two-centre bond. The six electrons for these bonds are provided by the lone pairs of the carbon atoms of the carbonyl groups. The remaining three valence orbitals of the chromium atom are occupied by lone pairs. The six electrons of the generalised chromium–ring bonds, the six electrons of the bonds formed by chromium with the carbonyl groups, and the six valence electrons of chromium make up a total of eighteen electrons in the valence level of chromium, that is the molecule obeys the EAN rule and is stable. When the chromium atom is replaced by the manganese atom, there will again be 18 electrons if the number of electrons

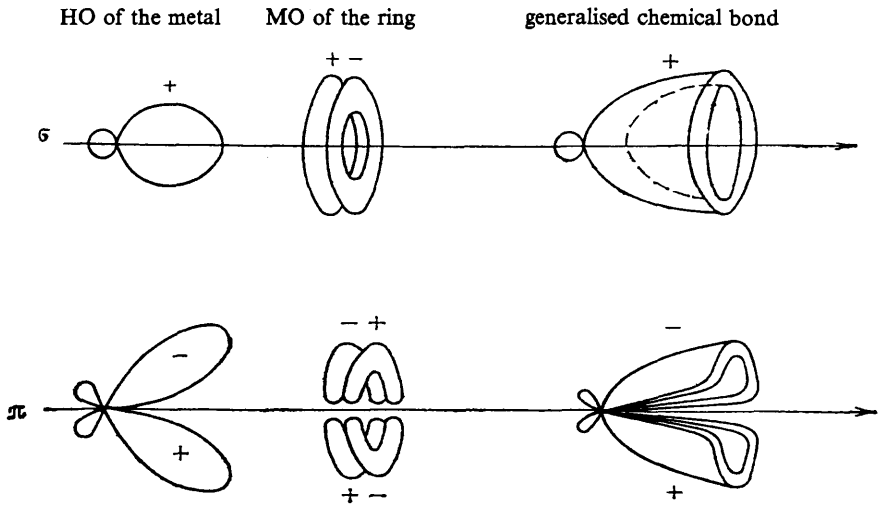
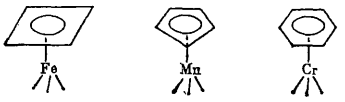


Figure 5. Generalised chemical σ- and π-bonds.

provided by the ring is reduced by one. In $(C_5H_5)Mn(CO)_3$, of the six electrons of the three bonds between the ring and the metal, one is provided by manganese, and five by the cyclopentadienyl ring, replacing the benzene ring. On going to iron, to satisfy the EAN rule, the cyclopentadienyl ring must be replaced by the cyclobutadienyl ring.



In the series of compounds considered, both the metal atom and the ring in the metal–ring bonds change, that is both partners of the generalised chemical bonds change. Nevertheless, the bonds with the carbonyl groups are not sensitive to this, and the arrangement and properties of the carbonyl groups remain almost unchanged in the series being considered.[42–48] Conversely, when the carbonyl groups are replaced by other groups, the changes in the properties of the ring also do not exceed those corresponding to the usual bond influences.[49–51] Thus generalised chemical bonds satisfy the requirement that they should be relatively independent of one another — the principal condition for the fruitful application of the concept of the chemical bond.

Two remarks may be added. Firstly, the similarity between the symmetry of the molecular π-orbital of the ligand and the symmetry of the atomic orbital of the transition metal can be only approximate. Generalised chemical bonds need not be as symmetrical as those between a metal and a ring. For example, the $Fe(CO)_3$ group can combine not only with cyclobutadiene but also with butadiene[52] and even with unsymmetrical heterobutadienes.[53,54] In this case, all that remains of the similarity in the symmetries of the orbitals of the metal and the ligand is the similarity in the distribution of the sign. The ligand π-orbital whose sign remains unchanged in the region between the ligand and the metal interacts with a hybrid σ-orbital of the metal; the ligand π-orbital whose sign changes only once in this region interacts mainly with hybrid π-orbitals of the metal, etc.

The second remark concerns the multiplicity of the metal–ligand bond.

For the atoms of transition metals in the middle of the series, the EAN rule applies rigorously, since they each have nine fully adequate valence orbitals. The ligand in a π-complex also has a whole set of molecular π-orbitals with different symmetry properties. Naturally, with the variety of these two sets of orbitals, it usually happens that there are not one but several pairs of orbitals in which the partners have symmetry suitable for interaction. Thus between a typical transition metal and a π-ligand, several generalised chemical bonds are formed simultaneously, that is the bonds in typical π-complexes are multiple bonds. For a metal of this kind, the bond with a π-ligand is much stronger than an ordinary metal–carbon σ-bond, so that competition between the two types of bond is unlikely.

For the transition metals at the start of the series, donor–acceptor bonds are weakened as a result of the high energy of the unoccupied *d*- and more particularly *p*-orbitals.[55] The formation of several such bonds is also unfavourable because it would lead to breakdown of the electrical neutrality principle, according to which the charges of the atoms in stable complexes should lie in the range from −1 to +1.[56] The most important feature, however, is that the small number of valence electrons in the metal atom excludes synergic stabilisation of the bonds as a result of the superposition of donor–acceptor and dative interactions. All this leads to breakdown of the EAN rule, and at the same time prevents the formation of additional generalised chemical bonds in π-complexes. Thus for example the compound Cp_2TiCl_2 can be described as a derivative of tetravalent titanium, whose four valence orbitals form two bonds with chlorine atoms and two bonds with the rings. The bond formed by titanium with the ring is an ordinary headlamp-shaped generalised chemical σ-bond. The strengths of the ordinary and generalised σ-bonds do not differ greatly from one another. This leads to competition between them.

An example is provided by the tetracyclopentadienyl derivatives of the transition metals at the start of the series. The competition between the ordinary and generalised chemical bonds in these molecules is also indicated by the easy exchange between the rings, joined to the metal in different ways,[57] and by the existence of a whole set of structures: with one h^5- and three h^1-rings (M = Mo [58]); with two h^5- and two h^1-rings (M = Ti,[59] Hf,[60] Nb, Ta [61]); with three h^5- and one h^1-ring (M = Zr [62]); and with four h^5-rings (M = U,[63] Th [64]). The EAN rule is not obeyed in any of these molecules.

Deviations from the EAN rule are also observed for the atoms at the end of the transition metal series. As a result of the rapid decrease in the energy of the *d*-orbitals of the transition metals at the end of the series, the *d*-electrons to a large extent lose the properties of valence electrons and become core electrons.[65] This brings to nought the synergic stabilisation of the donor–acceptor bonds by the dative interactions. At the same time, the increase in the difference in the energies of the *s*- and *p*-orbitals[66] leads to the successive exclusion of the latter from the bonding, leading to the appearance of 16-electron and then 14-electron complexes. The bonds formed by the π-ligands with the metal are no longer multiple bonds, and competition between the ordinary generalised chemical bond with the π-ligand and the ordinary simple two-centre metal–carbon bond again becomes possible.

Moving further down the periodic table does not lead to anything new in the development of the concept of the chemical bond. The non-transition elements of the subsequent periods are very similar to those of period III, and the transition metals of the later periods do not differ fundamentally from those of period IV.

VI. The chemical bond and electron-deficient compounds

The boron atom, like the carbon atom, has four valence orbitals, but only three valence electrons. The molecules of boron chloride BCl_3 and fluoride BF_3 are planar. The B–Hal bonds lying at an angle of 120° to one another are formed by the sp^2-hybrid orbitals of boron. The $2p_z$-orbital of boron remains unoccupied, but the p_z-orbitals of the halogens contain lone pairs of electrons. These pairs partly occupy the unoccupied p_z-orbital of boron, decreasing its unsaturation, and the molecules exist, although the two compounds are the strongest Lewis acids.[67] In boron hydride, the hydrogen atoms have nothing to give to the unoccupied p_z-orbital of boron and nothing with which to soften its unsaturation, and the hydride BH_3 does not exist, but dimerises. The structure of diborane B_2H_6 has been the subject of a discussion extending over several decades. The first workers[68–74] to establish the true structure of diborane included the Soviet scientists Nekrasov and Dyatkina.[70–74] Syrkin has told how Dyatkina's conclusion, based on quantum-chemical calculations, was not believed, because it was considered that the

structure of diborane had been established experimentally,[75,76] by methods including X-ray diffraction.[76] Diborane had been assigned an ethane-like structure. It was true that it was still not clear what held the two boron atoms together, since there were no electrons for a B—B bond (Fig. 6*a*). Many, including Lewis,[77] Sidgwick,[78] and Pauling,[79] tried to find a way out of this difficulty, and considered that the incomprehensible ethane-like structure of diborane had been "explained". Dyatkina was not stopped either by this Areopagus of theoreticians or by "experiment". Being a quantum chemist, she recalculated the diffraction pattern, and showed that the pattern agrees better with the diborane structure which she had proposed than with the ethane-like structure.[74]

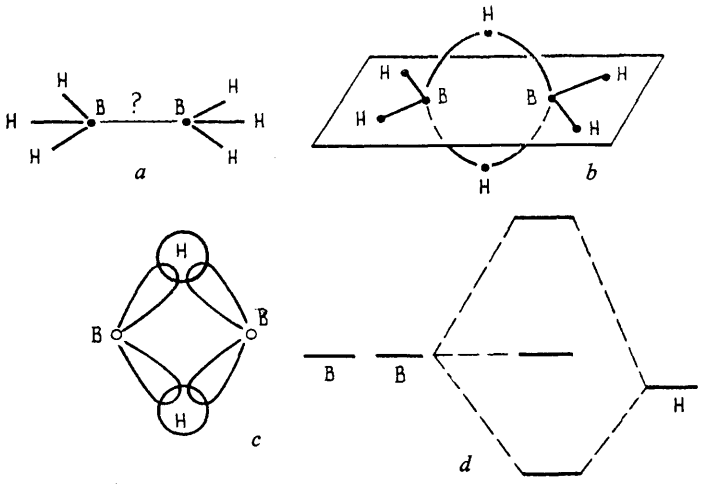


Figure 6. Diborane B_2H_6: *a*, ethane-like structure of diborane; *b*, actual structure of diborane; *c*, B—H—B bridging bonds of diborane; *d*, energy level diagram for the B—H—B bridging bond.

The structure of diborane has now been determined with limiting accuracy.[80] In the diborane molecule, four hydrogen atoms are joined to boron atoms by ordinary two-centre bonds. These four bonds lie in the horizontal plane, as in ethylene. The two remaining hydrogen atoms lie symmetrically above and below this plane, joining the boron atoms by two bent B—H—B bonds (Fig. 6*b*). The central part of diborane in the vertical plane is represented in Fig. 6*c*. These bonds are called bridging bonds.

The molecular orbitals of the bridging bond are constructed from the atomic orbitals of a hydrogen atom and two boron atoms. The three atomic orbitals give three molecular orbitals: bonding, non-bonding, and antibonding. The bonding orbital contains two electrons. A two-electron three-centre chemical bond is formed (Fig. 6*d*). Thus diborane contains a total of six two-electron localised bonds: four two-centre B—H bonds and two three-centre B—H—B bridging bonds. Thus 12 electrons are required, and these are provided by the six hydrogen atoms and two boron atoms.

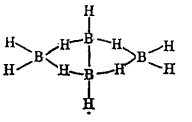
Diborane is a representative of the so-called electron-deficient compounds, that is compounds in which the number of valence electrons is smaller than the number of orbitals. When the number of electrons is greater than the number of atomic orbitals, lone pairs are formed. When the number of electrons ($2n$) is exactly equal to the number of atomic orbitals ($2n$), two-centre bonds are formed. The $2n$ atomic orbitals form $2n$ two-centre molecular orbitals; of these, n are bonding, and n are antibonding. All the valence electrons occupy the n bonding molecular orbitals. If however the number of electrons is smaller, then some of the two-centre bonding molecular orbitals remain unoccupied, but molecules are stable only if all the BMO are occupied. The result is the formation of three-centre bonds. As before, two electrons are involved in the three-centre bond, but it is constructed from three atomic orbitals. Thus when there are insufficient electrons, the extra atomic orbitals can be absorbed by three-centre bonds. If for each extra atomic orbital a three-centre bond is formed instead of a two-centre bond, then all the bonding molecular orbitals will be occupied, and the molecule will be stable.[13,81]

The principle of isolobal analogy suggests that the role of bridge need not necessarily be played by hydrogen, and that the latter can be replaced by any group isolobal with it, for example the methyl group $CH_3 \leftrightarrow H$. In fact, the dimer of trimethylaluminium is constructed in exactly the same way as diborane. It contains two bridging Al—CH_3—Al bonds. The carbon atoms of the remaining methyl groups lie in a plane perpendicular to the plane of the bridges, and are joined to aluminium by ordinary two-centre bonds.[82]

Thus in electron-deficient compounds a new type of bond appears — the two-electron three-centre bridging bond.

Next in order of complexity after diborane come the boron hydrides B_4H_{10} and B_5H_{11}. In the hydride B_4H_{10} [83,84] there are four boron atoms and therefore a deficit of four electrons. It should therefore contain four three-centre bonds to absorb the four extra atomic orbitals, so that the valence electrons will occupy all the BMO.

In fact, in the borane B_4H_{10} the boron atoms are joined by four hydrogen bridges. The remaining six hydrogen atoms are terminal, and are joined to boron by ordinary two-centre bonds. These ten bonds take up 20 electrons. The remaining two electrons join two boron atoms by a two-centre bond.



This description of one of the simplest boron hydrides is already not so simple, but, simple or complicated, it at least adequately reflects the structure of the molecule. Thus the structure is effectively described by more or less independent bonds with a definite location in space: seven two-centre and four three-centre bridging bonds. For the hydride B_5H_{11}, the situation is fundamentally less satisfactory. Before its structure is discussed, however, another type of three-centre bond can be considered (Fig. 7).

In the hypervalent compounds[26] examined above, the three-centre bond is produced because of a deficit of atomic orbitals; the central atom has only one orbital to form bonds with two ligands (Fig. 7*a*). The three-centre bridging bond,[13] formed because of a deficit of electrons, was then described. In this case the orbitals of the outer atoms overlap the orbital of the bridging atom (Fig. 7*b*). In addition to these open three-centre bonds, there exist central three-centre bonds,[13] where the atoms are situated at the vertices of a regular triangle, and their orbitals are directed towards the centre of the triangle. These three atomic orbitals give three MO: one

bonding and two antibonding. The symmetrical BMO contains the two electrons of the central three-centre bond joining three atoms (Fig. 7*c*).

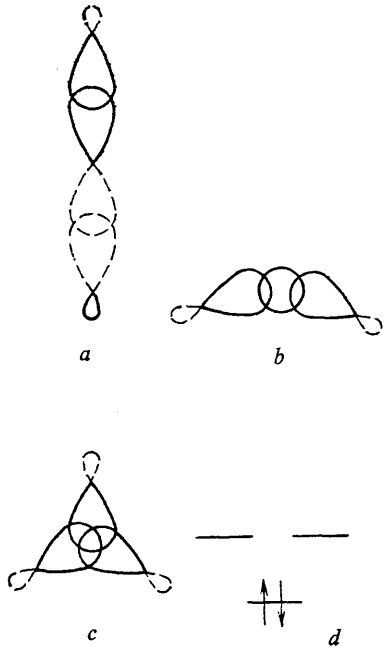
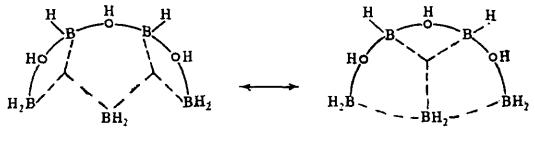


Figure 7. Three-centre bonds: *a*, three-centre bond in hypervalent compounds; *b*, bridging bond in electron-deficient compounds; *c*, central three-centre bond; *d*, energy level diagram of the central three-centre bond.

The boron hydride B_5H_{11},[85,84] in which there is a deficit of five electrons, has two central three-centre bonds and three bridging bonds with hydrogen bridges, that is five three-centre bonds are formed. The remaining eight hydrogen atoms are joined to boron by ordinary two-centre bonds. Another representation of the B_5H_{11} molecule is possible, however. All the localised bonds with hydrogen atoms, both the ordinary two-centre bonds and the three-centre bridging bonds, remain unchanged, but the bonding between the boron atoms can be represented not by two central three-centre bonds but by one central and one open, that is the B_5H_{11} molecule can be described by two different structures.



When a molecule can be described by different structures, it is a clear indication that the representation involving individual more or less isolated bonds does not correspond to chemical reality. The most complex non-conjugated organic molecule can be represented perfectly by a single structure, whereas the description of the simplest aromatic molecule, benzene, whose π-system forms a single whole, requires at least two structures.

The examination of aromatic systems is facilitated considerably by the fact that they are planar molecules whose framework is described by two-centre bonds. The indivisible whole is only their π-electron cloud, which in a first approximation does not interact with the framework[86,87] and can therefore be considered separately. The latent symmetry of π-systems,[88–90] and also the fact that they contain comparatively few electrons (one from each carbon atom), facilitate their examination considerably.

The situation with the boron hydrides is much more complicated. Boron hydrides form three-dimensional molecules, whose framework is usually a polyhedron. The framework of these molecules cannot be described by two-centre bonds. They can be described by a combination of two-centre and open and central three-centre bonds. A whole set of rules on how to do this has been developed[91] (some of these rules have been used implicitly in the description of the simplest hydrides given above). With increase in the size of the polyhedral molecule, the number of structures describing it increases. The description becomes ambiguous. The difficulties arise because the electronic system of the framework of these molecules is in fact a single whole. The attempt to break it down into individual bonds is artificial, and does not correspond to objective reality.

In contrast to the usual dismembering chemical approach, it is necessary to find a single indivisible system which can serve as a model of the electronic system of the boron hydrides, that is which can define their basic properties. The choice of such a model is suggested by the three-dimensional polyhedral structure of the boron hydrides. The greater the number of vertices in the polyhedron, the closer its similarity to the sphere on which its vertices are situated. The similarity between the three-dimensional structures of the boron hydrides and the sphere suggests the existence of an analogy in the basic properties of the wavefunctions of the electrons of these two systems.

Before describing the properties of the wavefunctions of an electron on a conducting sphere, however, the limits of applicability of this model can be considered, by comparing two polyhedra: the icosahedron with 12 vertices and 20 triangular faces, and its double the Archimedean polyhedron or dodecahedron, with 20 vertices and 12 pentagonal faces. The electron clouds of atoms situated at the vertices of the triangular faces of the icosahedron fill the entire face to its centre, so that the entire surface of the icosahedron is covered continuously by the electron cloud. The faces of the dodecahedron are much larger (Fig. 8), and in their central part the density of the electron cloud is negligible. The electrons do not cover the surface of the dodecahedron completely, but are localised along the edges. Thus the model of a sphere over which the electrons move in unhindered fashion is not appropriate for dodecahedral molecules. The model of the sphere is suitable for one-bond surfaces, and corresponds approximately only to polyhedra with triangular faces (Δ-polyhedra), that is Δ-polyhedral clusters.

The term "cluster" is used very broadly in chemistry.[92] It is often applied even to molecules containing simply two or more metal atoms joined to one another. Framework molecules such as cubane, prismane, dodecahedrane, etc. are also described as clusters.

For the present review, however, it is not specific molecules but the development of the concept of the chemical bond that is of interest. From this viewpoint, it is the Δ-polyhedral clusters that are of interest, and all the subsequent discussion will be devoted to them.

VII. The chemical bonding in Δ-polyhedral clusters

The form of the wavefunctions of electrons situated on a conducting sphere can be discussed.[93] The wavefunction of the ground state of an electron on a sphere has the same sign everywhere, and is distributed uniformly over the entire sphere. This totally symmetric state is one, and is conveniently represented as a ball uniformly coloured in a single colour. The next state on the energy scale can be described by a two-colour ball. The red half can be taken as corresponding to the positive sign of the wavefunction, and the blue half to the negative sign. The plane dividing the ball into red and blue halves—the equatorial plane—is the nodal plane of the function. On passing through this plane, the function changes sign, and on the actual plane the value of the function is zero. Thus in this state the wavefunction has one nodal surface.

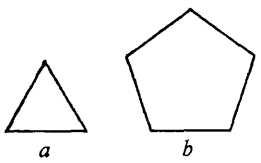


Figure 8. Comparative sizes of the faces of an icosahedron (*a*) and a dodecahedron (*b*) with edges of identical length.

In this case the electron density distribution is not uniform. The density is greatest at a pole, decreases gradually as the equator is approached, becomes equal to zero at the equator, and then increases again, reaching a maximum at the other pole.

The ball can be turned with its red pole upwards, forwards, or to the right. These three arrangements of the two-colour ball correspond to three states of the electron on the sphere with identical energies, that is to degenerate states.

The wavefunctions of the group of states next on the energy scale now have two nodal surfaces. There are five such states. These states are also degenerate. In each successive group of states on the energy scale, the number of nodal surfaces at which the wavefunction changes sign increases.

This is the most important property of the wavefunctions of an electron on a conducting sphere. The nodal properties of the wavefunctions are preserved even if the symmetry of the sphere is destroyed, for example by crumpling it. If bulges or dents appear on the sphere, the strict degeneracy of the wavefunctions is removed. Nevertheless, the ground state, in which the wavefunction has the same sign everywhere, is followed by a group of three wavefunctions with similar energies and one nodal surface, then by a group of five wavefunctions with similar energies and two nodal surfaces, etc.

The examination of the polyhedral boron hydrides can begin with the *closo*-hydrides. The *closo*-hydrides are hydrides in which the boron atoms are situated at the vertices of closed Δ-polyhedra. In these compounds, each boron atom is joined to a hydrogen atom, so that their formula is B_nH_n. The B—H bonds are directed outwards along the radius, and are *exo*-bonds. The *exo*-bonds are strongly localised, and undergo practically no interaction with the rest of the molecule. After the formation of one *exo*-bond, boron still has two electrons and three valence orbitals: one radial, directed towards the centre of the polyhedron, and two tangential, directed one along the parallel, and the other along the meridian. The bonding of the cluster framework involves these so-called framework electrons and orbitals. A boron hydride B_nH_n has a total of $2n$ framework electrons and $3n$ framework orbitals, of which n are radial, and $2n$ tangential. The $3n$ atomic orbitals of boron are used to construct the $3n$ molecular orbitals of the polyhedron. A pictorial representation of the structure of the molecular orbitals obtained from the radial atomic orbitals is provided by the wavefunctions of an electron on a conducting sphere, described above. A pictorial representation of the construction of the molecular orbitals from the tangential orbitals (although the nature of these orbitals is also determined by the form of the wavefunctions of an electron on a conducting sphere) is much more complicated. This will not be considered here, and the results will simply be presented.[94–96]

The most favourable lowest molecular orbital does not have a nodal surface, and the electron density is distributed uniformly over all the boron atoms. It is constructed only from the radial atomic orbitals of boron; the tangential orbitals cannot take part, from symmetry considerations. The $2n$ tangential orbitals of boron form $2n$ molecular orbitals, of which n are bonding, and n antibonding. The bonding molecular orbitals obtained from the tangential orbitals can interact with combinations of the radial orbitals having appropriate symmetry. As a result of this interaction, the bonding molecular orbitals are stabilised, but their number remains unchanged. This gives n bonding molecular orbitals constructed from tangential orbitals with an admixture of radial orbitals, and one totally symmetric bonding molecular orbital, constructed only from radial orbitals, that is a total of $n + 1$ bonding molecular orbitals.

These qualitative conclusions, based on the model approach, have been fully confirmed by MNDO calculations for the boranes.[97]

The $n + 1$ molecular orbitals obtained should contain $(n + 1)$ electron pairs. The boron *closo*-hydrides contain only $2n$ framework electrons, that is there is a deficit of two electrons. Since stability of the molecule requires that all the bonding molecular orbitals be occupied, the boron *closo*-hydrides are stable as the $B_nH_n^{2-}$ dianions.

The two electrons required can also be supplied to the polyhedron in other ways. The CH group also has three boundary orbitals, one σ and two π, that is the composition of the boundary orbitals is the same as that for the BH group, but the CH group has an extra electron. The two electrons required can therefore be obtained if the BH groups at two vertices of the boron hydride are replaced by CH groups. This gives the stable neutral *closo*-carboranes $C_2B_{n-2}H_n$.

The *closo*-boranes and *closo*-carboranes obtained can now be "broken down". This can be done for the case of the icosahedron, the hydride with 12 vertices. It has $12 + 1 = 13$ BMO, so that to be stable, it requires 26 framework electrons, that is this icosahedron will be stable (according to the general rule) either as the $B_{12}H_{12}^{2-}$ dianion (see its prediction,[98] synthesis,[99] and structure[100]) or as the carborane $C_2B_{10}H_{12}$ (see the synthesis of the 1,2-,[101–104] 1,7-,[105] and 1,12-isomers,[106,107] and the structure of the 1,2-,[108] 1,7-,[108] and 1,12-isomers[106]). The removal of BH from one of the vertices gives a molecule with a framework resembling a nest. These structures are called nest-like or *nido*-structures. In the distortion of the structure on going from the *closo*-borane to the *nido*-borane, the

number of bonding molecular orbitals remains unchanged,[109] that is the stability of the *nido*-borane still requires 26 electrons, but there are only 11 BH groups, that is there is a deficit of four electrons.

The electrons required can be obtained in very different ways:[110] the simplest is by replacing four BH groups by CH groups to give the neutral stable *nido*-carborane $C_4B_7H_{11}$. The four electrons can also be obtained by adding four hydrogen atoms to the $B_{11}H_{11}$ nest, to give the boron hydride $B_{11}H_{15}$. These four hydrogen atoms naturally are situated at the edge of the nest, as it were bringing the surface of the *nido*-borane up to spherical. The exact arrangement of these four hydrogen atoms has not been established. Different versions have been discussed: four bridges formed along the edge of the open pentagonal face, or an arrangement in which only some of these hydrogens are bridging, and the others terminal. These terminal B–H bonds are directed along the meridians towards the missing vertex (*endo*-bonds).

The removal of another vertex from the icosahedron gives a structure which is called a spider-web or *arachno*-structure. Surprisingly, this structure as it were preserves the memory of its origin from the icosahedron, and for its stability still requires the same 13 pairs of electrons.[109] Now, however, there remain only 10 vertices, so that there is a deficit of six electrons. Again, these can be obtained in different ways, for example as follows.

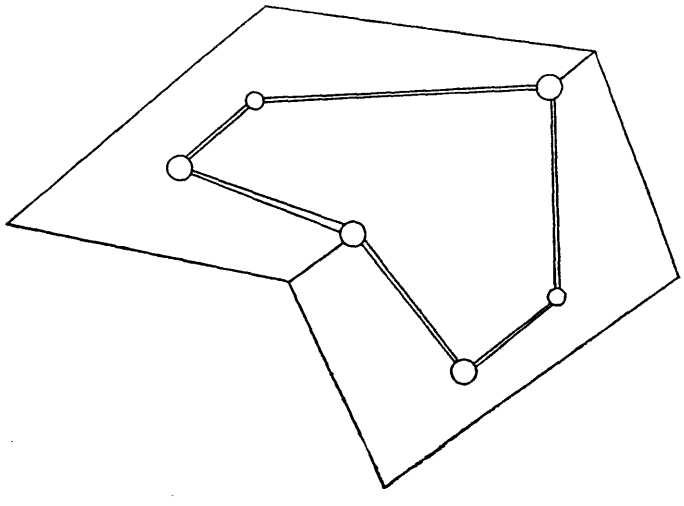


Figure 9. Boundary of the "hole" formed by the removal of two adjacent vertices of an icosahedron.

The edge of the hole produced by the removal of two vertices from the icosahedron forms a hexagon folded in half (Fig. 9). It would be possible to obtain the required six electrons by placing six bridging hydrogen atoms along the edge of this hexagon. They would interfere with one another, however, and the *arachno*-borane $B_{10}H_{16}$ is unstable.[110] Bridging hydrogen atoms are placed only on the two opposite sides of the hexagon farthest from the fold. The atoms in the position of the fold form *endo*-bonds with Lewis bases, which contribute their lone pairs to the cluster.[111] For example, the *arachno*-boranes $B_{10}H_{12}(CH_3CN)_2$,[112,113] $B_{10}H_{12}(NR_3)_2$,[114] and $B_{10}H_{12}(SR_2)_2$ [115] are formed in this way. The procedure involving breakdown of the icosahedron can be continued further. Another form of molecular design, based on the principle of isolobal analogy, that is on the replacement of a BH vertex in the neutral stable carborane $C_2B_{10}H_{12}$ by a group isolobal with it, can be considered. The alkylammonium group is naturally isolobal with the BH-group. The beryllium atom, like the boron atom, has four valence orbitals, but only two valence electrons. Thus to obtain a group isolobal with BH, Be must be joined to a base providing the electrons for the *exo*-bond. The $BeNR_3$ group is isolobal with BH. For the atoms of the group IV elements in the ground state, one valence electron is occupied by a lone pair, and the remaining three boundary orbitals contain two electrons, so that the tin atom, for example, is isolobal with the BH group.

More complex groups isolobal with the BH group can now be considered. The $Fe(CO)_3$ group can be taken first. Iron is a transition metal, so that it has nine valence orbitals. Of the eight valence electrons of the iron atom, six are situated in three valence orbitals, forming its lone pairs. Another three orbitals are involved in the formation of bonds with the carbonyl groups, which provide the electrons for these bonds. This leaves two electrons and three orbitals, one σ and two π. Thus the $Fe(CO)_3$ group, and also the $Ru(CO)_3$ group, are isolobal with the BH group. In the $(C_5H_5)Co$ group, cobalt is joined to the ring by three bonds: one headlamp-shaped σ-bond and two two-lobed π-bonds. The formation of these bonds uses three valence orbitals of cobalt and one of its electrons. Another three valence orbitals are occupied by the three lone pairs of cobalt. This leaves three valence orbitals and two electrons, that is the $(C_5H_5)Co$ group is also isolobal with the BH group. In the case of nickel, a group isolobal with the BH group is obtained when it combines with cyclobutadiene. In addition, the $Pd(C_4Ph_4)$ group is isolobal with the $Ni(C_4H_4)$ group, and hence with the BH group.

The isolobal groups

AlC_2H_5 (Ref.116) $\leftrightarrow$ $BeN(CH_3)_3$ (Ref.117) $\leftrightarrow$ Sn (Ref.118) $\leftrightarrow$

$Fe(CO)_3$ (Ref.119) $\leftrightarrow$ $Ru(CO)_3$ (Ref.120) $\leftrightarrow$ $Co(C_5H_5)$ (Ref.121)

$\leftrightarrow$ $Pd(C_4Ph_4)$ (Ref.122) $\leftrightarrow$ BH

can and do replace the BH group in the icosahedron of the carborane $C_2B_{10}H_{12}$. This gives metallocarboranes,[116–122] including compounds with transition metal atoms.

The ligands can be removed from a transition metal atom situated at a vertex of the icosahedron. This atom provided three valence orbitals and two electrons for the cluster. Six electrons form lone pairs. This leaves three valence orbitals, and if the transition metal is nickel, it leaves $10 - 2 - 6 = 2$ electrons, that is this icosahedron with the stripped nickel atom at a vertex forms a group isolobal with the BH group, so that it can replace this group in another carborane. This gives a structure in which two icosahedra have a nickel atom as a shared vertex (see its synthesis[123] and structure[124]). This iso-electronic cluster also exists for cobalt as the anion,[121] and for iron as the dianion.[125] These are the so-called *commo*-structures.[126]

The fruitfulness of the principle of isolobal analogy is sufficiently clear from the examples given. No more will be given, although it would be possible to describe a large number of other beautiful structures, since in accordance with the principle of isolobal analogy it is possible to replace other vertices and also to extend considerably the list of isolobal groups.

The chief importance of the principle of isolobal analogy is that it enables organometallic chemists to think freely about their field of chemistry. In other words, the principle of isolobal analogy in the chemistry of organometallic compounds fulfils a role analogous to that of the theory of chemical structure in organic chemistry. When the principle of isolobal analogy is used in this way, a considerable simplification of the definition of the isolobal nature of groups is possible. Groups can be described as isolobal if they have the same number of boundary orbitals and the same number of electrons in them. When these two conditions are observed, the requirement of an approximate correspondence in the three-dimensional structure, energy, and symmetry of the boundary orbitals[16] is usually satisfied automatically.

It should however be emphasised that the "isolobal analogy" suggests possibilities, but does not guarantee their existence.[16] The use of "libraries" of isolobal groups[16] may help to estimate more accurately the probability of realising conceived plans.

The naturally developed definition of isolobal groups, according to which the number of boundary orbitals should be the same and they should contain the same number of electrons, was adopted by Hoffmann slightly later,[16] and in his first papers[14,15] he emphasised that isolobal groups are groups with the same number of boundary orbitals, and the presence of the same number of electrons is not required. Although the definition now adopted undoubtedly has a much wider range of application, some advantages of the initial version of the definition of isolobal character are worth noting. In fact, analogous bonding ability and hence the possibility of the mutual replacement of groups are determined mainly by the number and nature of their boundary orbitals. The number of electrons required for bonding, however, can be provided in the most varied ways. Examples include the above-mentioned *commo*-polyhedra $(C_2B_9H_{11})_2Ni$, $[(C_2B_9H_{11})_2Co]^-$, and $[(C_2B_9H_{11})_2Fe]^{2-}$. All three groups $C_2B_9H_{11}M$ (M = Ni, Co, Fe) have the set of boundary orbitals required for the successful replacement of a BH vertex, and the electron deficit is made up by the fact that in the case of Co [121] and Fe [125] these structures are produced as singly- and doubly-charged anions.

The deficit of framework electrons is made up in an interesting way in the diferracarborane $[(C_5H_5)Fe]_2C_2B_6H_8$. In this *closo*-metallocarborane, two BH vertices are replaced by $Fe(C_5H_5)$ groups. The $Fe(C_5H_5)$ group also has the set of boundary orbitals required for the replacement of the BH vertex, but the three boundary orbitals of this group contain only one electron. It would therefore seem that the replacement would lead to a deficit of two framework electrons. In fact, this deficit is made up by the spontaneous ionisation of the iron atoms. This gives a paramagnetic cluster with two iron atoms in the ferricinium state and with the required (22) number of framework electrons.[127]

Another way of making up the deficit of framework electrons is found in the icosahedral rhodium cluster $[Rh_{12}(CO)_{27}Sb]^{3-}$.[128] In this complex, all the vertices of the icosahedron are occupied by rhodium atoms, from three rhodium tricarbonyls and two rhodium dicarbonyls. In the tricarbonyl, three valence orbitals of rhodium are involved in the formation of bonds with the carbonyl groups, which provide the electrons for these bonds. Three valence orbitals of rhodium are occupied by its lone pairs. The remaining three valence electrons of rhodium occupy its remaining three valence orbitals, that is this is a group with three boundary orbitals and three electrons in them. In rhodium dicarbonyl, two of its valence orbitals are involved in the formation of bonds with the carbonyl groups, four orbitals are occupied by lone pairs, and the three boundary orbitals contain only one electron. The rhodium atoms provide $(3 \times 3 + 9 \times 1) = 18$ electrons for the cluster,¶ but a total of 26 are required. From the charge of the cluster (–3), it follows that there is a deficit of five electrons. The cavity of the cluster, however, contains an antimony atom, which provides the five electrons required by the system of framework electrons.

This example introduces another type of bond — the interstitial bond. The interstitial atom is situated inside the cavity in the cluster; its valence orbitals interact with the framework bonding molecular orbitals of the cluster, stabilising them, without changing their number.

The cavities in transition metal clusters are naturally larger than those in boranes, and this method of satisfying the requirement for electrons and stabilising the structure is extremely common.[129] Clusters with interstitial hydrogen, carbon, nitrogen, phosphorus, arsenic, antimony, and sulphur are known.[129] The stabilising influence of the interstitial atom leads to the production of various exotic structures, such as the icosahedron of transition metal atoms given above.

Thus the isolobal analogy produces infinitely varied sets of clusters. The isolobal analogy clearly reveals the unity of the whole of chemistry, leading to the mutual replaceability of groups and atoms from completely different positions in the periodic table. In the attempt to emphasise the unity of chemistry, attention has been drawn primarily not to the differences between clusters but to what they have in common. What they have in common is determined by the similarity between the molecular orbitals of the cluster and the wavefunctions of the electrons of a conducting sphere,[94–96] which leads to the rule of $n + 1$ pairs of framework electrons.[130,131] Nevertheless, however, boranes and transition metal clusters differ significantly. Thus for boranes, polyatomic clusters and in particular icosahedral structures are stable, whereas for transition metal clusters, the octahedral structure is most characteristic. In the build-up of a cluster of transition metals, its polyhedron usually does not expand. Most frequently, the additional atom crowns a triangular face, and a cap consisting of the transition metal with its ligands appears above the face. What then happens to the framework MO? The metal–ligand group which has approached the face of the cluster has three boundary orbitals. The remaining six valence orbitals of the transition metal are involved in bonds with the ligands and are occupied by lone pairs. Of the three boundary orbitals, one is a σ-orbital, and the other two are π-orbitals. These orbitals should interact with the bonding MO of the cluster. Naturally, for this interaction the important feature is not the form of the MO as a whole but its structure at the face which the transition metal atom has approached. Among the BMO of the cluster there will always be some which will not change sign at this face, and some which will change sign once, that is σ- and π-orbitals. These will interact with the boundary orbitals of the approaching group. As a result of this interaction, the BMO of the cluster are stabilised, but their number remains unchanged. This is the so-called capping principle:[132] the number of framework electrons remains unchanged when a cap appears above a face of the polyhedron. Transition metal clusters grow mainly in this way; a cap appears above one face, then another, a third, and a fourth. Caps can appear, however, not only above

¶ The description is idealised. In fact, many of the carbonyl groups are bridging groups, but this does not alter the total electron count.

the original faces of the cluster but also above the newly formed faces. The more the cluster grows, the more frequently a part of the metal lattice can be recognised in its metallic framework.

How large must a cluster be to acquire the properties of the metal? There is as yet no definite answer to this question. The size of the cluster required for this, given by calculations using methods of the SCF-X_α-SW type (about 20 atoms), is much smaller than that given by EHM calculations.[133] In any case, when the number of atoms is sufficiently large, the cluster must be regarded basically as a metal particle.

Hoffmann, who so successfully built a bridge between organic and inorganic chemistry,[16] is now actively engaged in building a bridge between the theoretical approaches of quantum chemistry and the theory of the solid state.[134] This direction of the development of theory will not be considered here, and the review will end with a discussion of gold clusters.

Gold clusters apparently break all the cluster laws, but actually they provide clear confirmation that the electronic system of a cluster is a single entity, whose basic properties are determined by the properties of the wavefunctions of an electron on a conducting sphere.

VIII. The chemical bonding in gold clusters

In all the clusters examined so far in the present review — boranes, carboranes, heteroboranes, metallocarboranes, and transition metal clusters — the atoms of the cluster have formed framework bonds using three orbitals — one radial and two tangential.

This "material" has been used to construct the molecular orbitals of the clusters, which should be similar to the wavefunctions of an electron on a conducting sphere. These two features led to the rule of $n + 1$ electron pairs.

It has been seen how strictly this rule applies. It is possible to change the nature of the vertices in the cluster beyond recognition, it is even possible to remove them completely, yet when there are $n + 1$ electron pairs the framework of the cluster, no matter the number of atoms making it up, takes the form of an n-vertex polyhedron, or a fragment of one in the case where vertices have been removed.

Familiarity with clusters leads to never-ending amazement at the astonishing variety and refinement of the ways in which the rule is followed.

Gold does not obey this rule. What is happening?

Gold is the penultimate element in a transition metal series. At the end of a transition metal series, the energy of the *d*-orbitals is lowered considerably, and the lone pairs of electrons occupying them are gradually transferred to the core and become inactive. At the same time, the gap between the energies of the *s*- and *p*-orbitals increases. The *p*-orbitals become ineffective, and gradually cease to take part in bonding.

The cluster $(AuR)_n$ ($6 \leqslant n \leqslant 12$) can be considered.[135] The Au—R *exo*-bond is formed by an *sp*-hybrid orbital of gold, and is directed outwards along a radius of the cluster. The second *sp*-hybrid orbital of gold is directed along the radius towards the centre of the cluster. This is a radial orbital. The energies of the two unoccupied tangential *p*-orbitals of gold, directed along the parallels and meridians of the sphere, are high on the scale, and these orbitals practically do not function. Thus the gold cluster differs from all the clusters examined so far in the present review in that the tangential system of orbitals plays practically no part in bond formation, and the formation of the cluster involves only the interaction of the radial orbitals. Which of them form the molecular orbitals? The most favourable, that is the totally symmetrical orbital, is constructed only from radial orbitals (all clusters have one). This is followed (remembering the two-colour ball) by three orbitals with similar energies, each of which has one nodal surface. The next MO each have two nodal surfaces; in them, the sign of the function changes too frequently, and the orbitals are unfavourable and anti-bonding. Thus these radial orbitals give only four bonding molecular orbitals: one very favourable totally symmetrical orbital, and three orbitals with similar energies and one nodal surface. This statement is true, irrespective of the number of vertices in the cluster.

Thus because of the low effectiveness of the system of tangential orbitals, the number of BMO in the *closo*-clusters of gold ($6 \leqslant n \leqslant 12$) is four, so that the gold cluster is maintained by eight framework electrons. This is not quite enough for large clusters, but large gold clusters are stabilised by having an interstitial gold atom at the centre. The symmetry of the *s*- and *p*-orbitals of this atom ideally approaches that of the totally symmetrical and three degenerate BMO of the cluster, which are stabilised by the interstitial atom, without changing their number.

The cluster $[Au_{13}(PR_3)_{10}Cl_2]^{3+}$ can be taken as an example. It forms an icosahedron. The 12 gold atoms at the vertices of the icosahedron form *exo*-bonds with the 10 phosphine ligands and two chlorine atoms. The other Au atom is situated at the centre of the icosahedron. Of the 11 valence electrons of the gold atom, 10 are in deep-lying *d*-orbitals and have in fact entered the core, leaving only one electron from each gold atom. Of the total of 13 electrons, two are involved in bonds with the chlorine atoms (the electrons of the remaining *exo*-bonds are provided by the lone pairs of phosphorus), eight occupy the bonding molecular orbitals of the cluster, and three remain unused ($13 - 2 - 8 = 3$) and are removed. This cluster exists as the triply-charged cation.[136]

It is extremely interesting to compare the properties of gold clusters with those of other clusters. The absence of the tangential system of orbitals leads to significant differences between gold clusters and the clusters of other elements, and sometimes even to opposite properties. In particular, in other clusters, reduction leads to opening of the closed *closo*-structure, whereas in gold clusters, on the contrary, the addition of a pair of electrons leads to the conversion of the open toroidal structure of the cluster into a closed spheroidal structure.[135]

IX. Summary

The evolution of the concept of the chemical bond has been examined. The review began with the hydrogen molecule, which occupies a unique position among the millions of all molecules, since it is the only molecule for which the concept of the chemical bond has a completely unambiguous and rigorous significance. It has been shown how the concept of the two-electron chemical bond is transferred to polyatomic molecules, and that, despite the arbitrariness of this concept in polyatomic molecules, it is extremely fruitful, since it reflects the basic features of chemical reality.

The unusually broad range of applicability of the concept of two-centre bonds is due to the clearly-defined spatially directed character of the four hybrid valence orbitals of the atoms of the non-transition elements, as a consequence of which the bonds are relatively independent of one another. This explains the fruitfulness of the concept of individual bonds. If the number of electrons in an atom

is greater than the number required for the formation of two-centre bonds, no dramatic changes are observed; the extra electrons form lone pairs, and the number of bonds formed by the given atom decreases.

The change is more significant when the coordination number of the atom is greater than four, so that there are insufficient valence orbitals for the formation of two-centre bonds with all neighbouring atoms, and it is necessary to introduce the concept of three-centre bonds.

The comparatively large valence orbitals of transition metal atoms enable them to combine not with one but with several atoms of an unsaturated polyatomic ligand simultaneously. The presence of nine valence orbitals in a transition metal atom provides the prerequisite for the formation of a multiple metal–ligand bond (several multi-centre generalised chemical bonds) and hence leads to increased stability of the π-complex.

Thus both hypervalent compounds and transition metal π-complexes can be described in accustomed chemical fashion using three-centre bonds and multi-centre generalised chemical bonds in addition to two-centre bonds.

Thus neither the change from the elements of period II to the non-transition elements of later periods nor the introduction of transition metal atoms into the molecule requires the abandonment of chemistry's reigning ideology, since it is possible to retain the conceptual breakdown of molecules into individual more or less isolated bonds.

The changes in electronic structure resulting not from the replacement of individual atoms but from a change in the overall geometry of the molecule are much more radical. Thus for the atoms involved in the conjugation in planar conjugated systems, it is possible to distinguish valence orbitals having an axis of symmetry perpendicular to the plane of the molecule. The directed character of these orbitals is the same towards all neighbouring atoms. This is the reason for the strong interaction of the conjugated bonds and the delocalisation of the π-electrons in cyclic systems. The mesh of the network formed by the σ-framework of aromatic molecules is too large, so that the π-electron cloud is localised only in the region of the actual framework. Thus in this case there is one-dimensional (reticular) and not two-dimensional delocalisation of the electrons.†

Within the delocalisation region, the π-electrons move practically freely, and any conceptual breakdown of this single system into individual parts contradicts its factual integrity. Thus chemists are dealing every day with molecules to whose π-electron systems the concept of localised bonds is inapplicable.

Two-dimensional delocalisation of electrons takes place not in planar hexagonal network systems but in the closed or almost closed (*nido-*, *arachno-*, and *hypho*-clusters) surfaces of Δ-clusters, whose framework electrons also form a single integral system.

In three-dimensional space, in addition to one-dimensional (linear, reticular) and two-dimensional (Δ-clusters) delocalisation, three-dimensional delocalisation of electrons is also conceivable. It in fact exists in the depth of metals, but the study of this delocalisation belongs to physics. The traditional field of interest of chemistry deals with molecules. In a molecule, the negative cloud of delocalised electrons should be concentrated on a surface bounding a three-dimensional region, so long as positive nuclei are not introduced into this region. From this viewpoint, an example of compounds in which there is three-dimensional delocalisation of electrons is provided by interstitial compounds. These compounds are widely encountered, but they do not differ significantly from Δ-clusters.

It thus appears that all possible basic types of chemical bonding have been dealt with in the present review.

† The terms one-dimensional and two-dimensional are used in the mathematical sense.

References

1. N D Sokolov *Usp. Khim.*, 1988, **57**(2) 177 [English translation in *Russ. Chem. Rev.*, 1988(2)]
2. V A Legasov, A L Buchachenko *Usp. Khim.*, 1986, **55**(12) 1949 [English translation in *Russ. Chem. Rev.*, 1986(12)]
3. N P Gambaryan *Arm. Khim. Zh.*, 1988, **41** 194
4. L Pauling *Perspectives in Organic Chemistry*, Intersci. Publ., New York, 1956
5. B Pullman, A Pullman *Les Theories Electroniques de la Chimie Organique*, Masson, Paris, 1952, 665 pp
6. C A Coulson *Valence* (Translated into Russian), Izd. Mir, Moscow, 1965, 426 pp
7. G Herzberg *Molecular Spectra and Molecular Structure, Vol. I, Spectra of Diatomic Molecules* (Translated into Russian), Izd. Inostr. Lit., Moscow, 1949, 403 pp
8. C A Coulson *Valence*, Clarendon Press, Oxford, 1953, 338 pp
9. R Hoffmann *J. Chem. Phys.*, 1963, **39** 1397
10. L Pauling *J. Am. Chem. Soc.*, 1931, **53** 1367
11. J C Slater *Phys. Rev.*, 1931, **37** 481
12. J N Murrell, S F A Kettle, J M Tedder *Valence Theory* (Translated into Russian), Izd. Mir, Moscow, 1968, 520 pp
13. W H Eberhardt, B L Crawford, W N Lipscomb *J. Chem. Phys.*, 1954, **22** 989
14. M Elian, M M L Chen, D M P Mingos, R Hoffmann *Inorg. Chem.*, 1976, **15** 1148
15. J W Lauher, M Elian, R H Summerville, R Hoffmann *J. Am. Chem. Soc.*, 1976, **98** 3219
16. R Hoffmann *Angew. Chem. Int. Ed. Engl.*, 1982, **21** 711
17. F G A Stone *Angew. Chem. Int. Ed. Engl.*, 1984, **23** 89
18. E Hückel *Z. Phys.*, 1930, **60** 423
19. W G Penney *Proc. R. Soc. London, A*, 1934, **144** 166
20. W G Penney *Proc. R. Soc. London, A*, 1934, **46** 223
21. H B Gray *Electrons and Chemical Bonding* (Translated into Russian), Izd. Mir, Moscow, 1967, 234 pp
22. R Daudel *The Fundamentals of Theoretical Chemistry*, Pergamon Press, Oxford, 1969, 211 pp
23. J C Slater *Phys. Rev.*, 1930, **36** 57
24. J C Slater *Quantum Theory of Atomic Structure*, McGraw-Hill, New York–Toronto–London, 1960, Vol. 1, 502 pp
25. D A Bochvar, N P Gambaryan, L M Epshtein *Usp. Khim.*, 1976, **45**(6) 1316 [English translation in *Russ. Chem. Rev.*, 1976(6)]
26. R E Rundle *Rec. Chem. Progr.*, 1962, **23** 195
27. A Streitwieser *Molecular Orbital Theory for Organic Chemists* (Translated into Russian), Izd. Mir, Moscow, 1965, 435 pp
28. K S Pitzer *J. Am. Chem. Soc.*, 1948, **70** 2140
29. R S Mulliken *J. Am. Chem. Soc.*, 1950, **72** 4493
30. M W Schmidt, P N Truong, M S Gordon *J. Am. Chem. Soc.*, 1987, **109** 5217
31. J N Murrell, H W Kroto *J. Chem. Soc. Chem. Commun.*, 1977, 619
32. Th C Klebach, R Lourens, F Bickelhaupt *J. Am. Chem. Soc.*, 1978, **100** 4886
33.
34.
35.
36.
37.
38.
39.
40.
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48
49
50
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56
57
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61
62
63
64

33. T A Van Der Knaap, Th C Klebach, F Visser, et al. *Tetrahedron*, 1984, **40** 765
34. M S Gordon *J. Am. Chem. Soc.*, 1982, **104** 4352
35. D A Bochvar, N P Gambaryan *Arm. Khim. Zh.*, 1984, **37** 624
36. D M P Mingos, J C Hawes *Structure and Bonding*, Springer-Verlag, Berlin, etc.,1985, Vol. 63, p. 1
37. S P Gubin, G B Shul'pin *Khimiya Kompleksov so Svyazyami Metall–Uglerod* (The Chemistry of Complexes with a Metal–Carbon Bond), Izd. Nauka, Novosibirsk, 1984, 282 pp
38. L Pauling *The Nature of the Chemical Bond*, Cornell Univ. Press, Ithaca, New York, 1960, 644 pp
39. L Pauling *The Achievements and Future Development of Bio-organic Chemistry in Molecular Biology* (Translated into Russian), Izd. Nauka, Moscow, 1978, p. 3
40. D A Bochvar, N P Gambaryan *Metody Elemento-organicheskoi Khimii. Tipy Metallo-organicheskikh Soedinenii Perekhodnykh Metallov* (Methods of Organoelemental Chemistry. Types of Organometallic Compound of Transition Metals), Vol. 1, Izd. Nauka, Moscow, 1975, p. 9
41. D A Bochvar, N P Gambaryan, E M Brainina, et al. *Dokl. Akad. Nauk SSSR*, 1968, **183** 1324
42. B Rees, P Coppens *Acta Crystallogr., Sect. B*, 1973, **29** 2516
43. N S Chiu, L Schäfer *J. Organomet. Chem.*, 1975, **101** 331
44. D M Adams, R E Christopher, D C Stevens *Inorg. Chem.*, 1975, **14** 1562
45. P J Fitzpatrick, Y le Page, J Sedman, et al. *Inorg. Chem.*, 1981, **20** 2852
46. D M Adams, A Squire *J. Organomet. Chem.*, 1973, **63** 381
47. M I Davis, C S Speed *J. Organomet. Chem.*, 1970, **21** 401
48. D C Andrews, G Davidson *J. Organomet. Chem.*, 1972, **36** 349
49. M L H Green *Organometallic Compounds, Vol. 2, The Transition Metals* (Translated into Russian), Izd. Mir, Moscow, 1972, 456 pp
50. T V Nikitina *Metody Elemento-organicheskoi Khimii. Tipy Metallo-organicheskikh Soedinenii Perekhodnykh Metallov* (Methods of Organoelemental Chemistry. Types of Organometallic Compound of Transition Metals), Vol. 2, Izd. Nauka, Moscow, 1975, p. 585
51. J D Fitzpatrick, L Watts, G F Emerson, et al. *J. Am. Chem. Soc.*, 1965, **87** 3254
52. E O Fischer, H Werner *Metall-π-Komplexe* (Translated into Russian), Izd. Mir, Moscow, 1968, 264 pp
53. K Stark, J E Lancaster, H D Murdoch, E Weiss *Z. Naturforsch., B*, 1964, **19** 284
54. L V Rybin, A A Pogrebnyak, M I Rybinskaya, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 1596
55. C S G Phillips, R J P Williams *Inorganic Chemistry*, Oxford Univ. Press, Oxford, 1966, Vol. 2, 570 pp
56. L Pauling *J. Chem. Soc.*, 1948, 1461
57. E M Brainina, N P Gambaryan, B V Lokshin, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, 187
58. E O Fischer, Y Hristidu *Chem. Ber.*, 1962, **95** 253
59. J L Calderon, F A Cotton, B G Deboer, et al. *J. Am. Chem. Soc.*, 1970, **92** 3801
60. V I Kulishov, E M Brainina, N G Bokii, Yu T Struchkov *J. Organomet. Chem.*, 1972, **36** 333
61. E O Fischer, A Treiber *Chem. Ber.*, 1961, **94** 2193
62. V I Kulishov, E M Brainina, N G Bokii, Yu T Struchkov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, 2626
63. E O Fischer, Y Hristidu *Z. Naturforsch., B*, 1962, **17** 275
64. E O Fischer, A Treiber *Z. Naturforsch., B*, 1962, **17** 276
65. J C Slater *Phys. Rev.*, 1955, **98** 1039
66. C E Moore *Atomic Energy Levels*, US Department of Commerce, Washington, 1949, Vol. 1; 1952, Vol. 2
67. F A Cotton, G Wilkinson *Advanced Inorganic Chemistry* (Translated into Russian), Vol. 2, Izd. Mir, Moscow, 1969, 494 pp
68. W Dilthey *Angew. Chem.*, 1921, **34** 596
69. A F Core *Chem. Ind. (London)*, 1927, **5** 642
70. B V Nekrasov *Zh. Obshch. Khim.*, 1940, **10** 1021
71. B V Nekrasov *Zh. Obshch. Khim.*, 1940, **10** 1156
72. Ya K Syrkin, M E Dyatkina *Zh. Fiz. Khim.*, 1941, **15** 459
73. Ya K Syrkin, M E Dyatkina *Acta Physicochim. USSR*, 1941, **14** 547
74. M E Dyatkina, Ya K Syrkin *Dokl. Akad. Nauk SSSR*, 1942, **35** 200
75. S H Bauer *J. Am. Chem. Soc.*, 1937, **59** 1096
76. H Mark, E Pohland *Z. Kristallogr.*, 1925, **62** 103
77. G N Lewis *J. Chem. Phys.* 1933, **1** 17
78. N V Sidgwick *The Electronic Theory of Valency*, Clarendon Press, Oxford, 1927, 230 pp
79. L Pauling *The Nature of the Chemical Bond* (Translated into Russian), GONTI Khim. Lit., Leningrad, 1947, 440 pp
80. K W Hedberg, V Schomaker *J. Am. Chem. Soc.*, 1951, **73** 1482
81. W N Lipscomb *J. Phys. Chem.*, 1957, **61** 23
82. P H Lewis, R E Rundle *J. Phys. Chem.*, 1953, **21** 986
83. C E Nordman, W N Lipscomb *J. Phys. Chem.*, 1953, **21** 1856
84. E B Moore, R E Dickerson, W N Lipscomb *J. Phys. Chem.*, 1957, **27** 209
85. L R Lavine, W N Lipscomb *J. Phys. Chem.*, 1954, **22** 614
86. P G Lykos, R G Parr *J. Phys. Chem.*, 1956, **24** 1166
87. P G Lykos, R G Parr *J. Phys. Chem.*, 1956, **25** 1301
88. C A Coulson, G S Rushbrooke *Proc. Camb. Phil. Soc.*, 1940, **36** 193
89. C A Coulson, H C Longuet-Higgins *Proc. R. Soc. London, A*, 1947, **192** 16
90. T P Zivkovic *Int. J. Quantum Chem.*, 1987, **32** 313
91. R E Dickerson, W N Lipscomb *J. Chem. Phys.*, 1957, **27** 212
92. S P Gubin *Khimiya Klasterov* (The Chemistry of Clusters), Izd. Nauka, Moscow, 1987, 263 pp
93. D K Hoffman, K Ruedenberg, J G Verkade *Structure and Bonding, B, etc.*, Springer-Verlag, 1977, Vol. 33, p. 57
94. A J Stone *Polyhedron* 1984, **3** 1299
95. A J Stone *Inorg. Chem.*, 1981, **20** 563
96. A J Stone *Mol. Phys.*, 1980, **41** 1339
97. P Brint, J P Cronin, E Seward, et al. *J. Chem. Soc., Dalton Trans.*, 1983, 975
98. H C Longuet-Higgins, M de V Roberts *Proc. R. Soc. London, A*, 1955, **230** 110
99. A R Pitochelli, M F Hawthorne *J. Am. Chem. Soc.*, 1960, **82** 3228
100. J A Wunderlich, W N Lipscomb *J. Am. Chem. Soc.*, 1960, **82** 4427
101. M M Fein, J Bobinski, N Mayes, et al. *Inorg. Chem.*, 1963, **2** 1111
102. T L Heying, J W Ager, S L Clark, et al. *Inorg. Chem.*, 1963, **2** 1089
103. L I Zakharkin, V I Stanko, V A Brattsev, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1963, 2069
104. L I Zakharkin, V I Stanko, V A Brattsev, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1963, 2238
105. D Grafstein, J Dvorak *Inorg. Chem.*, 1963, **2** 1128

106. S Papetti, T L Heying *J. Am. Chem. Soc.*, 1964, **86** 2295
107. J F Sieckhaus, N S Semenuk, T A Knowles, et al. *Inorg. Chem.*, 1969, **8** 2452
108. H Schroeder, G D Vickers *Inorg. Chem.*, 1963, **2** 1317
109. A J Stone, M J Alderton *Inorg. Chem.*, 1982, **21** 2297
110. R E Williams *Adv. Inorg. Chem. Radiochem.*, 1976, **18** 67
111. R J Pace, J Williams, R L Williams *J. Chem. Soc.*, 1961, 2196
112. J V D M Reddy, W N Lipscomb *J. Am. Chem. Soc.*, 1959, **81** 754
113. J V D M Reddy, W N Lipscomb *J. Chem. Phys.*, 1959, **31** 610
114. M F Hawthorne, A R Pitochelli *J. Am. Chem. Soc.*, 1959, **81** 5519
115. D E Sands, A Zalkin *Acta Crystallogr.*, 1962, **15** 410
116. B M Mikhailov, T V Potapova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, 1152
117. G Popp, M F Hawthorne *J. Am. Chem. Soc.*, 1968, **90** 6553
118. R L Voorhees, R W Rudolph *J. Am. Chem. Soc.*, 1969, **91** 2173
119. M P Garcia, M Green, F G A Stone, et al. *J. Chem. Soc., Dalton Trans.*, 1985, 2343
120. A R Siedle *J. Organomet. Chem.*, 1975, **90** 249
121. M F Hawthorne, T D Andrews *J. Chem. Soc., Chem. Commun.*, 1965, 443
122. P A Wegner, M F Hawthorne *J. Chem. Soc., Chem. Commun.*, 1966, 861
123. L F Warren, M F Hawthorne *J. Am. Chem. Soc.*, 1967, **89** 470
124. D St Clair, A Zalkin, D H Templeton *J. Am. Chem. Soc.*, 1970, **92** 1173
125. M F Hawthorne, D C Young, P A Wegner *J. Am. Chem. Soc.*, 1965, **87** 1818
126. M F Hawthorne, D C Young, T D Andrews, et al. *J. Am. Chem. Soc.*, 1968, **90** 879
127. E K Nishimura *J. Chem. Soc., Chem. Commun.*, 1978, 858
128. J L Vidal, J M Troup *J. Organomet. Chem.*, 1981, **213** 351
129. J N Nicholls *Polyhedron*, 1984, **3** 1307
130. K Wade *J. Chem. Soc., Chem. Commun.*, 1971, 792
131. K Wade *Adv. Inorg. Chem. Radiochem.*, 1976, **18** 1
132. D M P Mingos, M I Forsyth *J. Chem. Soc., Dalton Trans.*, 1977, 610
133. E L Muetterties *Chem. Eng. News, Special Report*, 1982, (31) 28
134. R Hoffmann, S D Wijeyesekera, S Sung *Pure Appl. Chem.*, 1986, **58** 481
135. D M P Mingos *Polyhedron* 1984, **3** 1289
136. C E Briant, B R C Theobald, J W White, et al. *J. Chem. Soc., Chem. Commun.*, 1981, 201

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The structural study of liquid crystals

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ABSTRACT. Structural (mainly X-ray diffraction) studies of thermotropic liquid-crystalline mesophases have been reviewed. The classification of mesophases has been examined and refined. The discussion deals mainly with the structure of liquid crystals formed by rod-shaped molecules (calamitic mesophases). Mesophases of a new type, containing columnar associates of molecules joined by hydrogen bonds, have also been described.

The bibliography contains 141 references.

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I. Introduction

The study of liquid crystals (LC) began as early as last century,[1,2] and its hundredth anniversary has already passed. It now covers a remarkable scale, but the increase in the number and range of these studies has not been smooth. It was only about 25 years ago that it became clear that LC do not represent an exotic phenomenon; they are widely encountered in living and non-living nature, and have found a large number of practical applications in technology and medicine, and in recent years in chemistry (as orienting solvents in the study of NMR spectra and for carrying out topochemical reactions). The intensive study of LC has also led to the development of theoretical ideas which make up an integral and important part of present-day physical chemistry.

As in other fields of chemistry, structural data have here been extremely important. In structural chemistry, an independent branch referred to as "the structure of mesophases" has been distinguished.†

Even in the early stages of the study of LC, they were classified according to the degree and nature of the ordering as nematic, smectic, and cholesteric.[2] Thus structural studies from the beginning have played an important role in the investigation of LC, although in many cases the descriptions of the structure suffered from lack of clarity and specificity, and sometimes contradicted physicochemical data and the principle of close packing of molecules. Since like liquids they retain a considerable degree of disorder, liquid-crystalline phases naturally cannot be characterised structurally in the same detail as solid crystals. The statistical nature of their structure, however, reflects objective reality, so that in principle it should in each specific case be described in completely definite fashion, albeit in statistical language. Compared with liquids, experimental diffraction methods in this case give much more information, although, as in the case of liquid phases, the details of the structure of individual molecules remain out of reach.

The present review gives a systematic analysis of the structural aspects of studies of LC, carried out mainly in the last 25 years. Liquid-crystalline phases can be classified as thermotropic (produced from liquids or crystals by change in temperature) and lyotropic (formed in solution). Only the former are considered in the present review.

For a long time it was considered that the role of mesogens, that is compounds capable of existing in the thermotropic liquid-crystalline state, was played only by substances with rod-shaped molecules (so-called calamitic mesophases). In 1977, however, LC formed by disc-shaped molecules were reported,[4] and in 1987, liquid-crystalline phases consisting of cup-shaped molecules were described.[5] There is no doubt that, other types of mesogen will be detected. Usually, however, when LC are mentioned, it is calamitic mesophases that are meant. The present review also deals mainly with these LC (it is proposed to devote a separate review to the structure of disc-shaped mesophases).

In a rod-shaped molecule it is possible to distinguish a long axis, denoted L. The vector indicating the average direction of these axes is called the director (this concept is most useful for nematic mesophases). A calamitic mesophase can apparently be defined as a liquid crystal whose structure is regarded as sufficiently fully characterised if the arrangements of the molecular axes L are described (with allowance for statistics). This definition corresponds to the picture of molecules as cylinders with a circular cross-section. In some important cases (for flattened molecules), however, this description of the structure cannot be regarded as sufficient, and it is necessary to represent the molecules as cylinders with an elliptical cross-section. It is then necessary to add to the structural parameters the angles characterising the orientation of the ellipses perpendicular to the axes L.

† The term "mesophase" is now often used as a synonym for "liquid crystal"; this use of these concepts has also proved convenient in the present review. It should be borne in mind, however, that the concept of "mesophase" is sometimes given a more general meaning, to include various partly disordered (and partly ordered) phases occupying an intermediate position between ideal crystals and isotropic liquids.[3]

Liquid crystals are practically always molecular compounds, but liquid-crystalline phases show a number of distinctive features, compared with molecular crystals. In addition to the appreciably statistical nature of the structure, a domain structure is highly characteristic of LC. Domains with coherent boundaries apparently are also fairly frequently present in solid molecular crystals (more frequently than is usually assumed[6]). Nevertheless, this is not typical of solid crystals, whereas in LC domains are observed as the rule. They are readily rearranged and change their orientation under the influence of external factors, in particular electric and magnetic fields.

In a liquid-crystalline material, the domains are often arranged completely randomly. In an electric or magnetic field, they are ordered, leading to the formation of so-called oriented mesophases. It is these phases that are usually studied by X-ray diffraction. For solid crystals, the influence of an external field (and even temperature) on the structure is studied comparatively rarely (studies of this kind are only beginning to develop on a large scale), whereas for LC the study of structure as a function of field intensity and temperature has been customary for a long time.

In the study of the structure of LC it is important to bear in mind that their structure is dynamic. The problem in principle is to give a specific description of not only the average arrangement of the molecules, preserved for a more or less long time, but also the dynamics of the structure, that is the vibrational and rotational movements of the molecules, and also their diffusion and transfer from one molecular agglomerate to another. The information at present available, however, relates mainly to the averaged static structure of LC; this information is obtained by optical, dilatometric, and other physicochemical studies, but the main source of structural information is diffraction, in particular optical modelling of the diffraction pattern. Information on molecular dynamics is also provided by NMR and experiments on quasi-elastic neutron scattering.‡

II. The structural classification of calamitic mesophases

The first classification of LC having a structural basis was proposed in 1922 by Friedel,[2] who classified the 42 liquid-crystalline substances known to him as nematic, smectic, and cholesteric. The distinctive feature of nematic LC is that the molecules in them are arranged in approximately parallel fashion, that is they are characterised by approximately parallel orientation of the long axes. In smectic LC, the molecules again are approximately parallel, but in addition they are arranged in parallel layers. The local structure of a cholesteric mesophase is analogous to the structure of a nematic, on the other hand, cholesteric LC are characterised by a gradual change in the orientation of the vector L in space, leading to a spiral arrangement, as a result of which these crystals are optically active.

Subsequent studies showed that there is considerable variety in the properties and structures of smectic phases. This led to the classification of smectics as types A, B, C, D, E, F, and G by Sackmann and Demus.[8] This classification was based on experimental data on the miscibility of the mesophases, but it was already known at that time from X-ray diffraction studies[9] that the miscibility criterion corresponds to definite structural characteristics. Subsequently, X-ray diffraction studies made it possible to characterise specifically each of the types $A-G$, and also to add the types H, I, J, and K.

Generally speaking, the picture of the molecules as rods with cylindrical symmetry is inadequate for the description of these types of structure. A more adequate model is that of a cylinder with an elliptical cross-section, or a ribbon, and in some cases it is also necessary to take into account the non-equivalence of the two sides of this ribbon. In the simplest version, the structure of smectics of different types is usually described without taking into account the polarity of the molecules and the possibility of dimer formation. It is also assumed that the smectic phase consists of "monolayers", in that the centres of gravity of the molecules forming the layer lie approximately in the same plane, and that the thickness of the layer d is determined by the length of the molecule l ($d = l\cos\varphi$, where φ is the angle between the axis L and the normal to the layer).

In the description and classification of the structure "monolayer" smectics, account is usually taken of the nature of the packing of the molecules in the layer, whether or not the molecules lie at an angle to the normal to the layer ($\varphi = 0$ or $\varphi \neq 0$), and the presence or absence of correlation in the superposition of the layers. Four types of packing of the molecules in the layer are distinguished: 1) disordered, 2) "hexatic" (having only short-range order), 3) hexagonal, and 4) herring-bone. According to Goodby and Gray,[10] who summarised structural data on smectic phases, this gives the following classification of known smectics (the notation of the phases in which there is a correlation in the superposition of the layers is underlined):

Packing in the layer	$\varphi=0$	$\varphi'\neq0$	$\varphi''\neq0$
Disordered	*SmA*	*SmC*	
"Hexatic"	SmB_h	*SmI*	*SmF*
Hexagonal	*SmB*	*SmJ(G')*	*SmG*
Herring-bone	*SmE*	*SmK(H')*	*SmH*

This Table corresponds to Fig. 1, taken from Goodby and Gray,[10] which shows schematically the packing of the molecules in the smectic layers. Here, the circles denote vertically arranged molecules, whose effective symmetry is cylindrical as a result of the statistical character of the azimuthal orientations (or because of the domain structure of the layer, discussed below). The triangles denote sloping molecules with cylindrical symmetry (in the case of molecules with an elliptical effective cross-section, the slope of their long axes is indicated by arrows). Two versions of the slope of the molecules relative to the section of the layer are distinguished (φ' and φ''), giving two series of "sloping" smectics ($I-J-K$ and $F-G-H$). Fig. 2 gives a clearer picture of the arrangement of the molecules in the bulk of some smectics.

It should be emphasised that the representations of the structure of the layers in the hexatic phases in Fig. 1 are highly arbitrary. In fact, the following is understood. In contrast to hexagonal and herring-bone packing, in which the arrangement of the centres of gravity of the molecules is characterised by long-range positional order (although not so perfect as in true crystals), hexatic phases show only short-range positional order, and the molecular coordination number 6 is the most probable; the symmetry of the immediate environment of a molecule in the layer is therefore hexagonal or pseudo-hexagonal. At the same time, in these phases there is bond-orientational order, in which all the coordination hexagons are oriented in approximately the same way. Analogous

‡ This method detected the diffusion of molecules in a direction perpendicular to the smectic layers.[7]

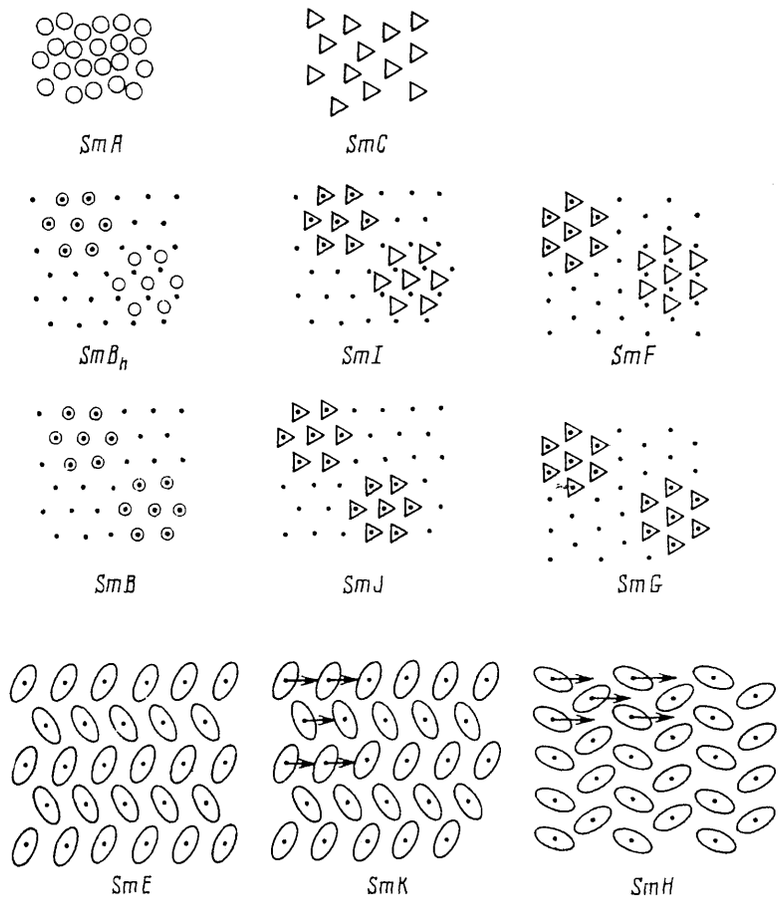


Figure 1. Arrangements of the molecules in smectic layers.[10]

phases with short-range order of a different type ("tetratic", etc.) are possible in principle, but these phases have not been reported in X-ray studies

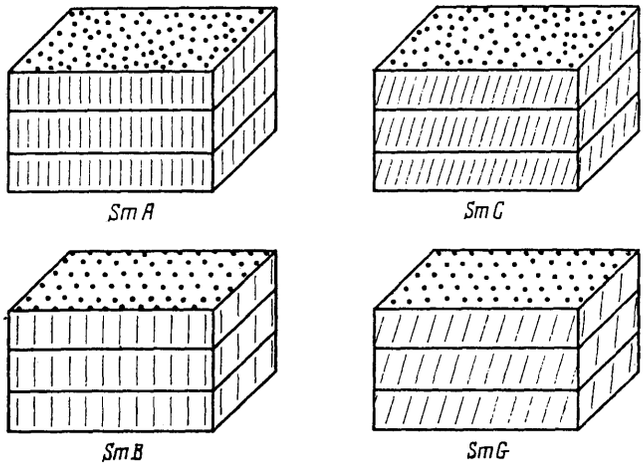


Figure 2. Schematic representation of the arrangement of the molecules in various smectics.

This classification gives a satisfactory description of experimental data on the structure of smectic mesophases. There is however some indeterminacy in the structural characterisation of *SmI* (this question will be examined later in section V). It should also be noted that the structural description sometimes contradicts experimental data on the miscibility of liquid-crystalline phases. The miscibility or immiscibility of two smectics apparently does not always indicate unambiguously a similarity or difference between their structures. A final conclusion can be reached only from special structural studies.

An unsatisfactory feature of the above systematisation is that it only reproduces the experimentally observed picture of the structure of smectics (more accurately, a set of models which has been used to interpret the experimental data); there is no possibility of predicting structures which are possible in principle but which have not yet been discovered.

A more *a priori* systematisation is that of de Vries,[11] which has been extended to lyotropic mesophases.[12] Here, the herring-bone arrangement of the molecules, denoted by the symbol "2", as taken as the basis of the structure of the smectic layers, but account is also taken of the possible production, at sufficiently high temperatures, of dynamic structures in which there is a spontaneous cooperative change in the azimuthal orientation, as a result of which the structure represented schematically in Fig. 3*a* is converted into the structure shown in Fig. 3*b*, and conversely. X-Ray diffraction records the

overall statistical structure (Fig. 3c), which is denoted by the symbol *m*. Moreover, according to de Vries it is possible to have a structure with three interconvertible azimuthal orientations of the molecules (Fig. 4), effectively having hexagonal symmetry (symbol "6"). To this is added a statistical structure with a non-fixed azimuthal orientation of the molecules, denoted by the symbol ∞.

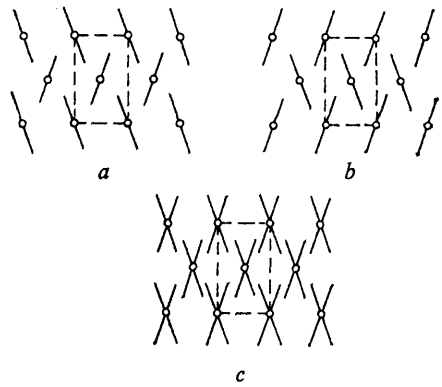


Figure 3. Structure of the layers 2 and *m* according to de Vries:[11] *a*, *b*, two equivalent herring-bone patterns; *c*, overall structure (detected by X-ray diffraction) in which versions *a* and *b* are equally probable.

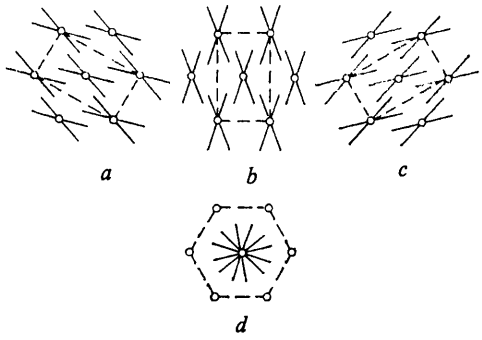


Figure 4. The formation of statistical layers according to de Vries:[11] *a*, *b*, *c*, three equivalent orientations of the layers *m*; *d*, overall structure.

The structure of a smectic phase as a whole is described by de Vries by means of a three-position symbol, where the type of packing of the molecules in the layer (2, *m*, 6, or ∞) is given by the first position, whether or not the director lies at a slope to the plane of the layer (∞ or *m*) is given by the second position, and the presence or absence of a correlation in the superposition of the layers (0 or 1) is given by the third position. This gives the 14 types of smectic structure shown in Table 1. De Vries identifies nine of them with types of smectic described in the literature; two types [*SmX* and *Sm*(*X*)] are said[11] to have been identified be de Vries and co-workers; and three types (6*m*1, 2∞0, 2*m*0) have apparently not yet been identified.

Table 1. Types of smectic mesophase (according to de Vries).

Type of packing of the molecules in the layer	Smectic mesophases			
	upright layers (∞)		sloping layers (*m*)	
	0	1	0	1
∞	∞∞0 (*SmA*)	—	∞*m*0 (*SmC*)	—
6	6∞0 (*SmB*)	6∞1 (*Sm*(*B*))	6*m*0 (*SmF*)	6*m*1 —
m	*m*∞0 (*SmX*)	*m*∞1 (*Sm*(*X*))	*mm*0 (*SmI*)	*mm*1 (*SmG*)
2	2∞0 —	2∞1 (*SmE*)	2*m*0 —	2*m*1 (*SmH*)

It should however be noted that there are discrepancies between de Vries' treatment and the structural systematisation of smectic phases described above.[10] This applies primarily to hexatic structures, which according to de Vries represent a fifth version of the packing of the molecules in the layer, so that they should be regarded as supplementing the 14 types listed in Table 1. At the same time, in de Vries' monograph,[10] the types *SmB*, *SmI*, and *SmF* are treated as hexatic phases (see also section V). Correspondingly, the interpretation of the types *SmI* and *SmG* as phases with structures corresponding to the symbols *mm*0 and *mm*1 differs from the description of these phases in de Vries' monograph.[10] In addition, de Vries' systematisation does not reflect different relations of the slope of the molecules to the section of the layer.

Moreover, the production of two or three spontaneously interconvertible orientations, proposed by de Vries, contradicts the principle of close packing, which should apparently be applicable not only to crystals but also to the liquid-crystalline state. A more probable model of the layers denoted by the symbols 6 and *m* is a domain structure (see Fig. 27) in which the boundaries of the domains can migrate either spontaneously or under the influence of external factors; there coexist three orientations of the domains in a layer of type 6, and two orientations in a layer of type *m*.

Another feature which apparently must be taken into account in an *a priori* systematisation of smectic phases is the following. It is known from organic crystal chemistry[13,14] that the characteristic packing of molecules includes not only the herring-bone pattern (layers with symmetry P_l2_1, P_lc, and P_l2_1/c) but also primitive packing with an oblique-angled cell (layers with symmetry P_l1 or $P_l\bar{1}$). If this mode of packing of the molecules in the layer is denoted by the symbol "1" and, following de Vries, the possible versions of the structure of a smectic with an oblique-angled planar cell are examined, then another four types of smectic phase are obtained: 1∞0, 1*m*0, 1∞1, and 1*m*1. Smectic phases of this type have not yet been detected by X-ray diffraction. This however is apparently due not to the fact that they do not exist in the systems studied but to the fact that the more symmetrical models used in the interpretation of the X-ray diffraction patterns have been fairly consistent with the experimental data. With increase in the accuracy

of X-ray diffraction studies, however, phases will possibly be found, whose X-ray diffraction patterns can be interpreted satisfactorily only on the basis of an oblique-angled structure of the smectic layers.

It is appropriate to supplement the above classification schemes by a parametric description of different types of liquid-crystalline structures. This description will make it possible to list structural parameters whose fixed values define the type of liquid-crystalline phase. An advantage of this approach is not only that it is quantitatively specific but also it makes it possible to regard polymorphic transformations of liquid-crystalline phases as the "de-freezing" (or "freezing") of individual degrees of freedom of the molecules. This opens up the way to a quantitative energetic analysis of mesomorphism.

The parameters characterising the structure of a calamitic LC include: 1) the angles φ, ψ, and θ describing the position of the long axis of the molecule and its azimuthal orientation (Fig. 5), 2) the distance between the axes of adjacent molecules D, and 3) for smectic phases, the thickness of the layer d. In the case of highly ordered smectics, the distances between the molecules are determined by the parameters of the two-dimensional lattice a and b (for hexatic phases by the parameters of the immediate environment a' and b'); for smectics with three-dimensional order, which in the literature are sometimes provisionally called "crystalline", the thickness of the layers is defined by the period c. Table 2 lists for each type of LC the parameters which make it possible to describe the principal features of the structure.

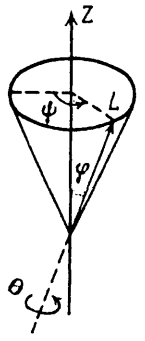


Figure 5. Angles characterising the orientation of a rod-shaped molecule.

For a more detailed characterisation of the structure, it is necessary to take account of the actual conformation and to indicate the way in which the axis L is selected. Moreover, in the study of the structure of specific mesophases, the formation of dimeric molecular agglomerates (they are often called "dimers", although they do not correspond to dimers in the chemical sense of the term) and "bilayer" structures are often encountered. (These questions will be examined later.)

It is also necessary to take account of the characteristics of the structure of LC arising in sloping ($\varphi \neq 0$) smectics in connection with the chirality of the molecules.[15] In this case, optically active mesophases *SmC**, *SmI**, and *SmF** are formed, in which the superposition of the layers of chiral molecules leads to spiral twisting, together with mesophases *SmI**, *SmG**, *SmK**, and *SmH**, in which this twisting does not take place[10] (the optical activity of the substance is due to the chirality of the molecules).

Table 2. Characteristic structural parameters of mesophases of different types.

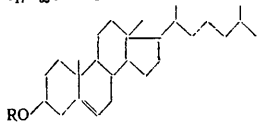
Type of mesophase	Notation	Fixed parameters
Nematics	*N*	$\varphi=0$, *D*
Smectics	*SmA*	$\varphi=0$, *D*, *d*
disordered	SmA_C	φ, *D*, *d*
	SmC	φ, ψ, *D*, *d*
hexatic	SmB_h	$\varphi=0$, $a'=b'$, $\gamma=120°$, *d*
	SmI	φ, $\psi=0$, $a'=b'$, $\gamma=120°$, *d*
	SmF	φ, $\psi=90°$, $a'=b'$, $\gamma=120°$, *d*
with three-dimensional order	*SmB*	$\varphi=0$, $a=b$, *c*, $\gamma=120°$
	SmG	φ, $\psi=0$, $a=b$, *c*, $\gamma=120°$
	SmI	φ, $\psi=90°$, $a=b$, *c*, $\gamma=120°$
	SmE	$\varphi=0$, $\theta=0$, 180°, *a*, *b*, *c*
	SmK	φ, $\psi=0$, $\theta=0$, 180°, *a*, *b*, *c*
	SmH	φ, $\psi=90°$, $\theta=0$, 180°, *a*, *b*, *c*

The calamitic mesogens for which X-ray diffraction data are available are listed in Table 3. They are arranged in a definite sequence (according to their chemical characteristics). Table 3 also gives the names of the compounds or groups of homologues, and the corresponding structural formulae. In some cases, letter abbreviations for the compounds, encountered in the literature, are given.

Table 3. List of calamitic mesogens studied by X-ray diffraction.

Compound	Name, abbreviation	Formula*
I	4-n-Octyl-4′-cyano-biphenyl	$C_8H_{17}—C_6H_4—C_6H_4—CN$
II	Alkoxycyanobiphenyl	$RO—C_6H_4—C_6H_4—CN$
III	n-Alkyl 4′-n-alkoxybiphenyl-4-carboxylate	$R'O—C_6H_4—C_6H_4—COOR$
IV	1α-Pentyl-4α-*p*-cyano-phenylbicyclo[2.2.3]octane	$C_5H_{11}—C_8H_{12}—C_6H_4—CN$
V	4′-n-Alkoxy-3′-nitrobiphenylcarboxylic acid	$RO—(NO_2)C_6H_3—C_6H_4—COOH$
VI	4′-n-Alkoxy-3′-cyanobiphenylcarboxylic acid	$RO—(CN)C_6H_3—C_6H_4—COOH$
VII	Alkylcyanotriphenyl	$R—C_6H_4—C_6H_4—C_6H_4—CN$
VIII	1-n-Heptyl-4-cyanobiphenyl-cyclohexane	$C_7H_{15}—C_6H_{10}—C_6H_4—C_6H_4—CN$
IX	1-n-Pentyl-4-ethylbiphenyl-cyclohexane	$C_5H_{11}—C_6H_{10}—C_6H_4—C_6H_4—C_2H_5$
X	1-n-Pentyl-4-X-biphenylcyclo-hexane	$C_5H_{11}—C_6H_{10}—C_6H_4—C_6H_4—X$, X = Cl, Br, CN, C_2H_5
XI	Cyanobiphenylpentylbicyclo-octane	$C_5H_{11}—C_8H_{12}—C_6H_4—C_6H_4—CN$
XII	4-Alkoxybenzylidene-4′-alkylaniline	$RO—C_6H_4—CH=N—C_6H_4—R'$
XIII	N-4-Cyanobenzylidene-4′-alkylaniline	$CN—C_6H_4—CH=N—C_6H_4—R$
XIV	N-4-Cyanobenzylidene-4′-octyloxyaniline	$CN—C_6H_4—CH=N—C_6H_4—OC_8H_{17}$
XV	2-Methylbutyl N-(4-n-decyloxybenzyl-idene)-4′-aminocinnamate	$C_{10}H_{21}O—C_6H_4—CH=N—C_6H_4—CH=CH—COO—CH_2—CH(CH_3)—C_2H_5$
XVI	n-Pentyl 4-phenylbenzylidene-4′-aminocinnamate	$C_6H_5—C_6H_4—CH=N—C_6H_4—CH=CH—COO—C_5H_{11}$
XVII	2-Chloropropyl 4-hexyloxybenzylidene-4′-aminocinnamate	$C_6H_{13}O—C_6H_4—CH=N—C_6H_4—CH=CH—COO—CH_2—CHCl—CH_3$

Table 3 (cont'd)

Compound	Name, abbreviation	Formula*
XVIII	4-(4-n-Alkoxybenzylidene-amino)-4'-cyanobiphenyl (n=7, HOBACB; n=8, OOBACB)	RO—C_6H_4—CH=N—C_6H_4—C_6H_4—CN
XIX	4-Nitrophenyl 4'-octyloxybenzoate	$C_8H_{17}O$—C_6H_4—CO—O—C_6H_4—NO_2
XX	4-Cyanophenyl 4'-octylbenzoate	C_8H_{17}—C_6H_4—CO—O—C_6H_4—CN
XXI	4-Butoxyphenyl 4'-decyloxybenzoate	$C_{10}H_{21}O$—C_6H_4—CO—O—C_6H_4—OC_4H_9
XXII	4-Cyanobiphenyl 4'-heptylphenylbenzoate	C_7H_{15}—C_6H_4—C_6H_4—CO—O—C_6H_4—C_6H_4—CN
XXIII	4-Pentoxyphenyl 4'-octyloxyphenylbenzoate	$C_8H_{17}O$—C_6H_4—C_6H_4—CO—O—C_6H_4—OC_5H_{11}
XXIV	4-Isopentylphenyl 4'-octyloxyphenylbenzoate	$C_8H_{17}O$—C_6H_4—C_6H_4—CO—O—C_6H_4—$CH_2CH(CH_3)C_2H_5$
XXV	p-Alkoxyazoxybenzene (n=1, PAA)	RO—C_6H_4—N(O)=N—C_6H_4—OR
XXVI	Ethyl azoxybenzene-p-dicarboxylate	C_2H_5O—CO—C_6H_4—N(O)=N—C_6H_4—CO—OC_2H_5
XXVII	1-Heptyl-4-p-cyanophenoxy-methylcyclohexane	C_7H_{15}—C_6H_{10}—CH_2—O—C_6H_4—CN
XXVIII	4-n-Pentylphenyl 4'-n-tetradecyloxythio-benzoate	C_5H_{11}—C_6H_4—S—CO—C_6H_4—O—$C_{14}H_{29}$
XXIX	4-Alkyl-4'-cyanostilbene	R—C_6H_4—CH=CH—C_6H_4—CN
XXX	4-Acetyl-4'-n-alkanoyloxy-azobenzene	R'—CO—C_6H_4—N=N—C_6H_4—O—CO—R
XXXI	Ethyl p-anisolamino-cinnamate	CH_3O—C_6H_4—NH—C_6H_4—CH=CH—COO—C_2H_5
XXXII	Bis-(4-n-hexyloxyphenyl)-mercury	$C_6H_{13}O$—C_6H_4—Hg—C_6H_4—OC_6H_{13}
XXXIII	1,2-Bis-(4-n-alkoxybenzoyl)-hydrazine	RO—C_6H_4—CO—NH—NH—CO—C_6H_4—OR
XXXIV	4-Nitrophenyl 4'-nonyloxy-benzoyloxybenzoate	$C_9H_{19}O$—C_6H_4—CO—O—C_6H_4—O—CO—C_6H_4—NO_2
XXXV	4-Cyanophenyl 4'-hexyl-benzoyloxybenzoate	C_6H_{13}—C_6H_4—CO—O—C_6H_4—O—CO—C_6H_4—CN
XXXVI	*trans*-1,4-Di-(n-octyloxy-benzoyloxy)cyclohexane	$C_8H_{17}O$—C_6H_4—CO—O—C_6H_{10}—O—CO—C_6H_4—OC_8H_{17}
XXXVII	2-Alkyl-1,4-di-(4'-n-octyloxy-benzoyloxy)benzene	$C_8H_{17}O$—C_6H_4—CO—O—C_6H_3R—O—CO—C_6H_4—OC_8H_{17}
XXXVIII	Terephthalylidene bis-4-n-alkylaniline (n=4, TBBA; n=5, TBPA; n=10, TBDA)	R—C_6H_4—N=CH—C_6H_4—CH=N—C_6H_4—R
XXXIX	Bis-(4'-n-alkoxybenzylidene)-1,4-phenylenediamine	RO—C_6H_4—CH=N—C_6H_4—N=CH—C_6H_4—OR
XL	α-Phenylazo-(methoxybenzyl-idene-α'-naphthylamine)	C_6H_5—N=N—$C_{10}H_6$—N=CH—C_6H_4—OCH_3
XLI	Bis-(4'-n-alkoxyphenyl)-2-chloro-1,4-phenylene-diamine	RO—C_6H_4—NH—C_6H_3Cl—NH—C_6H_4—OR
XLII	4-n-Octyloxybenzoyloxy-4'-cyanostilbene	$C_8H_{17}O$—C_6H_4—CO—O—C_6H_4—CH=CH—C_6H_4—CN
XLIII	4-n-Alkoxybenzoyloxy-4'-cyanoazobenzene	RO—C_6H_4—CO—O—C_6H_4—N=N—C_6H_4—CN
XLIV	Thallium stearate	$C_{17}H_{35}COO^-Tl^+$
XLV	Cholesteryl alkanoate	

*Here, R = C_nH_{2n+1}, R' = C_mH_{2m+1}.

Calamitic mesogenic molecules usually contain the following characteristic fragments: a) rigid rings (benzene, cyclohexane, adamantane, and heterocycle residues); b) bridges joining these rings [—CH=N—, CO—O—, —CH=CH—, —N(O)=N—, etc.]; c) groups joined to the rings (most frequently, alkyl or alkoxy groups). In Table 3, the compounds are arranged in the following order: 1) molecules not containing bridges (one-ring, two-ring, etc.) (I—XI); 2) molecules with one bridge (two-ring, three-ring, etc.) (XII—XXXIII); 3) molecules with two bridges (XXXIV—XLIII); 4) others (XILIV, XILV).

III. Nematic mesophases

Since the arrangement of the domains in non-oriented nematics is random, their X-ray diffraction patterns differ little from those of liquids. An oriented mesophase usually gives an X-ray diffraction pattern similar to that shown in Fig. 6. X-Ray diffraction patterns of this kind were obtained for compound XXV (n = 1, PAA) by Kast[16] (in an alternating electric field) and later by Kosterin and Chistyakov[17,18] (in direct and alternating fields). Here, equatorial and meridional reflections are observed. The former are usually represented by one or two pairs of intense crescent-shaped arcs, and are due to the approximately parallel orientation of the long axes of the molecules (L). The position of the equatorial reflections on the X-ray diffraction pattern makes it possible to determine the average distance between the long axes of neighbouring parallel molecules (D). The meridional reflections indicate the existence of a period a in the arrangement of the centres of gravity of the molecules along the direction of the direction **n**. This means that the nematic mesophase contains cylindrical rows of molecules (strings),[19] extending along **n** (Fig. 7). With the parallel orientation of the axes L this arrangement is the natural expression of the tendency to adopt a compact packing. The strings naturally exist only within certain molecular clusters (bundles). The width of the meridional reflections is determined by the average number of molecules in the string.

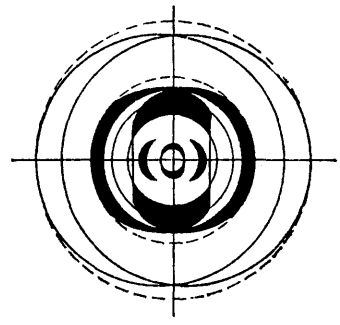


Figure 6. Diagram showing the positions of the reflections on the X-ray diffraction pattern of PAA (field intensity 4000 V cm^{-1}, temperature 123 °C).[17]

The PAA molecule shows negative dielectric anisotropy $\varepsilon_{\parallel} - \varepsilon_{\perp} < 0$ (the minimum value of ε in the direction of the long axis of the molecule with dipole moment forming an angle of 57° with this axis[20]). Thus in an electric field these molecules tend to be arranged in such a way that their axes L are perpendicular to the intensity vector (**n** ⊥ **E**). At the same time, in an electric field, a flux of the impurity ions usually present in the substance is produced; this flux also has an orienting influence, but it leads to the parallel arrangement of the axes L along the field lines (**n**||**E**).[21,22] The final result is determined by the competition between these two factors, and depends on the magnitude of the field strength. A published[17] set of X-ray diffraction patterns of a PAA mesophase at different direct field intensities shows that at E = 50 V cm^{-1}, only the orienting action of the field is felt (**n** ⊥ **E**), whereas at E > 10 V cm^{-1}, the

orienting action of the flux predominates (**n**||**E**). Similar X-ray diffraction patterns were obtained[23] for nematic specimens of compound XL.

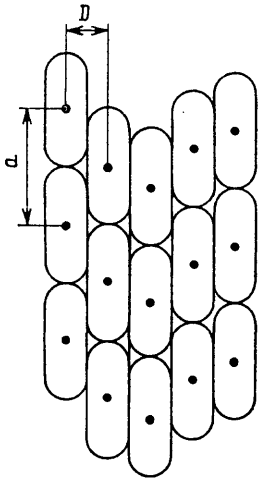


Figure 7. Arrangement of the molecules in a nematic mesophase.

Naturally, Fig. 7 gives a highly idealised picture of the structure of nematic mesophases. The relatively low intensities of the meridional reflections indicates that not all the molecules form periodic strings, and the weakness and vertical broadening of the equatorial reflections indicate that the orientation of the long axes of the molecules deviates from the strictly parallel. Distribution functions of the molecules with respect to orientation, and radial distribution functions of the atoms in the direction of the director, have been constructed.[17,18,23] The authors of these studies also report that they detected three preferred modes of relative azimuthal orientation of the molecules, corresponding to different values of D (D_1—the benzene rings of neighbouring molecules lie in the same plane, and their ends touch; D_2—the touching benzene rings are perpendicular to one another; and D_3—the benzene rings of neighbouring molecules are parallel). For PAA, these values were 6.2, 5.4, and 3.6 Å in a field with a strength of 200 V cm^{-1}, and 7.0, 5.3, and 3.6 Å in a field with a strength of 400 V cm^{-1}. Similar results were obtained for the nematic phase of compound XL. These data indicate that the effective shape of the molecule deviates from cylindrical.

A diffraction pattern similar to that described above is also obtained for cholesteric phases, in which the immediate environment of the molecules is approximately the same as in a nematic phase. In particular, this has been observed for specimens of derivatives of cholesterol (XLV, n = 8 and 13) which had not been subjected to special orienting treatment, but which evidently showed a considerable degree of orientation,[24] and for specimens oriented by a constant shear deformation (specimen in contact with a rotating rod).[25]

A more complex diffraction pattern was obtained for oriented nematic mesophases of homologues of compounds XXV and XLI.[26–28] An X-ray diffraction pattern typical of these phases is shown in Fig. 8. Here, the first meridional reflection has the form of a dumbbell, and the second meridional reflection is split. This type of meridional reflection indicates the appearance of order in a direction not coinciding with the director. To explain this pattern, de Vries[29] proposed the existence of so-called skewed cybotactic groups (Fig. 9), in which the molecules are arranged in layers§ as in the smectic *C*.



Figure 8. Schematic representation of the X-ray diffraction pattern of a nematic with splitting of the meridional reflections.[38]

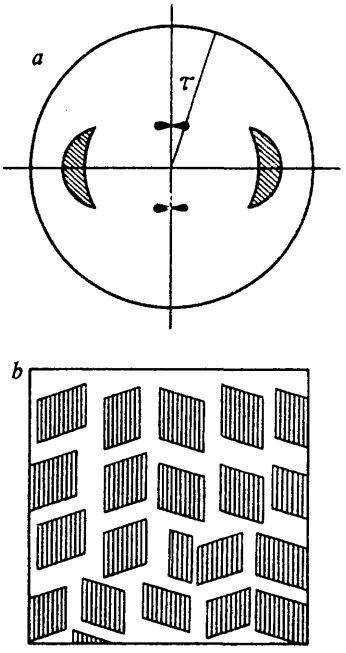


Figure 9. X-Ray diffraction pattern (*a*) and structure (*b*) of a nematic phase with cybotactic groups.

According to de Vries,[29] the angle τ on the X-ray diffraction pattern (Fig. 9*a*) is equal to the average value of the angle between the long axes of the molecules and the normal to the plane of the

§ The presence in liquid phases of cybotactic groups of molecules (that is molecular aggregates with definite spatial order) was first postulated by Stewart,[30] who later pointed out[31] that these groups apparently play an important role in nematic mesophases.

layer. This X-ray diffraction pattern also makes it possible to determine the average thickness of the layer d and the average distance D between the long axes of the molecules. The temperature dependence of these parameters and the intensity of the reflections was determined[32] for nematic phases of compound XLI (homologues with n = 6, 8, 10, 12) oriented in a magnetic field. Some of the numerical data are given in Table 4. With increase in temperature, the values of D and d increase, the former linearly, and the latter non-linearly. The angle τ also undergoes a corresponding non-linear change; with increase in temperature from the point of the transition into the nematic phase (T_N) to the point of the transition into the isotropic liquid (T_I), the value of τ decreases by $\sim 10°$. With increase in temperature, the intensities of the reflections naturally decrease, but for the homologues with n = 6 and 8 at high temperatures the intensity of the meridional reflections remains almost constant (including the range of existence of the isotropic liquid). The last feature was attributed[32] to the preservation of the cybotactic groups in the isotropic liquid phase.¶

Table 4. Geometric characteristics of the nematic phases of homologues of compound XLI.

n	T_N, K	T_I, K	d, Å at T_N	d, Å at 420 K	D, Å at 420 K	$(\Delta D/\Delta T)\times$ $\times 10^{-3}$, Å K^{-1}
6	371.9	471.5	24.05	26.54	5.015	2.60
8	334.0	453.7	27.04	30.30	5.066	2.80
10	384.9	440.9	32.16	35.92	5.066	2.53
12	406.7	432.7	36.32	37.46	5.090	3.14

De Vries[36] also studied the liquid and nematic phases of compound XII (homologues with n = 5–7). The value of D in the mesophase was determined from the equatorial reflections (the outer diffuse ring), and the value of a in the liquid phase was obtained from the meridional reflections (the inner diffuse ring). The presence of the inner ring on the X-ray diffraction pattern of the isotropic phase itself indicates the preferred orientation of at least some of the molecules; in the present case this orientation was evidently due entirely to the orienting action of the walls of the capillary. An increase in a was observed with decrease in the temperature of the liquid. Extrapolation of this relationship from the point of the liquid–nematic transition gave the value of a corresponding to the limiting elongated conformation of the molecule. For all three homologues, this value was found to be close to that obtained for a model in which the *trans*-conformation was assumed for the alkyl chains, and the chains were assumed to be coplanar with the benzene rings. The decrease in a with increase in temperature indicates that this conformation is lost, although the broadening of the inner ring may also be due to a decrease in the orientational order. In the nematic phases, with increase in temperature, a linear decrease in D from 4.94 Å to 5.03 Å was observed, as in the nematic phases described above.[32]

¶ Calculations carried out by the methods of molecular dynamics[33–35] also indicate the existence, in the instantaneous structure of the nematic phase, of molecular clusters, that is regions with higher orientational and translational order. These molecular clusters can apparently be identified with the cybotactic groups.

The layer associates (cybotactic groups) are usually present in nematics which on cooling form smectic phases. An exception is provided by the homologues of compound XXXVII with n = 0, 1, 3, 5, 9, 12, and 16, where n is the number of carbon atoms in the side chain, which does not lie along the axis of the ring in the molecule. In this series, with increase in n from 0 to 6, the angle of slope of the central aromatic fragment within the layers increases, and then decreases.[37] The explanation put forward by the authors cited[37] is that the short lateral "tail" hinders the parallel orientation of the molecules, but with increase in its length it becomes more flexible and can be arranged parallel to the long axis of the molecule.

According to Azaroff,[38] the explanation for the observed[26,27] broadening of the meridional reflections in a direction perpendicular to the meridian is that in the oriented nematic mesophase, the periodic strings of rigid molecules form layers (Fig. 10), and periodicity is also produced in a direction perpendicular to the strings. In the stack of parallel layers there is no periodicity along any direction not lying in the plane of the layer; at the same time, the stacks are arranged regularly in space. Azaroff considers that this model basically explains the intensity distribution on the X-ray diffraction patterns obtained,[26,27] although a real nematic phase also contains randomly arranged (non-correlating) molecular strings. On heating, the number and size of the stacks decrease, and the number of non-correlating strings increases, leading to splitting of the reflection, which acquires the form of a dumbbell.

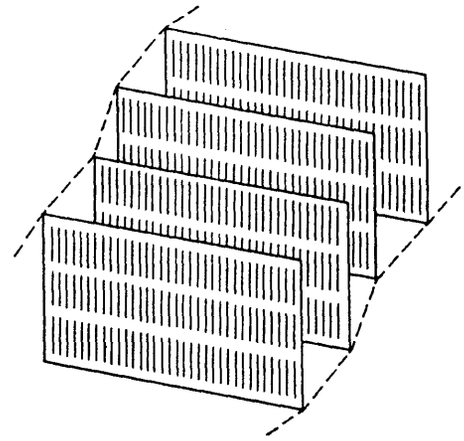


Figure 10. Stacks of parallel molecular layers in a nematic phase.[38]

Azaroff's model is criticised in a brief review by de Vries,[39] analysing published data on the structure of "cybotactic" nematics. The main argument against this model is that the existence of "planar layers" is not revealed in any properties of the nematic phase. According to de Vries, it is more probable that within this phase there are blocks of molecules with structures similar to those of the fragments of layers of the type *SmA* or *SmC*, whose appearance corresponds to the nucleation of the smectic layer order.

Optical modelling of diffraction on planar models of different molecular packings lead to similar conclusions about the structure of "cybotactic" nematics (Fig. 11).[40] In the opinion of the author cited, however, the value of the angle τ (see Fig. 9) is determined not by the slope of the molecules in the cybotactic groups (blocks) but by the average distance between these groups and their dimensions.

It is therefore suggested, in contrast to the work cited above,[32] that with increase in temperature the size of the blocks decreases.

Another possible increase in the complexity of the structure of the nematic phase may be due to the presence of dimeric associates of molecules, leading to the formation of molecular strings whose period is appreciably greater than the length of the molecule. This is apparently the situation in the cyanophenyl derivatives studied by Leadbetter and co-workers.[41-43] For these compounds, the ratio $a/l > 1$ and depends on the length of the aliphatic chains; at the same time, the period of the string a changes little with change in the central aromatic part of the molecule.

This last feature indicated to the authors cited a form of packing of the molecules in which their aromatic parts overlap (come into contact). The structure of the string is given approximately by the diagram in Fig. 12 (proposed by the present authors). The authors cited[41-43] talk about "bilayer" packing, but in the opinion of the present authors, when discussing the nematic phase, it is better to say that the string contains molecules oriented in antiparallel fashion, or that the strings are formed by dimers, which in the present case are most probably stable associates of molecules. These dimers are stabilised, in particular, by electrostatic interaction, since the molecules have an appreciable dipole moment (3.5–4.0 D).

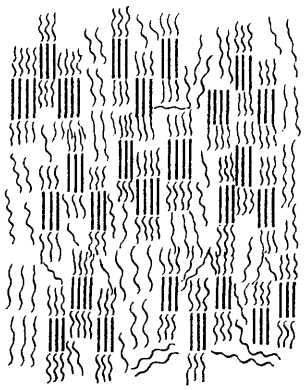


Figure 11. Model of the structure of a "cybotactic nematic", obtained by optical modelling.[40]

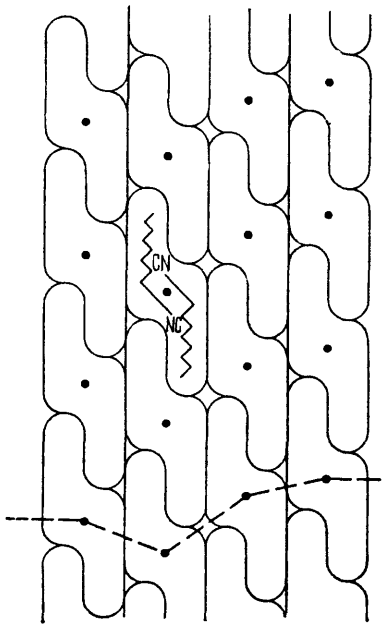


Figure 12. Structure of a nematic phase made up of dimers (for the case of cyano-derivatives).

Table 5 gives the values of l and a for a series of cyano-derivatives.[43] An interesting feature is that for compounds IV, VII, and XI, in addition to the reflectance given by the period a corresponding to the dimeric organisation of the strings, additional reflections indicating the existence of a period $a_2 < l$ are observed. This indicates the presence of strings in which dimers are not observed, and the molecules possibly do not have the most elongated conformation. The temperature dependence of the intensity of the reflections shows that strings with the period a_2 predominate at low temperatures, and strings with the period a_1 predominate at high temperatures.

A picture similar to that described above is also observed for a number of other compounds, for example compounds XXIX and X.[44,45] In the last case, the ratio a/l shows a marked dependence on the substituent, having the value ~1.4 for the cyano-derivatives, and ~1.1 for the halogeno-derivatives.

Table 5. Comparison of the lengths of the molecules (l) and the periods (a_1 and a_2) in the nematic phases of cyano-derivatives.

Compound	l*, Å	a_1, Å	a_2, Å
(II, n=6)	20.5	27.7	—
(IV)	19	24.9	13.2
(VII)	22	30.9	20.4
(XI)	23.5	30.7	18
(XX)	24	31.7	—
(XXVII)	22.2	32.2	—

* l is the maximum length of the molecule for the most elongated conformation.

IV. Smectic *A* and *C* phases

The X-ray diffraction patterns of a smectic mesophase oriented in an electric or magnetic field often have the form shown schematically in Fig. 13*a*. X-Ray diffraction patterns of this type have been obtained[46] for compound XXXI, and also in other studies.[47-52] In contrast to the X-ray diffraction patterns of nematics, in this case the meridional reflections have the form of fairly distinct spots. According to the simplest treatment, this type of X-ray diffraction pattern corresponds to an ideal smectic *A*, in which the molecular axes L are perpendicular to the layers ($\varphi = 0$); if however the axes L lie at a slope to the plane of the layer ($\varphi \neq 0$), that is in the case of an ideal smectic *C*, the straight line passing through the centres of the meridional reflections should make an angle ω with the equator (Fig. 13*b*). This picture has been observed fairly infrequently, however, and only for single-domain specimens. The distance between the meriodional reflections is determined by the thickness of the layer d, and the position of the equatorial reflections, as in the case of nematics, can be used to calculate the value of D.

In fact, smectics have a more complex structure. In particular, the condition $\varphi = 0$ for smectics *A* is usually satisfied only statistically.

Oriented liquid-crystalline specimens of compounds XXVI, XXXII, and XLIV, obtained on freshly split mica plates, have been studied by X-ray diffraction.[53] The X-ray diffraction patterns had the form corresponding to the type *SmA* (Fig. 13*a*), but the best agreement with experiment was given by a model in which the molecules were displaced relative to one another along their long axes by 5–6 Å, and their slope to the normal to the layer was 30° and 43° for compounds XXVI and XLIV respectively (for compound XXXII, a structural model corresponding to the experimental diffraction data could not be obtained). The structural analysis carried out in this study was based on an examination of the width and intensity of the meridional reflections as functions of the order of diffraction; these relationships should be different for different trial models, of which the following were considered: 1) monolayer *SmA*, 2) bilayer *SmA*, and 3) bilayer *SmC* (with allowance for the degree of disorder of the para-crystalline type). The best model was found to be the third model, which was constructed using X-ray diffraction data obtained for single crystals of these compounds or their analogues. Thus the order of the type *SmA* ($\varphi = 0$) is here achieved only effectively, as a result of averaging of the orientations with respect to the para-crystalline domains and with respect to the thickness of the specimen. Estimation of the linear dimensions of the crystallites gave the value ~400–800 Å.

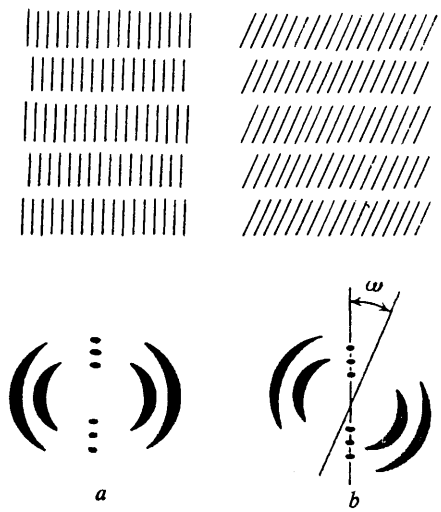


Figure 13. Arrangement of the molecules in upright (*a*) and sloping (*b*) smectic mesophases, and a schematic representation of the corresponding X-ray diffraction patterns.

For a deeper structural analysis of LC it is necessary to take into account the fact that the form of the molecules often differs significantly from cylindrical; this applies particularly to molecules containing long terminal aliphatic chains, which may extend in a direction which differs considerably from the direction in which the rigid central part extends.

The X-ray diffraction pattern obtained[54] for the smectic phase of compound XXXIX ($n = 6$) in a magnetic field had the form represented schematically in Fig. 14 ($\omega = 43°$). Assuming that the molecules retain the conformation found in the crystalline substance (the angle between the straight line passing through the centres of the benzene rings and the direction in which the aliphatic chains extend is 59°), the authors cited constructed a multi-domain model of this smectic. One of the two orientations of the layers represented in Fig. 15 is produced in each domain. Within the layer, the axes of the central parts of the molecules are arranged in sloping fashion, and make an angle of 47° with the plane of the layer, whereas the aliphatic chains are almost perpendicular to the plane of the layer (~74°). The proposed structure was confirmed by optical modelling. Here, a definite analogy with the structure of a nematic containing cybotactic groups is observed (Fig. 9). The smectic phase differs in that in it the layers are much more extensive than the cybotactic groups, and extend to the boundaries of each domain.

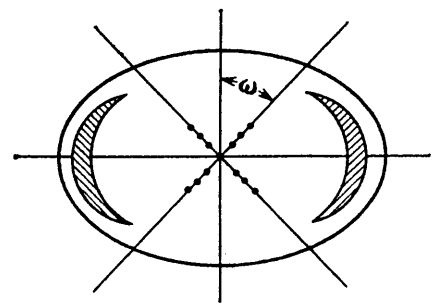


Figure 14. Schematic representation of the X-ray diffraction pattern compound XXXIX ($n = 6$).[54]

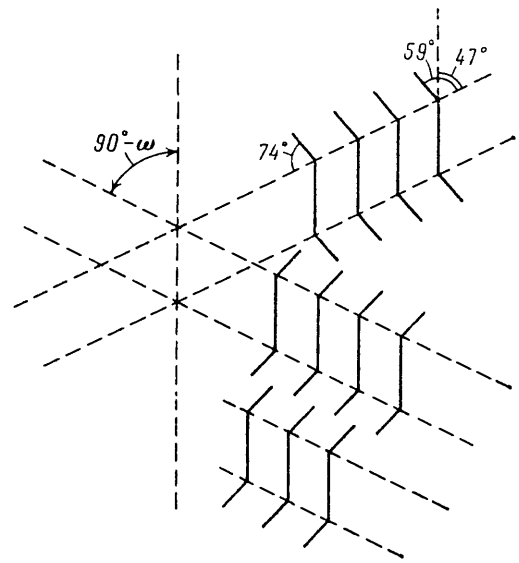


Figure 15. Polydomain model of the smectic phase of compound XXXIX ($n = 6$).[54]

The example given shows that allowance for the non-linearity of the molecules (an attempt to make this allowance was also undertaken in the work cited above[53]) blurs the classical structural representations of the calamitic phases *SmA* and *SmC*. To this must be added the possible sinusoidal corrugation of the layers, allowance for which, for example, gives best agreement with experiment in the optical modelling of the diffraction pattern of the smectic mesophase of compound XXV (n = 7).[55] The authors cited proposed the examination of various hypothetical layer structures formed from rod-shaped and zigzag molecules to explain the extended (parallel to the equator) form of the meridional reflections. The best model was found to be the model of type $SmA\tilde{}$ discussed below.

Recent studies have shown that in many cases, smectic phases have a bilayer structure. This important feature of their structure is usually related to the non-linear configuration and polarity of the molecules.

One of the first investigations in which the bilayer structure of a smectic mesophase was detected involved an X-ray diffraction and dilatometric study of compound I at different temperatures.[56] The proposed structural model, constructed with allowance for the angular configuration of the molecules, is shown in Fig. 16.

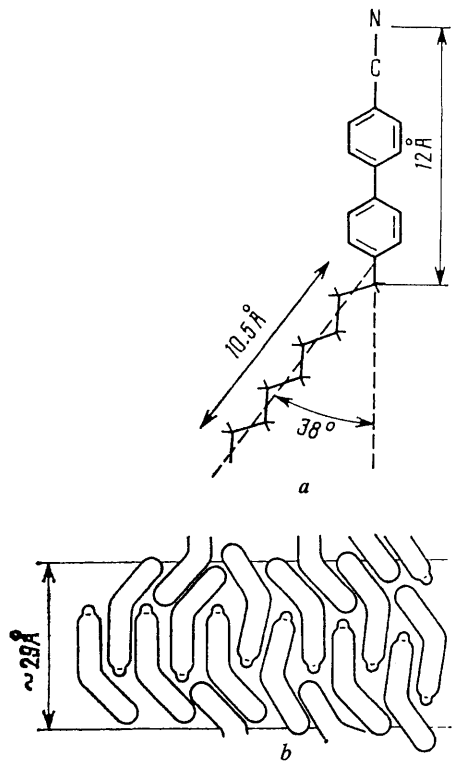


Figure 16. Structure of the molecule of compound I (*a*) and the packing of the molecules in the smectic phase (*b*).[56]

Dilatometric and X-ray diffraction data[57,58] were also combined in a study of the structure of the mesophases of compound XXX, of the type *SmA*. Two homologous series (m = 0 and 1) were studied, in each of which the central aromatic part remained unchanged, and the aliphatic chain joined to the ester group was varied (n = 1–16). The dilatometric study gave the molar volume, and the X-ray diffraction study gave the layer thickness (d) throughout the temperature range of existence of the mesophase. In the opinion of the authors cited, the experimental data show best agreement with the "bilayer" model (Fig. 17). The central part of the "bilayer" consists of the aromatic sub-layer, which contains practically no aliphatic "tails" and is therefore comparatively rigid and highly ordered. On both sides of the aromatic sub-layer there are much less ordered sub-layers consisting of aliphatic chains. The axes of the aromatic fragments of the molecules of the lower homologues of the series with m = 0 make an angle of 70–75° with the average plane of the layer, but are arranged approximately at right angles for the higher homologues and for all members of the series with m = 1. The thickness of the aromatic sub-layer for m = 0 and n = 2 is 16.7 Å, and for m = 0 and n = 14 it reaches 18.0 Å, which is practically equal to the length of the aromatic part, found from the model of the molecule; on going from one homologue to another, the total thickness of the layer increases by an average of 1.51 Å (m = 0) and 1.35 Å (m = 1), although according to model representations the increment in the length corresponding to a CH_2 group is 1.27 Å. This last feature is due to the specific structure of the bilayer. For m = 0, the thickness of the aliphatic part of the layer is determined by the average slope of the chains to the plane of the layer, which is equal to ~40°; for m = 1, the thickness of this part of the layer decreases, and the degree of order also decreases. With increase in temperature, the thickness of the bilayer increases slightly, according to a linear law. Using the X-ray diffraction patterns and the data on the structure of smectics described above, the authors cited tried to obtain information on the structure of the layers in the crystalline forms of the smectogens XXX being considered.[59] Unambiguous results could not be obtained, however (in principle, both bilayer and monolayer packings of the molecules are possible).

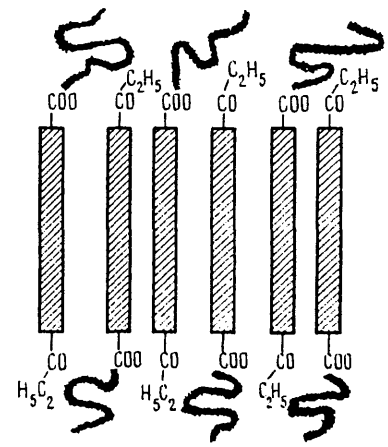


Figure 17. Structure of a smectic "bilayer".[57]

Similarly, a small-angle X-ray diffraction study[60] detected a "bilayer" structure in the phase of type *SmA* formed by compound VIII (the nematic phase of this substance contains molecular dimers, represented schematically in Fig. 12).

In addition to the nematic phases described in the previous section, smectics of the cyano-derivatives II (n = 10, 13, 16, 18), VII (n = 8), and XXII have been studied.[41–43] Here, three features are noteworthy. Firstly, for the phase *SmA* of compound XXII, decrease in temperature leads to the appearance of dumbbell-shaped reflections, indicating the production of skewed cybotactic groups, and the lines drawn through the centres of gravity of the molecules making up the cybotactic group make an angle of 27° with the *SmA* layers. Secondly, in this case also, bilayers in which the molecules are arranged in antiparallel orientations and are apparently joined to form dimers are also observed. Thirdly, and finally, in the smectic phase† of compound VII (n = 8), as in the nematic phase, a double periodicity is observed ($d_1 \simeq 1.4l$, $d_2 \lesssim l$). This apparently indicates the coexistence of bilayers and monolayers in which the molecules on the average have the parallel orientation.

Double periodicity of the smectic phase has also been observed[50] for compound XIX. In the weakly oriented state of the mesophase, splitting of the meridional reflections is observed; instead of the period 24.9 Å, periods of 32.5 Å and 26.6 Å appear for orientation in an electric field, and of 31.6 Å and 21.3 Å for orientation in a magnetic field. The authors cited pointed out, however, that both the existence of double periodicity in the packing of the layers and the presence of domains in which the smectic layers have the form of coaxial cylinders are possible in this case. According to Mineev,[51] the diffraction of X-rays on cylindrical smectic layers should lead to the observed splitting of the reflections.

The general picture of the bilayer structure of smectics, the phenomenon of double periodicity, and the reflection of these effects on the X-ray diffraction patterns were examined by Hardouin and co-workers.[61–63] According to the authors cited, there are three sub-types of mesophases *SmA* (Fig. 18) constructed from polar molecules: 1) the smectic A_1, consisting of non-polar monolayers (in a special case, the molecules in this layer may be joined to form dimers); in this smectic, $d \simeq l$; 2) the smectic A_2, consisting of double layers, each of which includes two polar monolayers; in this case, $d \simeq 2l$; and 3) the smectic A_d, formed by bilayers, where $l < d < 2l$. To this must be added the phase of type $Sm\tilde{A}$ with periodic modulation.[61]

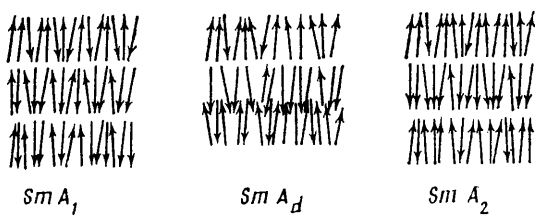


Figure 18. Structure of mesophases *SmA* belonging to different sub-types.

Fig. 19 compares the diffraction patterns (meridional reflections) characteristic of these three types of smectic with that for the nematic mesophase. The two diffuse haloes on the X-ray diffraction pattern of the nematic are characterised by the wave vectors $\mathbf{q}_2 = (2\pi/l)\mathbf{n}$ and $\mathbf{q}_1 > (2\pi/2l)\mathbf{n}$, where $\mathbf{n}$ is a vector showing the direction of the director; the vector $\mathbf{q}_1$ is due to the periodicity of the strings formed by individual molecules, and the vector $\mathbf{q}_2$ is due to the periodicity of the strings consisting of dimers. The smectic A_2 gives two Bragg peaks, corresponding to the polar monolayers and the double layers. For the smectic A_d, two Bragg peaks are observed, corresponding to the first and second order of diffraction from the bilayers. Here, however, a diffuse halo is usually observed in the region corresponding to the wave vector $\mathbf{q}_2 = (2\pi/l)\mathbf{n}$; this is due to the fact that the bilayer structure generally contains regions having a monolayer structure (see Fig. 23). For the smectic A_1, a Bragg peak corresponding to monolayer packing is observed, together with a diffuse halo, which indicates that this smectic is usually impregnated with the bilayer structure. The modulation of the layers, characteristic of smectic *A*, leads to doubling of the meridional reflection. If this modulation is sinusoidal, the reflection may be not split, but elongated along the equator.

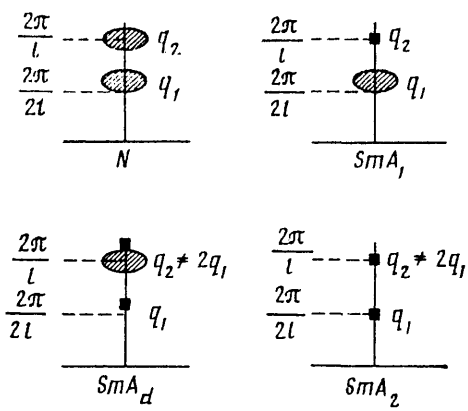


Figure 19. Schematic representation of the X-ray diffraction patterns of a nematic and of mesophases *SmA* belonging to different sub-types.[63] The black points denote the Bragg peaks corresponding to highly ordered elements of the structure; the hatched regions represent the diffuse peaks corresponding to structural features with a low degree of order.

These characteristics of the X-ray diffraction patterns can be established and studied systematically only by highly accurate measurements, examples of which have been published.[63] Thus compound XXXV in a narrow temperature range is converted from the nematic to the smectic phase SmA_d, and then to SmA_2. A mixture of compounds XXXV and XXXVIII (n = 4) with decrease in temperature passes through stages involving the formation of a nematic and then the successive phases SmA_1 and SmA_2. A study of the temperature dependence of the thickness of the smectic layer, carried out[64] for individual compounds and mixtures, showed that in the transformation $SmA_d \rightarrow SmA_2$ the value of d increases smoothly and continuously, indicating, in the opinion of the authors cited, that this transformation is not a phase transformation. Examples of mixtures of mesogens whose structure corresponds to the type $Sm\tilde{A}$ have been given.[61]

† This phase is a phase of the type *SmE*; these smectics are described in section V.

phases $N(1)$ and $N(2)$ reduces to a difference in the structures of the strings, which have a larger period in the first case. The lateral interaction of these strings in the regions of the equilibrium diagram corresponding to the nematic mesophases is insufficient for their relative displacement to be detected. When the nematic is converted into the smectic phase, a rearrangement takes place, as a result of which the layer structure is detected.

The structural interpretation of the transformations proposed by Cladis and co-workers,[66] and also the model represented in Fig. 21, apparently have an arbitrary element; the existence of dimers is assumed *a priori*, although in fact they may not be present in some of the phases examined. In one of their papers,[65] the authors cited also took account of the possibility of rearrangement (or breakdown) of the dimers in the phase transformation, but this alternative does not appear in their subsequent paper.[66]

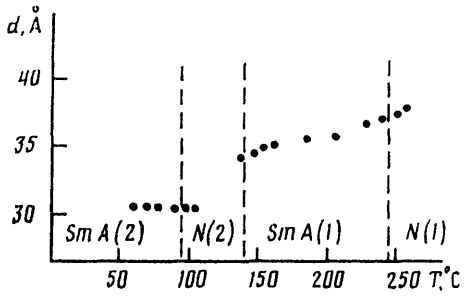


Figure 22. Temperature dependence of the thickness of the smectic layers of compound XLII.[69]

A completely different interpretation of the reverse mesomorphism observed for compound XLII was given by other workers.[68,69] In this case the following chain of thermotropic transformations was detected:

$$C \xleftrightarrow{95\,^\circ C} SmA\,(2) \xleftrightarrow{96\,^\circ C} N\,(2) \xleftrightarrow{138.9\,^\circ C} SmA\,(1) \xleftrightarrow{247\,^\circ C} N\,(1) \longleftrightarrow I,$$

where C represents the crystal, and I the isotropic liquid. The thickness of the layer in the phase $SmA(2)$ in fact is independent of temperature and approximately equal to the length of the molecules (31.4 Å), whereas in the phase $SmA(1)$ the thickness of the layer increases considerably with increase in temperature (Fig. 22). The diagram in Fig. 22 confirms the difference in the periods of the strings in the nematics $N(1)$ and $N(2)$ mentioned above. The authors cited[68,69] also measured the average distances between the long axes of the molecules D for all the phases:

Phase	Temperature, °C	d, Å
N (1)	263	5.3
SmA (1)	150	5.1
N (2)	115	5.0
SmA (2)	75	4.85

They consider that the structure $SmA(2)$ is a monolayer structure, and that $SmA(1)$ is predominantly bilayer. At the same time, with decrease in temperature, the X-ray diffraction patterns of the phase $SmA(1)$ show an additional periodicity, corresponding approximately to four times the length of the molecules (~120 Å). This last feature was attributed to the appearance of monolayer regions. A schematic representation of the structure of the mesophase assumed by the authors cited in this temperature range is shown in Fig. 23, which explains the modulation with a period of ~120 Å. A study of the diffuse spots corresponding to small angles of scattering on the X-ray diffraction patterns of the phase $N(2)$ indicated the presence of cybotactic groups, which are similar to the monolayers of the phase $SmA(2)$ in the lower part of the temperature range, and similar to the bilayers of the phase $SmA(1)$ in the upper part; in the middle of this range, both types of group are observed.

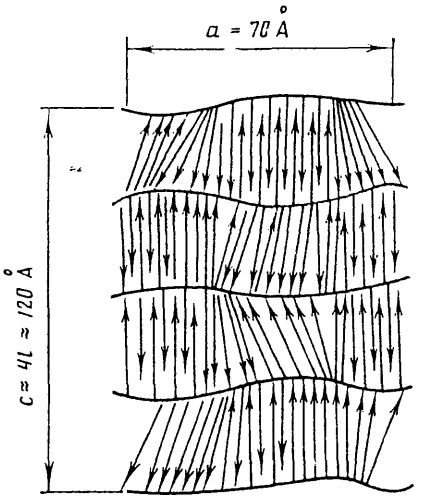


Figure 23. Structure of the mesophase of compound XLIII.[69]

Similar results were obtained[7] for the compound XLIII (n = 9), which differs from the compound XLII studied by Hardouin and co-workers[68,69] only in the bridging group: the group $-CH=CH-$ is replaced by the group $-N=N-$. Here, the following phase transformations are observed:

$$C \xrightarrow{94.0\,^\circ C} N\,(2) \xrightarrow{116.0\,^\circ C} SmA\,(1) \xrightarrow{212.4\,^\circ C} N\,(1) \xrightarrow{242.9\,^\circ C} I.$$
$$\searrow SmA\,(2) \swarrow 70.9\,^\circ C$$

The temperature dependence of the value of d for specimens oriented in a magnetic field is analogous to that represented in Fig. 22, but in this case it was also possible to measure the change in the period of the strings in the range corresponding to the reverse nematic $N(2)$. Here, the interpretation of the results is similar; it is considered that the phase $SmA(2)$ consists of monolayers, the phase $SmA(1)$ is partly bilayer, and in the range of existence of the phase $N(2)$ there is a gradual change from the first to the second structure.

The same compound XLIII (n = 9) and its homologue with n = 8 has been studied at a high pressure.[71] For the homologue with n = 8, reverse mesomorphism was not observed; the change in the temperature of the transformation of the monolayer phase $SmA(1)$ into the nematic phase was linear (Fig. 24*a*). A fundamentally different result was obtained for the bilayer reverse phase $SmA(1)$ of the homologue with n = 9 (Fig. 24*b*). In the last case the phase boundary is represented by a symmetrical curved line; at a pressure of 0.51 kbar the bilayer phase $SmA(1)$ disappears. Thus pressure

stabilises the monolayer structure and destabilises the bilayer structure, converting the latter into a nematic structure (the authors cited point out that their interpretation of the results was based on the model proposed by Cladis and co-workers[65,66]).

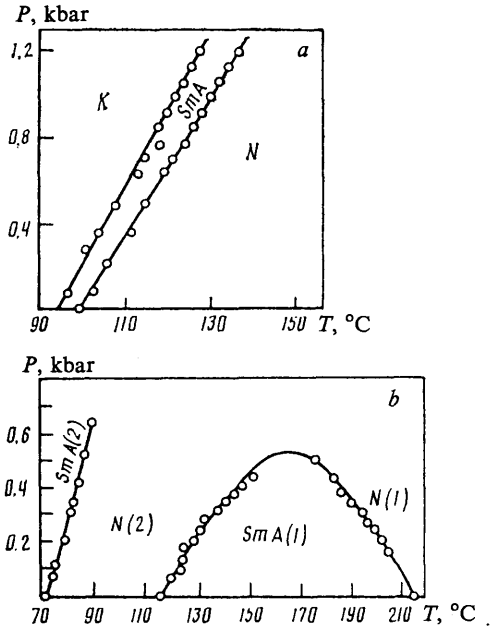


Figure 24. Equilibrium diagrams of homologues of compound XLIII:[71] *a*, homologue with $n = 8$; *b*, homologue with $n = 9$.

In a recent paper[72] it was shown that the number of smectic–nematic reverse phase transformations observed in a single system may be fairly large. Thus for compound XXXIV the following sequence of mesomorphic phases (in the notation of the authors cited) is observed; the types of phase were confirmed by X-ray diffraction data:

$$I \xrightarrow{224\ ^\circ C} N \xrightarrow{195\ ^\circ C} Sm(\text{bilayer}) \xrightarrow{156\ ^\circ C} N(1R) \xrightarrow{138.5\ ^\circ C} Sm(\text{bilayer})$$
$$\xrightarrow{124\ ^\circ C} N\,(2R) \xrightarrow{121\ ^\circ C} SmA\,(1) \xrightarrow{119\ ^\circ C} SmC \xrightarrow{100\ ^\circ C} SmA\,(2) \xrightarrow{96\ ^\circ C} SmC\,(2).$$

The authors cited relate this variety of phases, firstly to the change with change in temperature in the conformational mobility of the terminal alkyl chains, leading to a change in the effective length of the molecule, and secondly to the possible formation or breakdown of dimers.

Before considering papers dealing with the study of smectics of type *C*, it may be noted that X-ray diffraction data on these mesophases are fairly sparse. The tilt angle φ of the molecules in the phase *SmC* is determined in different ways: 1) from the position of the reflections on the X-ray diffraction patterns, 2) from the ratio of the length of the thicknesses of the layers in the phases *SmC* and *SmA* of a given compound. These estimates are clearly always more or less approximate, since they involve the assumption that the molecules have a cylindrical form, or (and) other approximations.

For compound XXV ($n = 7, 8$), the phase *SmC* is formed directly from the nematic, and the angle φ (~30°) changes little compared with the angle of slope of the molecules in the cybotactic groups of the nematic phase.[73] For a typical representative of smectics of type *C*, namely compound XXXVIII (TBBA), the classical sequence of phase transformations $N \rightarrow SmA \rightarrow SmC$ is observed on cooling. The transformation $SmA \rightarrow SmC$ is accompanied by an increase in the angle φ from 0 to 25 °C, and the results of the direct measurement of φ from the X-ray diffraction patterns (the value φ_P) and its calculation from the thickness of the smectic layers ($\cos\varphi_X = d_C/d_A$) show good agreement.[74]

The temperature dependence of the angle φ in *SmC* has been studied[37] for compound XXI; with increase in temperature, the angle φ increases, and φ_P and φ_X diverge. The authors cited attribute this last feature to the zigzag form of the molecules, and suggest that the thickness of the smectic layer be described by the expression

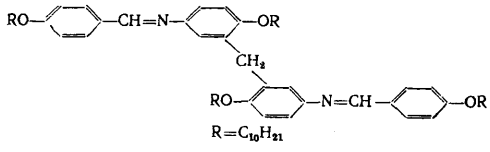
$$d = a_0 \cos\varphi_1 + (l_1 + l_2)\cos\varphi_2,$$

where a_0, l_1, and l_2 are the lengths of the central aromatic part and the terminal fragments of the molecule, and φ_1 and φ_2 the angles of slope of the aromatic ring and the "tails" to the plane of the layer ($\varphi_1 = \varphi_P$). It was found that in the substance studied, the terminal chains are arranged almost at right angles to the layer, and the aromatic rings are sloping.

The thickness of the smectic layer of the phase *SmC* of compound XXV ($n = 7$) has been measured at different pressures up to 1.5 kbar [75] and up to 3.8 kbar,[76] and the angle of slope of the molecules to the plane of the layer determined. For $d = 23.5$ Å, atmospheric pressure, and a molecule length of 32.1 Å (found from the model), $\varphi = 43°$. An interesting feature is that with increase in pressure, the value of *d* and hence the angle of slope remain practically unchanged. The authors cited[76] point out that the nature of the change in the structure with the smectic *C* is compressed is still not clear. The $P-T$ diagram shows a triple point at a pressure of 6.67 kbar and a temperature of 164 °C. Above this pressure, the solid phase is converted directly into the nematic phase.

A characteristic feature of the smectic phase of the chiral compound XV [75] is its spiral character (type *SmC**). This phase is produced from the phase *SmA* with increase in pressure, and the thickness of the layer, which in *SmA* was independent of pressure, decreases considerably in *SmC** (the slope of the molecules increases) (Fig. 25); the substance is then converted into *SmI**. The authors cited compared the behaviour of this substance with that of compound XXV ($n = 7$); in the last case the phase *SmC* is formed directly from the nematic phase (the stage *SmA* is not observed), and the thickness of the sloping smectic layer is practically independent of temperature and pressure. An attempt to relate the difference described to the structures of the molecules of the compounds being compared was unsuccessful, however.

An analysis of the structure of mesophases of the type *SmC* for the compound



proved to be extremely complicated, because of the conformational non-rigidity of the molecules and the possible coexistence of completely different conformers in the same mesophase. Three

specimens (obtained in different ways) of this compound, called "Siamese twins", were studied.[77] Specimen *A*, obtained by crystallising from a solvent, in both the crystalline (28 °C) and the smectic (122 °C) phases gave a diffraction maximum indicating the presence of layers with d = 23 Å. Specimen *B*, obtained by cooling the melt, at the same temperatures in both the crystalline and smectic phases gave a maximum corresponding to layers with d = 32 Å. Finally, for specimen *C*, obtained by rapid heating to 125 °C, a diffraction pattern with two maxima (d = 23 Å and 32 Å) was observed. The authors cited consider that the phases *A* and *B* are formed by different conformers (*a* and *b*) (this naturally leads to the production of layers with different structure and thickness), and that the phase *C* is a mixture of the conformers and contains two types of smectic domain. In the interpretation of the results, the conformers *a* and *b* were assigned structures in which the $C_{10}H_{21}O-C_6H_4-CH=N-C_6H_3(OC_{10}H_{21})$ chains are directed in different directions in one case, and in the same direction in the other. It was also noted that the smectic phase of the compound $C_{10}H_{21}O-C_6H_4-CH=N-C_6H_4-O-C_{10}H_{21}$ (corresponding approximately to half of the "twins" molecule) also give a diffraction maximum corresponding to a layer with d = 32 Å. (This obviously means that in specimens *A* and *B* the extended parts of the molecules are oriented in different ways relative to the planes of the smectic layers.) It is clear, however, that the interpretation of the diffraction data given in the work cited is indefinite. Such complex molecules have an extremely wide range of conformational possibilities; these molecules can also be arranged in layers in different ways.

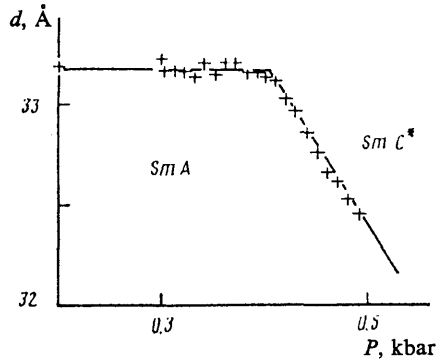


Figure 25. Pressure dependence of the thickness of the smectic layer in compound XV.[75]

Like the smectic phases of the *SmA* type, the sloping smectics show monolayer structures (SmC_1) and structures with double layers (SmC_2).[61] Cases of modulation of the layers are known,[78,79] giving the sub-type *SmC*; here, sinusoidal modulation is replaced by corrugation of the layers, "like the teeth of a saw".[78]

V. Smectic phases with a high degree of ordering

This section is devoted to a systematic examination of X-ray diffraction studies of "crystalline" smectics (the two lowest rows in Fig. 1), and then the less ordered hexatic smectics (second row in Fig. 1). This sequence of presentation is dictated by the chronology: the first detailed studies of the structure of "crystalline" LC preceded slightly the detailed study of hexatic phases.

It should be emphasised that the term "crystalline smectic" indicates the possibility of the experimental determination of the three parameters of a statistical lattice, but does not imply the three-dimensional periodicity characteristic of solid crystals. In addition to local breakdown of the order (for example, faults in the orientation due to the isometric character of the molecules in certain directions), considerable dispersion of the orientational and positional parameters is usually observed in this case, and domain structures of different types are often encountered, together with structural modulations which do not correspond to the effective period. In this case the dynamic parameters naturally have values appreciably higher than those characteristic of solid crystals. It is also important to emphasise that many liquid-crystalline systems are sufficiently ordered (suitable for structural studies) only under special conditions (for example in an electric or magnetic field).

A significant contribution to the study of highly ordered smectic phases was made by Doucet, who summarised his work in a review.[80] In particular, "crystalline" smectics of the compound XXXVIII (n = 4) (TBBA) were studied by X-ray diffraction;[81] the following transformations were observed between the large number of mesomorphic phases:

$$C(9) \xrightarrow{-33\,^\circ C} C(8) \xrightarrow{113\,^\circ C} (SmG)\,(5) \xrightarrow{144\,^\circ C} SmC\,(4) \xrightarrow{172\,^\circ C}$$
$$52\,^\circ C \uparrow \qquad \uparrow 84\,^\circ C$$
$$(7) \xrightarrow[68\,^\circ C]{} (6)$$
$$\longrightarrow SmA\,(3) \xrightarrow{200\,^\circ C} N\,(2) \xrightarrow{236\,^\circ C} I\,(1).$$

A "single crystal" of phase (5), obtained by melting the single crystal (8) without applying an external field, gave two types of X-ray diffraction pattern. These X-ray diffraction patterns, and the arrangements of the molecules deduced from them are shown in Fig. 26. When the X-ray beam is perpendicular to the long molecular axes *L*, the diffraction pattern (Fig. 26*a*) consists of a series of parallel diffuse bands (layer lines), the distances between which are proportional to the reciprocal of the length of the molecule (1/29 Å). This indicates the presence of molecular string along the *c* axis. The thickness of the diffuse layer lines depends on the extent of the ordered section of the string; in the present case it is close to 200 Å, which corresponds to approximately seven molecules. The length of the diffuse bands can be used to find the mean-square deviations of individual molecules from the direction of the string (2°) and the mean-square displacements of the molecules along the string (2.5 Å). Unlike the diffuse bands given by nematics, the diffuse bands in the present case are not curved, indicating that there is little departure from the parallel arrangement of the strings. The intense spots forming a regular row on the layer lines are produced by the smectic layers. The angle between the long molecular axes and the normal to the plane of the layer is 32° at 115 °C (it can be measured directly on the X-ray diffraction pattern). Strings are formed when the layers are superimposed.

The other X-ray diffraction pattern (Fig. 26*b*) corresponds to the equatorial plane *ab*, which is perpendicular to the long axes of the molecules. The 6 Bragg reflections observed in this case indicate two-dimensional translational ordering of the smectic layers (a pseudo-hexagonal lattice). This X-ray diffraction pattern also contains diffuse spots, which can be grouped into three sets of four, lying at an angle of 120 ° to one another. This last feature was interpreted as corresponding to three orientations of the domains. Doucet[80] constructed a scheme for the coherent coupling of

domains oriented in different ways (Fig. 27). Within each domain the cell is monoclinic. The X-ray diffraction patterns described, and also the "powder diagrams", were used to determine the parameters of this cell (at 125 °C):

$$a=10.10(5),\ b=5.18(2),\ c=28.3(2)\ \text{Å},\ \beta=119.0(5)^\circ.$$

According to the current structural classification of smectics (see section II), this structure of the domain corresponds to the type *SmH*. The coexistence of three orientations of the domains, leading to the pseudo-hexagonal nature of the layers, makes it possible to assign the mesophase described to the type *SmG*. In the works cited,[80,81] this mesophase was first regarded as a representative of the smectics of type *SmB* (from the miscibility criterion). Having established the sloping arrangement of the molecules relative to the layers, Doucet suggested that the smectics of type *B* be sub-divided into "upright" (B_A) and "sloping" (B_C). In his review,[80] however, he points out that the X-ray diffraction data show that the phases classified as *SmG* according to the miscibility criterion are identical to phases of the type SmB_C.

In the model described for the structure of the phase (5) of TBBA, the question of the nature of the azimuthal disorder remains open; it may be static (there are no reorientational movements of the molecules involving rotation of the molecules about their long axes) or dynamic (reorientational movements take place, so that the orientation of the domains is constantly changing). Inelastic neutron scattering has shown[82] that the molecules in the phase being considered change their orientation, by rotating through 60°. This is consistent with the proposed model (Fig. 27) if it is assumed that the molecules situated at the vertices of the cell and at its centre are rotated through 60° relative to one another and that they change their orientation in synchronous fashion.

The degree of crystallinity, revealed in the correlation of the relative arrangement of the smectic layers, can be estimated by analysing the profile of the diffuse spots surrounding the Bragg reflections (Fig. 28). An analysis of the phonons generating these diffuse spots at different temperatures was carried out.[80] The intensity profile of the diffuse scattering is described by the function $I(q) = I/q^\alpha$, where q is the distance from the centre of the reflection in reciprocal space, and α the crystallinity criterion. If there is no correlation between the layers of the smectic phase, then, as shown by de Gennes and Sarma,[83] $\alpha < 2$. On the contrary, for phase (5) close to the point corresponding to its formation from the crystal, the value of α is close to 2, indicating a high degree of crystallinity.

A similarity is observed between the structures of the phase (5) and the crystals (8). According to X-ray diffraction data,[84] the crystals (8) contain molecular layers parallel to the plane *ab*, and also strings extending along the *c* axis. The lattice parameters are: $a = 17.56$, $b = 5.75$, $c = 53.2$ Å, $\beta = 115.47°$, structural class $C2/c$, $Z = 8(1)$. Thus the structures of the layers in the mesophase (5) and in the crystalline substance (8) differ considerably, but the

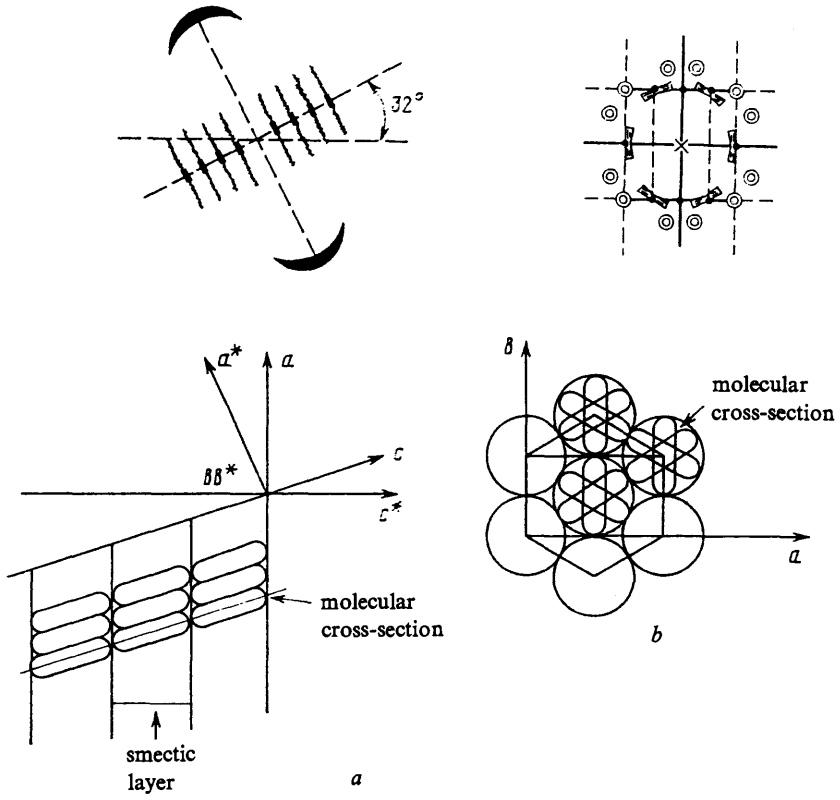


Figure 26. X-Ray diffraction patterns (schematic representations) and arrangement of the molecules in the highly ordered smectic phase of the compound TBBA:[80] *a*, projection perpendicular to the axis *L*; *b*, projection along the axis *L*.

angle between the long axes of the molecules and the normal to the plane of the layer in the crystals is 35°, that is it is close to the corresponding value found for the smectic phase (5). Disorder is observed in the arrangement of the terminal methyl groups, and there is extremely little penetration of the butyl chains into adjacent layers. These two factors weaken considerably the cohesion of the layers, enabling the latter, on fusion of the crystal, to be converted into the smectic phase with comparatively little rearrangement.

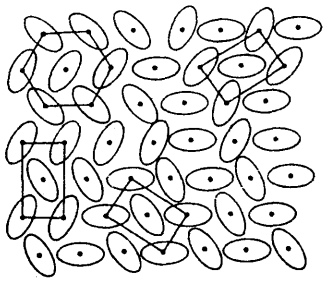


Figure 27. Arrangement of the molecules in the smectic layer of the highly ordered mesophase of compound XXXVIII;[80] three orientations of the cell of the layer are shown.

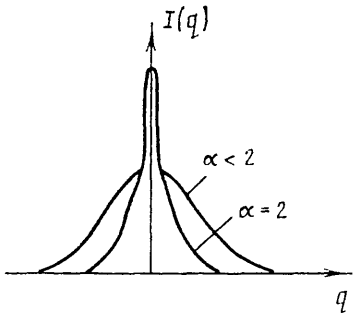


Figure 28. Profile of a Bragg peak surrounded by a background of diffuse scattering.

The conversion of the phase (5) into the crystalline state takes place with the formation of the intermediate mesophases (6) and (7), which are also highly ordered smectics. The X-ray diffraction patterns of phase (6) are similar to those of phase (5), but differ in that only four diffuse spots, that is one orientation of the domains, is observed. Thus the phase (6) can be classified as type *SmH*. In this case the monoclinic cell parameters are: a = 10.38, b = 5.24, c = 28.31 Å, β = 123°. The disorder apparently involves mainly rotation of the molecules through 180° about their long axes (statistical distribution in two azimuthal orientations), in agreement with neutron scattering data.[85] In the phase (7), doubling of the period along the long molecular axes is observed (cell parameters: a = 10.17, b = 5.27, c = 55.24 Å, β = 122.3°). According to the current classification, the phase (7) is evidently a bilayer smectic of the same type.

The X-ray diffraction data[80,85] indicate that the structures of the phases (5) and (6) of TBBA are similar to those of the phases *SmB* and *SmE* of compound XVI (n = 5). The latter undergoes the following mesomorphic transformations:

$$C \overset{92\,^\circ C}{\longleftrightarrow} SmE \overset{101.5\,^\circ C}{\longleftrightarrow} SmB \overset{168\,^\circ C}{\longleftrightarrow} SmA \overset{204\,^\circ C}{\longleftrightarrow} I.$$

The phases *SmB* and *SmE* of compound XVI (n = 5) differ from the phases (5) and (6) of TBBA in that the molecules are approximately perpendicular to the plane of the layer. The X-ray diffraction patterns of the phase *SmB* of this compound do not contain rings with index l equal to 1, indicating a decrease in the correlation of the layers in the transformation *SmE* → *SmB*. Doucet[80] points out that this is not a property typical of all smectics of type *B*; in other compounds, phases of type *B* give reflections with l = 1.§ In the phase *SmB* the azimuthal disorder is such that all the molecules behave as translationally equivalent; this evidently corresponds to the existence of three orientations of the domains with the "herring-bone" arrangement of the molecules. In the phase *SmE* the disorder corresponds to reorientational rotations of the molecules round their long axes through 180°. Neutron diffraction data[87] indicate that this disorder is dynamic.

The phase *SmE* of the homologue of compound XVI with n = 4 has been studied.[88,89] In contrast to the work of Doucet and co-workers,[80,86] it was established that the smectic is "bilayer" (in this case this term apparently means that in a period perpendicular to the plane of the layers *ab* there are two "sub-layers", whose thickness (26.8 Å) is slightly greater than the length of the molecule (25.3 Å); each "sub-layer" is displaced by a distance $a/2$ relative to its neighbour, as shown by X-ray diffraction data for the crystalline phase). The conversion of the crystals into the mesophase *SmE* is accompanied by a marked change in entropy (70% of the entropy effect of the conversion of the crystal into the isotropic liquid). This corresponds to an appreciable structural rearrangement; the angle between the long axis of the molecules and the normal to the layer decreases from ~40° to a value close to 0°.[89] In the specimens obtained by melting the crystal, domains with six different orientations are observed. Incoherent quasi-elastic neutron scattering showed that the relaxation time of the azimuthal rotation of the molecules does not exceed 10^{-10} s, and this rotation is not free (height of the barrier ~10 kT).

"Bilayer" packing of the molecules in a smectic of type *SmE* was also found for compound XVIII (n = 7).[90] X-Ray diffraction showed that the phase *SmE* has an orthogonal cell with parameters a = 8.29, b = 5.17, c = 58.0 Å. By making use of the nature of the absences, which indicates the presence of a glide plane of reflection n, and also by constructing close packing from three-dimensional models of the molecules (with length L = 29.5 Å), the authors cited obtained a model of the structure of the meso-phase (Fig. 29). In their opinion, the unfavourable contact between the CN groups of molecules belonging to different layers (Fig. 29*a*) is compensated by the close packing in the layers, where the benzene rings are in contact with the alkyl chains.

For compound XVIII (n = 7), the following sequence of mesomorphic transformations was observed:

$$C(II) \overset{65\,^\circ C}{\longleftrightarrow} C(I) \overset{73\,^\circ C}{\longleftrightarrow} SmE \overset{95\,^\circ C}{\longleftrightarrow} SmB \overset{111\,^\circ C}{\longleftrightarrow} N_1 \overset{140\,^\circ C}{\longleftrightarrow}$$
$$\underset{51\,^\circ C}{\overset{\uparrow}{\underset{\downarrow}{S_X}}}$$
$$\rightarrow SmA \overset{222\,^\circ C}{\longleftrightarrow} N_2 \overset{273\,^\circ C}{\longleftrightarrow} I.$$

§ According to the ideas presented in section II, the phase *SmB* of compound XVI (n = 5) is to some extent hexatic (*SmB*$_h$).

It is suggested that the transformation *SmE* → *SmB* is accompanied by a relative displacement of the layers, which acquire a hexagonal structure as a result of the orientational disorder, by the magnitude of the vector 1/6*a* + 1/2*b* to give packing of the type ...*ABAB*... With further increase in temperature, on formation of the phases N_1 and *SmA*, adjacent molecules are displaced relative to one another to give "dimers" in which the aromatic parts of the molecules are in contact; this produces a "bilayer" structure with $d/L > 1$ (layer thickness 41.5 Å). At the same time, a non-matching density wave with a period of 34.5 Å is produced. This is interpreted as due to the coexistence of dimers and monomers. The packing of the paired molecules ("dimers" with a bulky central region) in the smectic layers leads to the production of cavities between the alkyl chains. These cavities are occupied by monomers (the ratio of the numbers of dimers and monomers is 1 : 1).

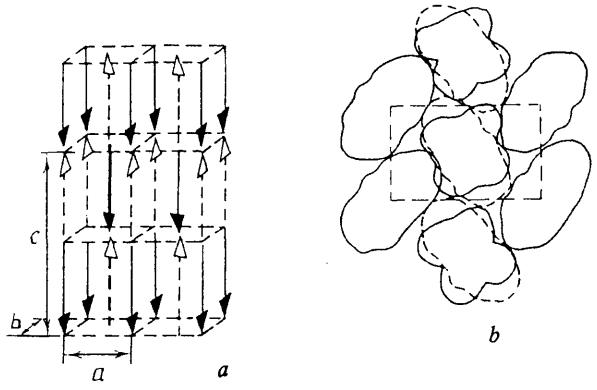


Figure 29. Structure of the phase *SmE* of compound XVIII: *a*, arrangement of the molecules in the volume; the arrows indicate the positions of the CN groups; *b*, section perpendicular to the long axes of the molecules.[90]

A number of detailed studies of the structure and transformations of smectics of type *B* have been carried out in recent years.

Thus Pershan and co-workers[91] studied the phase *SmB* of compound XII ($n = 4$, $m = 8$), which undergoes the following mesomorphic transformations:

$$C \overset{33\,^\circ C}{\longleftrightarrow} SmB \overset{49.6\,^\circ C}{\longleftrightarrow} SmA \overset{63.6\,^\circ C}{\longleftrightarrow} N \overset{78.8\,^\circ C}{\longleftrightarrow} I.$$

Specimens oriented by a magnetic field were studied on a three-circle diffractometer. It was established that the phase *SmB* has three-dimensional long-range positional order. At the same time, an appreciable contribution is made by diffuse scattering. Fig. 30 gives a diagram showing the arrangement of the molecules in the layer and the way in which the layers are superimposed; the packing of the layers is of the type ...*ABAB*... The correlation length is close to 1.4 μm (1.4×10^4 Å) in the plane of the layers, and about 0.14 μm in the perpendicular direction. In the phase *SmA* the correlation length in the plane of the layer is ~20 Å. Thus the conversion of *SmB* into *SmA* is accompanied by very considerable disordering.

The phase *SmB* of this compound was also studied with a higher resolution (synchrotron radiation).[92] The specimens consisted of suspended films, so that it was possible to study the orientational structure of the layers. Sufficiently thick films (number of layers $N = 100$) showed the existence of three-dimensional long-range order. With decrease in the thickness of the film, the inter-layer correlation decreased. In thin films ($N = 4$), which are actually two-dimensional crystals, a correlation length of more than 800 Å was observed, indicating long-range positional order within the layers.

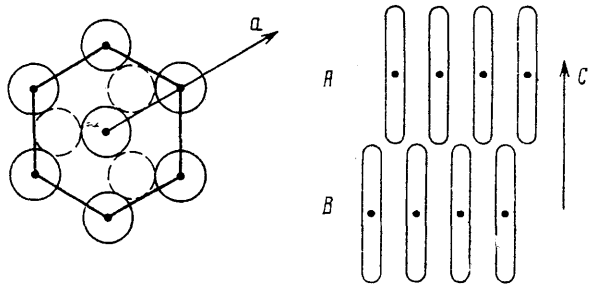


Figure 30. Schematic representation of the superposition of the layers in the smectic phase *B*.

Strong diffuse scattering, not characteristic of ordinary crystals, was also observed for this phase.[82] This scattering was attributed to the existence of a soft displacement mode of the molecular vibrations, due to the weakness of the interaction of the layers. The weakness of this interaction is confirmed by the fact that compound XII ($n = 4$, $m = 8$) in the range 27–5 °C undergoes three structural phase transformations involving a change in the way in which the layers are superimposed. This last feature indicates that the potential energy of the interaction of the layers depends little on their relative displacement.

Similar studies of the phase *SmB* of the compounds XII ($n = m = 4$) and XXXVI established in these cases also the existence of long-range positional order in all three dimensions.[93]

A new and effective method for obtaining oriented single-domain specimens on a hydrophobised support[94] has been used[95,96] to study the mesophases of compound XVIII ($n = 7$), which are formed in the following sequence:

$$X - SmE - SmB - N_{reverse} - SmA - N.$$

The phase originally denoted *X* was found to be a reverse smectic of type *SmB*. This is the first case of the detection of a phase *SmB* below the temperature of the existence of the phase *SmE*.

The structure of the smectic phase of the type *SmG*, and the change in the structure of the LC in the *SmB* → *SmG* transformation, were studied[97–99] for compound XII ($n = 5$, $m = 7$), for which the following phase transformations are observed (°C):

$$C \overset{15\,^\circ C}{\longleftrightarrow} SmG \overset{36\,^\circ C}{\longleftrightarrow} SmB \overset{51\,^\circ C}{\longleftrightarrow} SmC \overset{54\,^\circ C}{\longleftrightarrow} SmA \overset{64\,^\circ C}{\longleftrightarrow} N \overset{78\,^\circ C}{\longleftrightarrow} I.$$

The smectic *SmG* has a monoclinic base-centred (*C*) cell with parameters: $a = 9.54$, $b = 5.02$, $c = 27.9$ Å, $\beta = 114.8°$. The period *c* is approximately equal to the length of the molecule; from this it

follows that the long axes of the molecules form an angle of ~25° with the normal to the plane of the layer. The hexagonal phase *SmB* has a cell with parameters: a = 5.07 Å, c = 28.4 Å.

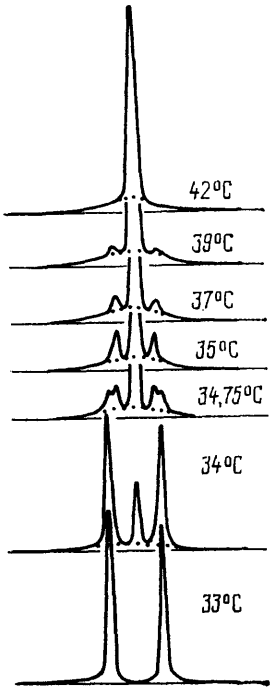


Figure 31. Temperature dependence of the profile of the meridional reflections (l = 1) in the region of the transformation *SmB* → *SmG* for compound XII (n = 5, m = 7).[97]

On the X-ray diffraction pattern of the phase *SmB*, the meridional reflections are extensively broadened and contain a pair of satellite spots, which become stronger and more isolated with decrease in temperature (Fig. 31). The transformation *SmB* → *SmG* leads to doubling of the meridional reflections (only the satellite spots remain). This transformation is preceded by the production of sinusoidal modulation (parallel to the layers) with a wavelength of ~78 ± 3 Å, which is approximately 17 times the period a of the hexagonal lattice. This last result follows from an analysis[98] of the evolution of the satellite spots with change in temperature. The authors cited consider that these spots are produced by the modulated displacement of the molecules at right angles to the layers with an amplitude H, and that the intensity of the satellites is proportional to H^2. The broadening of the meridional reflections is due to the bending of the layers, and the discrete satellite reflections are generated by the wave character of these bends. The amplitude of the modulation increases regularly with decrease in temperature, and reaches a maximum value (4 Å) at 35.5. °C, when the phase *SmG* is produced. There is an abrupt change in the orientation of the long axes of the molecules, which make an angle of 25° with the normal.

The corrugated character of the layers in the phase *SmB* of compound XII (n = 5, m = 7) is confirmed by a study[100] using optical modelling. In the opinion of the authors cited, the diffraction pattern shows best agreement with a model containing, between the layers, cavities separated from one another by an average of 80 Å (Fig. 32). It is suggested that this model is dynamic—the cavities migrate along the layers. The fluidity of this phase was attributed to this migration.

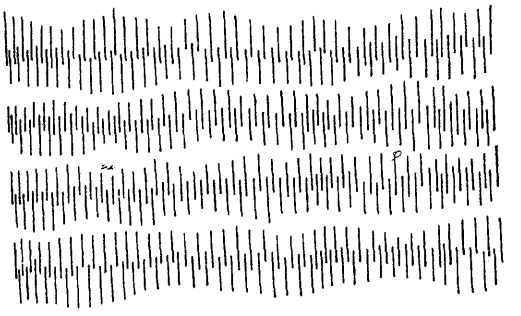


Figure 32. Schematic representation of the arrangement of the molecules in the phase *SmB* of compound XII (n = 5, m = 7), from optical modelling data.[100]

The dynamics of the mesophase of this compound were studied by neutron diffraction. Incoherent quasi-elastic neutron scattering showed[101] that the constant characterising the reorientation of the molecules round their long axes is 1.8 × 10^{11} rad^2 s^{-1} for the phase *SmB* and 1.7 × 10^{11} rad^2 s^{-1} for the phase *SmG*. In the second of these phases, two azimuthal orientations of the molecules, differing by rotation through 180°, predominate. Movement in the direction of the long axes of the molecules is observed in both phases, with a mean-square displacement of 1.4 Å in *SmB* and 1.1 Å in *SmG*. The relaxation time of this movement is comparable with the rotation time of the molecule round its long axis (~5 × 10^{11} s).

The coherent inelastic scattering of neutrons on a completely deuteriated specimen oriented in a magnetic field showed[102] that the relaxation time associated with the modulation of the phase *SmB* is close to 10^{-7} s. Since the longitudinal displacements of the molecules (1.4 Å) takes place in ~5 × 10^{-11} s, the authors cited[102] conclude that the modulation of the phase *SmB* is static (for dynamic modulation the relaxation time should be close to 5 × 10^{-11} s). Thus increase in the amplitude of the modulation with decrease in temperature ensures a minimum value of the free energy; simultaneously, in the opinion of the authors cited, synchronisation of the wave distortion of the layers takes place (more accurately, the displacement with respect to phase for adjacent layers tends to zero), leading to the phase transformation *SmB* → *SmG*.

The description of smectics ordered in three dimensions can be concluded by considering the phases *SmJ*(*SmG'*) and *SmK*(*SmH'*), detected for compound XXXIX (n = 7):[103]

$$C \xrightarrow{127\ ^\circ C} C_1 \xrightarrow{130\ ^\circ C} C_2 \xrightarrow{146\ ^\circ C} SmH' \xrightarrow{154\ ^\circ C} SmG' \xrightarrow{157\ ^\circ C} SmI \xrightarrow{164\ ^\circ C} \rightarrow SmC \xrightarrow{197\ ^\circ C} N \xrightarrow{241\ ^\circ C} I.$$

These phases, however, were also encountered earlier for compounds XVII (the phase *SmG'*) [104] and XXIV (the phases *SmG'* and *SmH'*).[105] The phase *SmX* has been reported[106] for compound XXVIII, whose structural characteristics can be obtained from Table 1. The existence of these phases was not confirmed in subsequent papers, however.

Hexatic phases were predicted in theoretical studies,[107,108] and aroused considerable interest because of an important specific characteristic: with no inter-layer correlations and with only short-range positional order within the layers in these phases, it was suggested that there is long-range order in the orientation of the vectors connecting the centres of gravity of the molecules (bond-orientational order). According to the theoretical hypotheses,[109–111] these phases should be produced by the step-wise fusion of solids. Hexatic character was apparently first established for the smectics *F*. Here, however, the phases of type *B* will be considered first, since they represent the most characteristic hexatic structure, which has also been the subject of a theoretical analysis.

As already noted, different degrees of correlation of the layers in the phases *SmB* have been detected in a number of studies (in particular, temperature-dependent inter-layer correlations have been studied[101]). In addition to the phases *SmB* with crystalline order described above, phases in which there is no inter-layer correlation have been detected.[112] The X-ray diffraction patterns of these phases showed extended rods of scattering with a length of $\sim \pm C^*$, parallel to c^* and centred at sites of the reciprocal lattice *hkl* of low order. Compound XXIII, which exists in the form of a phase *SmB* in the temperature range 107–119 °C, has been studied.[103] The complete absence of reflections *hkl* indicated disordered superposition of the layers. An analysis of the profile of the reflections gave the value of the correlation length within the layer; this was found to be $\gtrsim 350$ Å, which apparently indicates the existence of only short-range order in the layers.

An X-ray diffraction study of freely suspended films of compound III in the phase *SmB*[93] with a thickness of 4 molecular layers established definitely that this phase is hexatic. In this case, analysis of the profile of the peak gave the correlation length $\xi = 150$ Å. At the same time, the very broad form of the maximum for the inter-layer correlations indicates that the latter extend to only one layer.

Smectic phases of the type *F* were first detected in experiments on miscibility in the 1970's; they were later studied by X-ray diffraction[101,103,105,113,114,115,116] in the compounds XXXVIII ($n = 5$) (TBPA) and XXXVIII ($n = 10$) (TBDA), for which the following sequence of phase transformations is observed:

$$C \xrightarrow{68\,^\circ C} SmG \xrightarrow{140\,^\circ C} SmF \xrightarrow{149\,^\circ C} SmC \xrightarrow{179\,^\circ C} SmA \xrightarrow{212\,^\circ C} N \xrightarrow{233\,^\circ C} I$$
$$\nwarrow SmH \overset{61\,^\circ C}{\swarrow}$$

$$C \xrightarrow{73\,^\circ C} SmG \xrightarrow{120\,^\circ C} SmF \xrightarrow{150\,^\circ C} SmI \xrightarrow{158\,^\circ C} SmC \xrightarrow{160.8\,^\circ C} SmA \xrightarrow{192.4\,^\circ C} I.$$

Single-domain specimens obtained by slowly melting single crystals or by cooling the isotropic liquid (with a transition through the phase *SmA*), and a polycrystalline (polydomain) specimen, placed in a capillary subjected to a strong magnetic field, and then cooled in the absence of the field to the temperature corresponding to the formation of the phase *SmF*, were studied.[116]

X-Ray diffraction patterns of two types were examined. In the first case the primary beam was directed parallel to the smectic layers. In this case, sharp 00*l* ($l = 1, 2$) reflections were observed, indicating a layer structure (similar to the phase *SmG*). The *hk*0 reflections (in contrast to those observed for the phase *SmG*) were elongated along the c^* axis, that is along the normal to the layers, and *hkl* reflections with $l \neq 0$ were not observed at all. These features indicate the absence of three-dimensional order. The elongated *hk*0 reflections, which had the form of rods, correspond to the two-dimensional lattice of the layer.

The X-ray diffraction patterns of the second type were obtained with the beam directed parallel to the long molecular axes. Here, six diffuse *hk*0 reflections were observed, indicating (as in the case of the phase *SmG*) a pseudo-hexagonal arrangement of the axes *L* (no signs of herring-bone packing of the molecules were detected).

The X-ray diffraction patterns of polydomain specimens gave the following values of the parameters of the monoclinic *C*-centred cell (Fig. 33): for TBPA at 132 °C, $a = 9.62$, $b = 5.14$, $c \simeq 31.2$ Å, $\beta = 114°$; for TBDA at ~120 °C, $a = 9.64$, $b = 5.22$, $\beta \simeq 112°$ (the angle $180° - \beta$ characterises the slope of the axes *L* to the plane of the layer).

Thus the structure of the phase *SmF* is extremely similar to that of the phase *SmG*. The main differences are that in the phase *SmF* there is almost no inter-layer correlation and, apparently, no elements of the herring-bone pattern in the layers (isotropic rotation or *pseudorotation* of the molecules about the axes *L*).¶

The general features of the X-ray diffraction patterns obtained for the phase *SmI* of compound XXXVIII ($n = 10$) are similar to those for the phase *SmF*; here, however, instead of the rods with indices 200, an extended reflection with indices 020 appears (Fig. 33). This last feature is due to a change in the direction of the axis *L* relative to the lattice of the layer. At 152 °C, the lattice parameters of the phase *SmI* have the values: $a \simeq 5.57$, $b \simeq 9.0$, $c \simeq 42$ Å, $\beta \simeq 116°$. As in the case of *SmF*, the angle $180° - \beta$ is equal to the angle of slope of the axis *L* to the plane of the layer, but in this case the axis *L* forms this angle not with the long period but with the short period of the orthogonal lattice of the layer (Fig. 33). Here, as in *SmF*, the molecules are most probably in a state of rotation or pseudo-rotation about their long axes.

The mechanism of the *SmF* → *SmI* transformation assuming the existence of a phase boundary along which molecules with coordination 5 and 7 alternate in the layer (Fig. 34)[116] is of considerable interest. The displacement of this boundary leaves the positions of the axes *L* unchanged, but rotates the lattice of the layer through 30°. In the opinion of the authors cited,[116] however, an alternative interpretation of the transformation as a collective change in the direction of the axes *L* is possible.

An important part of the works cited[103,116,117] was the analysis of the profile of the diffraction maxima. It was established that the profile of the diffuse "rods" in the direction perpendicular to c^* is described by a Lorenzian curve with correlation length $\xi > 50$ Å for *SmF* and $\xi > 180$ Å for *SmI*. Thus the degree of ordering of the molecules is greater in the layers *SmI* than in the layers *SmF*, although the phase *SmI* is produced at a higher temperature. This is confirmed by the X-ray diffraction patterns of the "polycrystalline" specimens, where the half-width of the diffuse *hk*0 rings for *SmI* is one quarter of that for *SmF*.

Finally, mention may be made of one of the latest practical applications of highly-ordered smectics, closely related to their structure, namely the use of LC as orienting solvents in organic synthesis.[118–120] An example is provided by the isomerisation of benzenesulphonates.

¶ Interestingly, the transformation *SmG* → *SmF* is of first order for TBPA and of second order for TBDA.

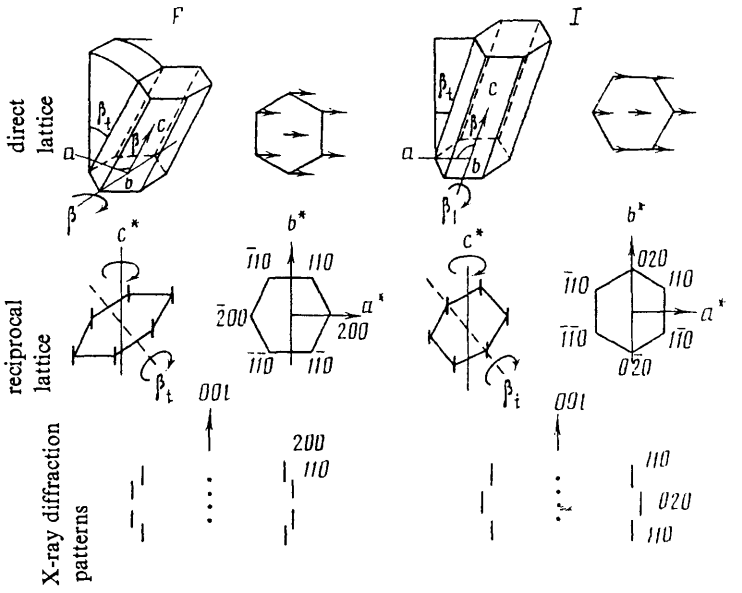
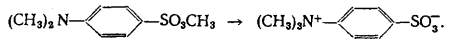
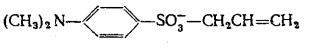


Figure 33. Real and reciprocal lattices and X-ray diffraction patterns of the phases *SmF* and *SmI*, obtained by recording along the layers (specimens oriented in a magnetic field);[103] the arrows indicate the direction of slope of the axes *L*.

Thus the isomerisation of methyl *p*-(dimethylamino)benzenesulphonate, involving the intermolecular migration of a methyl group:



has been studied in detail.[118,121,122] At room temperature, this reaction takes place in the crystal, where the arrangement of the molecules is convenient for this (antiparallel), but does not take place in solution (this question has been examined in detail[123]). The isomerisation of the related compound



does not take place either in solution or in the crystal. Both of these benzenesulphonates isomerise, however, when dissolved in the smectic phase of compound IX,[118] for which the following phase transformations have been detected:

$$C \xleftrightarrow{34.4\,^{\circ}C} SmB \xleftrightarrow{146.4\,^{\circ}C} N \xleftrightarrow{164.7\,^{\circ}C} I$$

An interesting feature is that the isomerisation takes place only in the temperature range of existence of the phase *SmB*. X-Ray diffraction data[121,122] indicate that this phase is highly ordered. The distances between the molecules in the layer (5.50 ± 0.03 Å) differ little from the distances *D* in the nematic phase (5.52 ± 0.06 Å). The thickness of the layer (21.4 ± 0.2 Å) is close to the length of the molecule (23.5 ± 0.5 Å), indicating a perpendicular arrangement of the molecules. Rigid aromatic sub-layers situated between less rigid aliphatic layers are distinguished. Benzenesulphonate molecules have almost no influence on the geometic characteristics of the phase *SmB*. It is suggested that clusters (dimers or larger agglomerates) of the benzenesulphonate molecules are inserted in "head to tail" fashion into the aromatic sub-layer of the phase SmB. This creates conditions for the migration of the methyl groups from one molecule to another for both benzenesulphonates studied. The influence of the molecular packing on the isomerisation is proved by the sharp decrease in its rate on going to the nematic phase of the solvent.

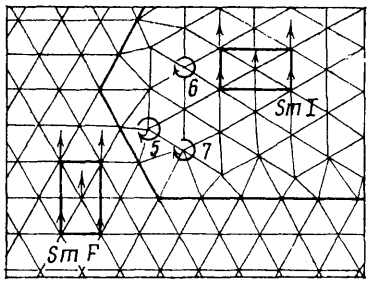


Figure 34. Structure of the boundary separating the phases *SmF* and *SmI*, consisting of 5-, 6-, and 7-coordinate molecules;[116] the arrows indicate the slope of the axes *L*.

VI. Cubic phases

A unique place among calamitic mesophases is occupied by the LC called smectics *D*, although it will be seen that this name does not give a correct picture of their structure. The first homologous series of compounds for which mesophases of this type were found as synthesised in 1957 [124] (compounds V, VI, and XXXIII in Table 3). The homologues of compound V with $n = 16$ and 18

undergo the following phase transformations, detected by differential scanning calorimetry:[125]

$$n=16: C \xleftrightarrow{126.8\,^\circ C} SmC \xleftrightarrow{171.0\,^\circ C} SmD \xleftrightarrow{197.2\,^\circ C} SmA \xleftrightarrow{201.9\,^\circ C} I,$$

$$n=18: C \xleftrightarrow{124.6\,^\circ C} SmC \xleftrightarrow{158.9\,^\circ C} SmD \xleftrightarrow{195.0\,^\circ C} I.$$

X-Ray diffraction showed[126] that the phases *D* do not have the layer arrangement of the molecules characteristic of smectics. Here, the X-ray diffraction patterns of polycrystalline specimens revealed a cubic lattice (space group $Ia3d$) with parameter a = 102 Å and $Z \simeq 1150$ molecules per cell.

A sufficiently well-founded model of the arrangement of the molecules in this mesophase has not yet been constructed. It is considered that in this case, as a result of hydrogen bond formation (or other sufficiently strong intermolecular interactions), the molecules are joined in stable associates as spherical or rod-shaped micellar formations similar to the supermolecular formations in lyotropic LC. (These micelles form a cubic lattice.) The important role of specific intermolecular interactions in the formation of the phase *D* is indicated by the fact that the replacement of the nitro-group in compound V by Cl, Br, or CH_3 leads to the disappearance of this phase.

A cubic phase is also formed by the acid VI (n = 16, 18), which is similar to compound V, but in which the NO_2 group has been replaced by CN. A recent study[127] of the homologue of this compound with n = 18 detected a primitive cubic lattice with symmetry $P23$ or $Pm3$ and parameter a = 86 Å.

The study of the phases *D* is made difficult by the fact that they are formed by only a limited number of compounds. Examples are the hydrazine derivatives XXXIII, which undergo the following sequence of phase transformations:

$$C \rightarrow SmD \rightarrow SmC \rightarrow I.$$

The homologues of compound XXXIII with n = 8, 9, and 10 have cubic lattices with parameters a = 45.7, 48.8, and 51.7 Å respectively.[128] In this case it is considered that intermolecular H-bonds between the NH and CO groups are responsible for the formation of the cubic phase. The polymorphic forms of the compound with similar structure containing the $-CH=N-$ group instead of the $-CO-NH-$ group (which excludes the formation of H-bonds) do not form a cubic phase (the phase *SmC* of this compound with n = 10 has the usual structure for LC of this type).

Another type of mesophase with a cubic lattice is the so-called cholesteric "blue" phase, which exists in a narrow temperature range (less than 1 K) between the ordinary cholesteric phases, which have a one-dimensional spiral structure, the blue phase shows three-dimensional spatial periodicity. This phase has been studied mainly by the optical methods, the use of which in this case is analogous to X-ray diffraction studies, since here the parameter of the cubic lattice is commensurate with the wavelength of visible light.

The present state of structural studies of the blue phases has been reviewed.[129,130]† Several possible models are discussed, including: 1) a three-dimensional lattice of disclinations, and 2) an emulsion model, which assumed that the isotropic liquid is disseminated in the cholesteric structure. None of these models has yet been reliably established, however.

† Since the present manuscipt was prepared, another review has been published: H Stegemeyer, T Blümel, K Hiltrop, et al. *Liq. Cryst.*, 1986, **1** 1

VII. Phases with columnar H-associates

The previous sections dealt with mesophases formed by rod-shaped molecules. The liquid-crystalline state is also often observed for compounds whose molecules have a quite different shape. These include primarily the disc-like mesophases, which have been intensively studied in recent years and are the subject of a number of reviews.[131–133] They are formed by molecules containing a rigid disc-shaped nucleus (benzene, triphenylene, truxene, etc.) with alkoxy or alkanoyl substituents attached. The most characteristic forms of discotic is the columnar mesophase, in which the molecules are arranged in periodic or aperiodic stacks. It has recently been found, however, that thermotropic columnar LC may be formed by molecules with shapes completely different from discs. In this case the construction of the columns involves the formation of a system of hydrogen bonds. Examples of these compounds are described below.

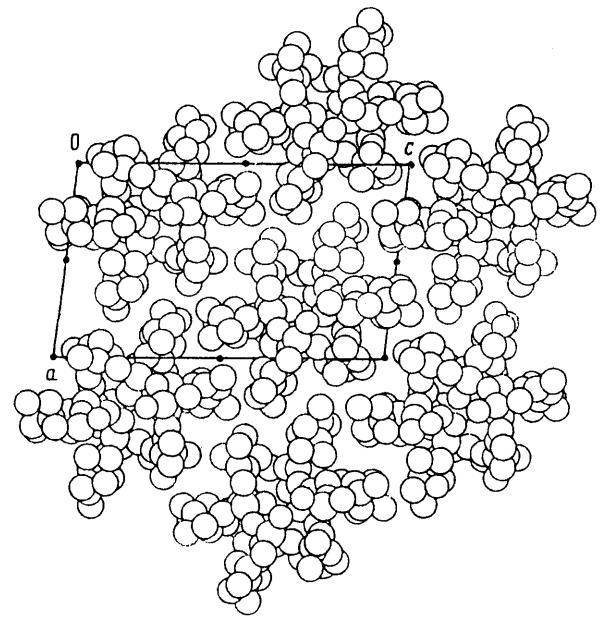
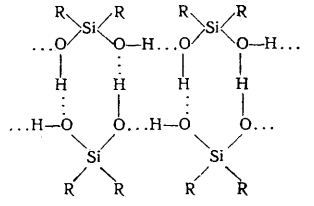


Figure 35. Projection of the crystal structure of $[(n\text{-}Pr)_2Si(OH)]_2O$ on the (010) plane, perpendicular to the axes of the columns.[140]

As early as the 1950s it was noted that a mesophase is formed by the silanol $R_2Si(OH)_2$ with R = iso-Bu, whereas other members of the series (R = Me, Et, Ph, iso-Pr, t-Bu) did not show mesomorphism.[134,135] At the time, this mesophase was characterised as smectic, but it was later established[136] that the optical texture of the mesophase of $(iso\text{-}Bu)_2Si(OH)_2$ is similar to that of discotics (in addition, unlimited miscibility of this substance with the classical discotic benzenehexa-n-heptanoate was observed). In the opinion of the authors cited,[136] the similarity in the heats of the phase transformations $C \rightarrow$ LC and LC $\rightarrow I$ (7.6 kJ mol^{-1} and 7.2 kJ mol^{-1} respectively) indicates that each of these transformations involves the rupture of a certain fraction of the H-bonds present in the crystal.

An X-ray diffraction study of single crystals of this compound could not be carried out. An X-ray diffraction study of close homologues of this compound (R = iso-Pr, t-Bu) showed,[137,138] however, that the crystals are made up of infinite H-associates containing cyclic dimers:

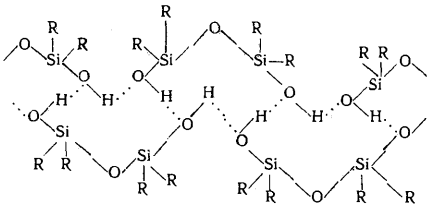


The silanediol with R = iso-Bu should apparently have a similar structure. The authors cited[136] liken this associate to a discotic column, where the role of the discs is played by "platforms" approximately perpendicular to the ribbon and each containing two SiR_2 groups.

Similar phase transformations were also observed for various dihydroxysiloxanes. The most extensively studied $[(n\text{-}Pr)_2Si(OH)]_2O$ undergoes the following transformations:[139]

$$C \xrightarrow[29.3\ kJ\ mol^{-1}]{43\ ^\circ C} LC \xrightarrow[20\ kJ\ mol^{-1}]{69\ ^\circ C} I.$$

An X-ray diffraction study[140] of a single crystal of this siloxane grown in a capillary directly from the mesophase showed that in the crystal the molecules are joined in columns (Fig. 35). The outer layer of the columns is formed by the aliphatic substituents, and the core of the column consists of a cooperative system of H-bonds:



The packing of the columns is pseudohexagonal (the crystal belongs to the triclinic system); the averaged parameter of the pseudo-hexagonal two-dimensional lattice is a = 12.66 Å. A planar hexagonal lattice with a = 12.58 Å was also detected in the mesophase of this compound. This suggests that cylindrical columnar H-associates similar to those found in the crystal are preserved in the mesophase. This is confirmed by the similarity in the spectral characteristics of the crystal and the mesophase.

The number of examples of this kind should apparently increase considerably in the near future. It will then be possible to speak of a separate class of liquid-crystalline phases, differing considerably from both calamitic and discotic mesophases.

References

1. O Lehmann *Z. Phys. Chem.*, 1989, **4** 462
2. T A Komarova, A S Kir'yanov *Istoriya i Metodologiya Estestvennykh Nauk. Vypusk XXVIII. Khimiya* (The History and Methodology of the Natural Sciences. No. XXVIII. Chemistry), Izd. Moskov. Gos. Univ., Moscow, 1982, p. 183
3. V K Pershin, Vl K Pershin, P M Zorkii *Problemy Kristallokhimii* (Problems of Crystal Chemistry), Izd. Nauka, Moscow, 1988, p. 30
4. S Chandrasekhar, B K Sadashiva, K A Suresh *Paramana*, 1977, **9** 41
5. L Lin *Mol. Cryst. Liq. Cryst.*, 1987, **146** 41
6. P M Zorkii, Ya M Nesterova *Zh. Strukt. Khim.*, 1986, **27**(1) 115
7. A J Leadbetter, R M Richardson, J C Frost *J. Phys. (France)*, 1979, **40** C3–125
8. H Sackmann, D Demus *Mol. Cryst. Liq. Cryst.*, 1973, **21** 239
9. H Sackmann, D Demus *Mol. Cryst.*, 1966, **2** 81
10. J W Goodby, G W Gray *Smectic Liquid Crystals*, Glasgow, 1984, 156 pp
11. A de Vries *Mol. Cryst. Liq. Cryst.*, 1981, **63** 215
12. S A Seleznev, A de Vries *Zh. Fiz. Khim.*, 1986, **60**(4) 817 [English translation in *Russ. J. Phys. Chem.*, 1986(4)]
13. A I Kitaigorodskii *Organicheskaya Kristallokhimiya* (Organic Crystal Chemistry), Izd. Akad. Nauk SSSR, Moscow, 1955, 559 pp
14. P M Zorkii *Fizicheskaya Khimiya. Sovremennye Problemy* (Physical Chemistry. Current Problems), Izd. Khimiya, Moscow, 1982, p. 134
15. J Billard *J. Chim. Phys. Phys.-Chim. Biol.*, 1983, **80** 127
16. W Kast *Z. Phys.*, 1931, **71** 39
17. E A Kosterin, I G Chistyakov *Kristallografiya*, 1968, **13** 295
18. E A Kosterin, I G Chistyakov *Kristallografiya*, 1969, **14** 321
19. R S Bear, O E A Bolduan *Acta Crystallogr.*, 1950, **3** 236
20. V Tsvetkov, V Marinin, *Zh. Eksp. Teor. Fiz.*, 1949, **18** 641
21. K Herrmann, A H Krummacher, K May *Z. Phys.*, 1932, **73** 419
22. V N Tsvetkov *Acta Physicochem. URSS*, 1937, **6** 865
23. I G Chistyakov, B K Vainshtein *Kristallografiya*, 1963, **8** 570
24. J H Wendorff, F P Price *Mol. Cryst. Liq. Cryst.*, 1973, **24** 129
25. L I Mineev, I I Sushkin, I G Chistyakov *Dokl. Akad. Nauk SSSR*, 1983, **272** 607
26. I G Chistyakov, W M Chaikovskii *Mol. Cryst. Liq. Cryst.*, 1969, **7** 269
27. I G Chistyakov, V M Chaikovskii *Kristallografiya*, 1973, **18** 293
28. A de Vries *Mol. Cryst. Liq. Cryst.*, 1970, **10** 219
29. A de Vries *J. Phys. (France)*, 1975, **36** C1–1
30. G W Stewart, R M Morrow *Phys. Rev.*, 1927, **30** 232
31. G W Stewart *Phys. Rev.*, 1931, **38** 931
32. V M Sethna, A de Vries, N Spielberg *Mol. Cryst. Liq. Cryst.*, 1980, **62** 141
33. V K Pershin, S A Skopinov *Fiz. Tverd. Tela*, 1979, **21** 496
34. V K Pershin, S A Skopinov *Ukr. Fiz. Zh.*, 1981, **26** 1978
35. V H Pershin, S A Skopinov *Kristallografiya*, 1981, **26** 178
36. A de Vries *Mol. Cryst. Liq. Cryst.*, 1973, **20** 119
37. N E Keller, E Nachaliel, D Davidov, C Böffel *Phys. Rev. A*, 1986, **34** 4363
38. L V Azaroff *Mol. Cryst. Liq. Cryst.*, 1980, **60** 73
39. A de Vries *J. Mol. Liq.*, 1986, **31** 193
40. V A Gudkov *Kristallografiya*, 1986, **31** 350
41. A J Leadbetter, R M Richardson, C N Colling *J. Phys. (France)*, 1975, **36** L–69
42. A J Leadbetter, J C Frost, J P Gaughan, et al. *J. Phys. (France)*, 1979, **40** 375
43. G J Brownsey, A J Leadbetter *J. Phys. Rev. Lett.*, 1980, **44** 1608

44. S Bhattacharjee, L V Azaroff *Mol. Cryst. Liq. Cryst.*, 1987, **144** 317
45. I H Ibrahim *Z. Naturforsch.*, 1987, **42** 444
46. I G Chistyakov, L S Shabishev, R I Yarenkov, L A Gusakova, *Mol. Cryst. Liq. Cryst.*, 1969, **7** 279
47. S Diele, P Brand, H Sackmann *Mol. Cryst. Liq. Cryst.*, 1972, **17** 163
48. J Falgueirettes, P Delord *Liquid Crystals and Plastic Crystals* (Edited by G W Gray, P A Winsor), Hardwood, Sussex, 1974, Vol. 3, p. 62
49. A J Leadbetter, J P Gaughan, B A Kelly, et al. *J. Phys. (France)*, 1979, **40** C3–178
50. I G Chistyakov, Z B Radzhabova, L K Vistin', et al. *Zhidkie Kristally i ikh Primenenie. Mezhvuzovskii Sbornik Nauchnykh Trudov* (Liquid Crystals and their Applications. Collected Scientific Papers from Higher Educational Establishments), Ivanovo, 1980, p. 3
51. L I Mineev *Zhidkie Kristally i ikh Primenenie. Mezhvuzovskii Sbornik Nauchnykh Trudov* (Liquid Crystals and their Applications. Collected Scientific Papers from Higher Educational Establishments), Ivanovo, 1981, p. 18
52. K A Suresh, R Shashidhar, G Heppke, R Hopf *Mol. Cryst. Liq. Cryst.*, 1983, **99** 249
53. W R Krigbaum, J C Poirier, M J Costello *Mol. Cryst. Liq. Cryst.*, 1973, **20** 133
54. L Kamenchuk, E A Kosterin, O Vladimirova *Zhidkie Kristally i ikh Primenenie. Mezhvuzovskii Sbornik Nauchnykh Trudov* (Liquid Crystals and their Applications. Collected Scientific Papers from Higher Educational Establishments), Ivanovo, 1982, p. 24
55. E H Pape, K Schröder, P Zugenmaier *Mol. Cryst. Liq. Cryst. Lett.*, 1987, **4** 165
56. A J Leadbetter, J L A Durrant, M Rugman *Mol Cryst. Liq. Cryst. Lett.*, 1977, **34** 231
57. G Albertini, E Fanelli, D Guillon, et al. *J. Chem. Phys.*, 1983, **78** 2013
58. G Albertini, E Fanelli, D Guillon, et al. *J. Phys. (France)*, 1984, **45** 45
59. G Albertini, E Fanelli, S Melone, et al. *Mol. Cryst. Liq. Cryst.*, 1983, **99** 331
60. W Haase, H Paulus, H T Müller *Mol. Cryst. Liq. Cryst.*, 1983, **97** 131
61. F Hardouin, A M Levelut, M F Achard, G Sigaud *J. Chim. Phys. Phys.-Chim. Biol.*, 1983, **80** 53
62. F Hardouin *Physica*, 1986, **A140** 359
63. K K Chan, P S Pershan, L B Sorensen, F Hardouin *Phys. Rev. A*, 1986, **34** 1420
64. S K Prasad, R Shashidhar, B R Ratna, et al. *Liq. Cryst.*, 1987, **2** 111
65. P E Cladis, R K Bogardus, W B Daniels, G N Taylor *Phys. Rev. Lett.*, 1977, **39** 720
66. P E Cladis, R K Bogardus, D Aadsen *Phys. Rev. A*, 1978, **18** 2292
67. B Jha, B Bhattacharjee, S Paul, R Paul *Phys. Status Solidi*, 1983, **76** 461
68. F Hardouin, G Sigaud, M F Achard, H Gasparoux *Solid State Commun.*, 1979, **30** 265
69. F Hardouin, A M Levelut *J. Phys. (France)*, 1980, **41** 41
70. K A Suresh, R Shashidhar, G Heppke, R Hopf *Mol. Cryst. Liq. Cryst.*, 1983, **99** 249
71. S K Prasad, R Shashidhar, K A Suresh, et al. *Mol. Cryst. Liq. Cryst.*, 1983, **99** 185
72. E Fontes, P A Heiney, J L Haseltine, A B Smith *J. Phys. (France)*, 1986, **47** 1533
73. A J Leadbetter *The Molecular Physica of Liquid Crystals* (Edited by G R Luckhurst, G W Gray), Acad. Press, New York, 1979, p. 285
74. J Doucet, A M Levelut, M Lambert *Mol. Cryst. Liq. Cryst.*, 1973, **24** 317
75. D Guillon, J B Stamatoff, P E Cladis *J. Chem. Phys.*, 1982, **76** 2056
76. R Shashidhar, S Chandrasekhar *Mol. Cryst. Liq. Cryst.*, 1983, **99** 297
77. A C Griffin, N W Buckley, W E Hughes, D L Wertz *Mol. Cryst. Liq. Cryst. Lett.*, 1981, **64** 139
78. F Hardouin, N H Tinh, M F Achard, A M Levelut *J. Phys. Lett. (France)*, 1982, **43** L–327
79. V A Gudkov, Z B Radzhabova *Kristallografiya*, 1985, **30** 518
80. J Doucet *The Molecular Physics of Liquids* (Edited by G R Luckhurst, G W Gray), Acad. Press, New York, 1979, p. 317
81. J Doucet, A M Levelut, M Lambert *Phys. Rev. Lett.*, 1974, **32** 301
82. A M Levelut *J. Phys. (France)*, 1976, **37** C3–51
83. P G de Gennes, G Sarma *Phys. Lett. A*, 1972, **38** 219
84. D P Lesser, A de Vries, J W Reed, G H Brown *Acta Crystallogr., Sect. B*, 1975, **31** 653
85. F Volino, A J Dianoux, H Hervet *J. Phys. (France)*, 1976, **37** C3–55
86. J Doucet, A M Levelut, M Lambert, et al. *J. Phys. (France)*, 1975, **36** C1–13
87. A J Leadbetter, R M Richardson, C J Carlile *J. Phys. (France)*, 1976, **37** C3–65
88. A J Leadbetter, J C Frost, M A Mazid, J P Gaughan *J. Phys. (France)*, 1979, **40** C3–185
89. A J Leadbetter, M A Mazid, K M A Malik *Mol. Cryst. Liq. Cryst.*, 1980, **61** 39
90. S Diele, D Jaeckel, D Demus, H Sackmann *Cryst. Res. Technol.*, 1982, **17** 1591
91. P S Pershan, G Aeppli, J D Litster, R J Birgeneau *Mol. Cryst. Liq. Cryst.*, 1981, **67** 205
92. D E Moncton, R Pindak *Phys. Rev. Lett.*, 1979, **43** 701
93. R S Pindak, D E Moncton, S C Davey, J W Goodby *Phys. Rev. Lett.*, 1981, **46** 1135
94. S V Val'kov, I E Chistyakov *Zh. Eksp. Teor. Fiz.*, 1982, **52** 791
95. S V Val'kov, O B Akopova *Kristallografiya*, 1983, **28** 964
96. S V Val'kov *Zhidkie Kristally. Mezhvuzovskii Sbornik Nauchnykh Trudov* (Liquid Crystals. Collected Scientific Papers from Higher Educational Establishments), Ivanovo, 1985, p. 19
97. A J Leadbetter, M A Mazid, B A Kelly *Phys. Rev. Lett.*, 1979, **43** 630
98. P A C Gane, A J Leadbetter *J. Phys. C: Solid State Phys.*, 1983, **16** 2059
99. R F Bryan *Transactions Am. Cryst. Ass.*, 1981, **17** 99
100. V A Gudkov, Z B Radzhabova *Kristallografiya*, 1987, **32** 427
101. A J Leadbetter, M A Mazid, R M Richardson *Liquid Crystals* (Edited by S Chandrasekhar), London, 1980, p. 65
102. R M Richardson, A J Leadbetter, et al. *J. Phys. (France)*, 1984, **45** 1061
103. P A C Gane, A J Leadbetter, P G Wrighton *Mol. Cryst. Liq. Cryst.*, 1981, **66** 247

104. J Doucet, P Keller, A M Levelut, P Porquet *J. Phys. (France)*, 1978, **39** 548
105. A J Leadbetter, J P Gaughan, B A Kelly, et al. *J. Phys. (France)*, 1979, **40** 178
106. A Ekachai, A dr Vries, M E Neubert, N Spielberg *J. Chem. Phys.*, 1981, **74** 4048
107. P G de Gennes, G Sarma *Phys. Lett. A*, 1972, **38** 219
108. R J Birgeneau, J D Litster *J. Phys. Lett. (France)*, 1978, **39** 399
109. B I Halperin, D R Nelson *Phys. Rev. Lett.*, 1978, **41** 121
110. D R Nelson, B I Halperin *Phys. Rev. B*, 1979, **19** 2457
111. J M Kosterlitz, D J Thouless *J. Phys. C*, 1973, **3** 1181
112. A J Leadbetter, J C Frost, M A Mazid *J. Phys. Lett. (France)*, 1979, **40** 325
113. J J Benattar, J Doucet, M Lambert, A M Levelut *Phys. Rev. A*, 1979, **20** 2505
114. J W Goodby, G W Gray, A J Leadbetter, M A Mazid *J. Phys. (France)*, 1980, **41** 591
115. J J Benattar, F Moussa, M Lambert *J. Phys. Lett. (France)*, 1981, **42** L67
116. J J Benattar, F Moussa, M Lambert *J. Chim. Phys.*, 1983, **80** 99
117. P A C Gane, A J Leadbetter, et al. *Phys. Rev. A*, 1981, **24** 2694
118. B Samori, L Fiocco *J. Am. Chem. Soc.*, 1982, **104** 2534
119. W J Leigh, S Jakobs *Tetrahedron*, 1987, **43** 1393
120. R L Treanor, R G Weiss *Tetrahedron*, 1987, **43** 1371
121. P de Maria, A Lodi, B Samori, et al. *J. Am. Chem. Soc.*, 1984, **106** 653
122. B Samori, P de Maria, P Mariani, et al. *Tetrahedron*, 1987, **43** 1409
123. V E Shklover, T V Timofeeva *Usp. Khim.*, 1985, **54**(7) 1057 [English translation in *Russ. Chem. Rev.*, 1985(7)]
124. G W Gray, B Jones, P Marson *J. Chem. Soc.*, 1957, 393
125. D Demus, D Marzotko, N K Sharma, A Wiegeleben *Krist. Tech.*, 1980, **15** 311
126. A Tardieu, J Billard *J. Phys. (France)*, 1976, **15** C3
127. G Etherington, A J Leadbetter, X J Wang, et al. *Liq. Cryst.*, 1986, **1** 209
128. D Demus, A Gloza, H Hartung *Cryst. Res. Technol.*, 1981, **16** 1445
129. V A Belyakov, V E Dmitrienko *Usp. Fiz. Nauk*, 1985, **146** 369
130. P P Crooker *Mol. Cryst. Liq. Cryst.*, 1983, **98** 31
131. C Destrade, Nguen Huu Tinh, H Gasparoux, et al. *Mol. Cryst. Liq. Cryst.*, 1981, **71** 111
132. A M Levelut *J. Chim. Phys.*, 1983, **80** 149
133. T V Timofeeva, P M Zorkii, A P Polishchuk *Problemy Kristallokhimii* (Problems in Crystal Chemistry), Izd. Nauka, Moscow, 1990 (in the press)
134. C Eaborn *J. Chem. Soc.*, 1952, 2840
135. C Eaborn, N H Hartshorne *J. Chem. Soc.*, 1955, 549
136. J D Bunning, J E Lydon, C Eaborn, et al. *J. Chem. Soc., Faraday Trans. 1*, 1982, 713
137. N H Buttrus, C Eaborn, P B Hitchcock, A K Saxena *J. Organomet. Chem.*, 1985, **284** 291
138. N H Buttrus, C Eaborn, P B Hitchcock, P D Lickiss *J. Organomet. Chem.*, 1986, **302** 159
139. N N Makarova, N N Kuz'min, Yu N Godovskii, E A Mukhina *Dokl. Akad. Nauk SSSR*, 1988, **300** 372
140. A P Polishchuk, N N Makarova, M Yu Antipin, et al. *Kristallografiya*, 1989 (in the press)
141. A P Polishchuk, N N Makarova, T V Timofeeva, et al. *Kristallografiya*, 1989 (in the press)

Translated from *Uspekhi Khimii*, **58** 2011–2034 (1989) U.D.C. 542.91:542.952.1:547.333.3:547.446.5

Amines acting as hydride ion donors in reactions with unsaturated electrophilic compounds

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ABSTRACT. The reactions involving reduction of electrophilic double bonds (C=C, C=O, C=N, and N=N) with amines (usually tertiary) that contain hydrogen atoms at the α-position have been classified. The key stage in such reactions is formation of an iminium salt, which can formally be regarded as the transfer of a hydride ion from the amine to the compound with a double bond, although the actual mechanism may be different. The subsequent reactions of the intermediates formed (iminium cations, enamines, aminocarbenes), including acylation and cycloaddition, are examined. The synthetic potentialities of these reactions for obtaining different functionally substituted linear and heterocyclic compounds are discussed.

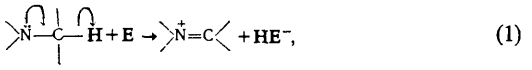
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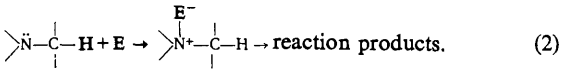
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I. Introduction

Aliphatic, alicyclic, and heterocyclic amines that contain hydrogen atoms at the α-position are potential donors of hydride ions and can participate in the reduction of sufficiently active electrophilic compounds [equation (1)]. This ability to eliminate a hydride ion and form an iminium cation is in many cases suppressed by competing reactions which start with addition of the electrophilic partner [equation (2)].[1]

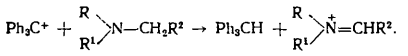


(1)



(2)

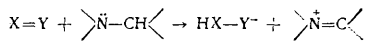
Nevertheless, oxidation reactions of hydrocarbon residues in amines occur quite widely and can be effected by treatment with stronger or weaker oxidising agents such as free halogens,[2,3] other inorganic oxidising agents,[4] and also classical hydride ion acceptors[5,6] such as triarylcarbenium ions:1,7–12



A reaction of the latter type is responsible for the thermal decolorisation of triarylmethane dyes containing a carbocation site together with dialkylamino groups.[13]

The electrochemical oxidation of amines is also well known.[14] Their fermentative oxidation is of considerable significance in nature.[4]

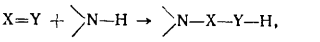
Among those reagents capable of reactions which may formally be regarded as the elimination of a hydride ion from the α-position of the amine are various unsaturated electrophilic compounds containing double bonds—activated olefins, carbonyl compounds, their hetero analogues, etc. Quite a considerable amount of material on reactions of this type [equation (3)] has been collected to date.



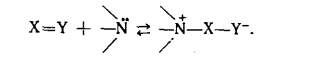
(3)

An attempt has been made in this review to classify this material, with thermal reactions mainly being studied. The electrochemical[14] and photochemical[15] oxidation of amines have been the subjects of extensive reviews.

Tertiary amines are usually involved in reactions of type (3), secondary or primary amines are involved less frequently. This is probably because in the latter cases there is the possibility of other reactions, mainly addition to the double bond [equation (4)]. Tertiary amines can also add on to double bonds such as C=C[16–19] or C=O[20–22] but as a rule these reactions are reversible [equation (5)].



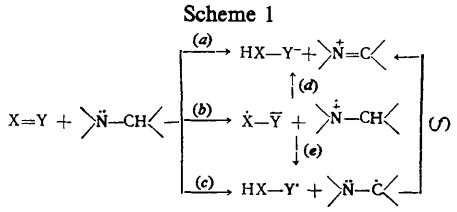
(4)



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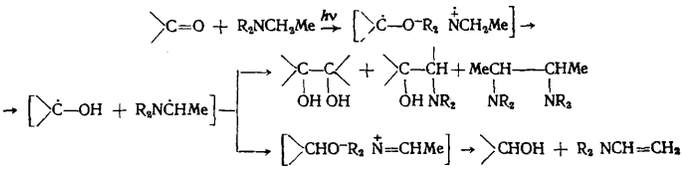
In principle reactions of type (3) can occur by at least four routes (Scheme 1): 1) direct hydride transfer (*a*); 2) transfer of e^- to form a radical ion pair [usually via a charge-transfer complex (CTC)], then transfer of H^+ and transfer of e^- again (*b*)–(*e*)–(*f*); 3) transfer of e^-, then transfer of $H^\cdot$ (*b*)–(*d*); 4) transfer of $H^\cdot$ followed by transfer of e^- (*c*)–(*f*).

Scheme 1



Sometimes the direct transfer of a hydride ion [variant (1)] is assumed for these types of reactions, but mechanisms involving the formation of an intermediate CTC [variants (2) and (3)] would usually appear to be more likely.[4,23–27] Evidence in favour of these is the frequently observed instant colour change when the reactants are mixed and the frequent cases of complexes of amines with different electron acceptors being formed, unaccompanied by further reactions.[23–25,28,29]

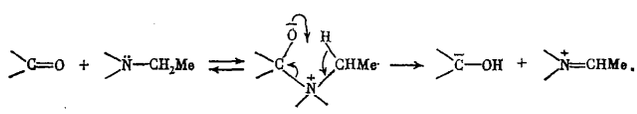
Variant (2) usually occurs in the photochemical oxidation of amines.[15,30–33] Free radicals formed at stage (*e*) can both disproportionate to an anion and cation [stage (*f*) and also couple,[15,30–32,34–37] for example:



In addition, these free radicals can be identified using t-nitrosobutane as a "trap".[38] It cannot be excluded that in certain photochemical reactions a radical pair is formed directly from the reactants by H· transfer [variant (4)] and avoiding the radical ion stage.[32,39,40] There is evidence that the mechanism depends on the nature of the solvent; in nonpolar media a radical pair is formed directly while in polar media the reaction occurs via radical ions.[39,40]

Variant (3) usually occurs in thermal reactions and formation of free radicals is not observed†[23] (compare, however, the results of Ohno et al.[43]). The overall trend is that in photochemical reactions mainly free-radical coupling products are formed (for example, pinacones from carbonyl compounds[15,30–32]), while in thermal reactions products derived from the reaction of iminium salts are formed.

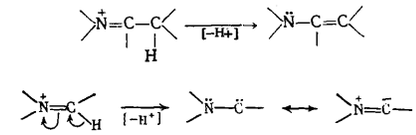
One further possible scheme for the oxidation of an amine by an unsaturated compound is fragmentation of the intermediate betaine with an "unconventional" transfer of the electron pair on cleavage of the C–N bond,[44–46] for example:‡



But however the reaction might occur—via a CTC, via a betaine, or as a result of direct hydride ion transfer—the oxidation of the amine leads to an iminium salt. In the majority of cases the actual mechanism has not been investigated; nevertheless, taking the result of the reaction as a basis, this type of conversion is usually called a hydride transfer.

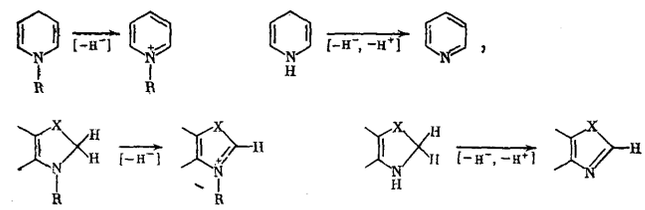
In some cases the iminium salt is the final product, in other cases it is an intermediate (identified by NMR, for example, or only postulated).

The anion component of the iminium salt HX–Y⁻ (⁻CHO⁻, ⁻CHN⁻, etc.) can add on a proton from the medium or deprotonate the iminium cation. An enamine is formed as a result of elimination of a proton from the β-position. When there are no hydrogen atoms at this position, an aminocarbene can be formed by α-elimination:



These reactive species are usually not isolated but undergo further reactions, for example, those involving a further molecule of the initial unsaturated compound.

Some of the most effective donors of hydride ions are dihydroaromatic heterocycles such as 1,4-dihydropyridines,§ thiazolines, and imidazolines. Thus, they can reduce hexafluoroacetone,[49,50] hexachloroacetone,[28,51,52] thiobenzophenone,[53] trifluoroacetophenone,[26,27] imines and enamines,[54] unsaturated carbonyl compounds,[55–57] haloquinones,[23] and carboxylic acid chlorides.[58] The driving force of these reactions is formation of an aromatic system:



However, sufficiently electrophilic double bonds can also be reduced by normal aliphatic, aliphatic-aromatic, or saturated heterocyclic amines.

It should be emphasised that the redox conversions that occur when amines react with unsaturated compounds are important from different viewpoints. Thus they can be used to synthesise from simple and accessible reactants, compounds which are difficult to obtain by another route. Typical examples are the syntheses based on triethylamine via an unstable intermediate diethylvinylamine (see below). Moreover, it is necessary to take into account the limitations that are imposed by the possibility of side reactions with the traditional use of tertiary amines as basic (or nucleophilic) reactants or catalysts.

II. Reduction of a C=C bond

For an olefinic double bond to have sufficient electrophilic reactivity, it must be activated with electron-withdrawing substituents. This condition is also necessary in the case of reactions with amine hydride ion donors.

1. Fluoroolefins

Fluoroolefins are fairly active in reactions with nucleophiles. However, tetrafluoroethylene does not react under normal conditions with tertiary amines. Some tertiary amines have been used as

† The acidity of radical cations of tertiary amines is low ($pK_a \sim 15$). This fact, together with the substantial decrease in strength of the α-C–H bond on going from an amine to its radical cation, is evidence in favour of variant (3) involving H· transfer.[41] For the different routes of radical cation fragmentation see Todres.[42]

‡ A "conventional" route is taken to mean the transfer of the bonding electron pair to the positively charged nitrogen atom, leading to decomposition of the betaine to the initial components.

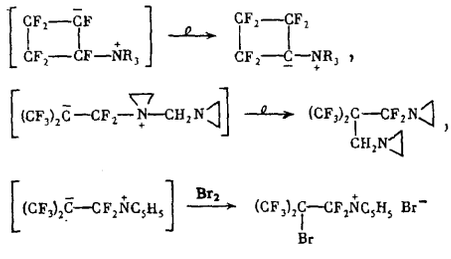
§ Coenzymes of the type NADH, which contain a dihydropyridine ring, play a most important part in biochemical oxidation-reduction processes.[47,48]

stabilisers to prevent spontaneous polymerisation of tetrafluoroethylene.[59] The reaction of tetrafluoroethylene with triethylamine on exposure to γ-radiation leads only to telomerisation products $Et_2NCHMe(CF_2CF_2)_nH$.[60]

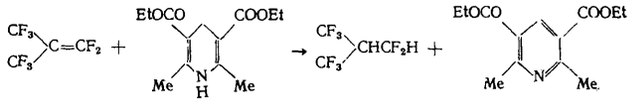
The more electrophilic perfluorocyclobutene and perfluoroisobutylene when reacted with tertiary amines evidently give bipolar ions, for example:

$$(CF_3)_2C{=}CF_2 + NR_3 \rightleftarrows (CF_3)_2\bar{C}{-}CF_2\overset{+}{N}R_3.$$

Indirect confirmation of this type of reaction is that the capacity of tertiary amines to catalyse the dimerisation of bis(trifluoromethyl)ketenimines is suppressed by the addition of perfluoroisobutylene (the rate of reaction is reduced by a factor of over 100).[16] In certain cases products derived by reaction of bipolar intermediates, being formed by rearrangements[16,17,61] or by reaction with an "external" electrophile,[62] have been isolated.



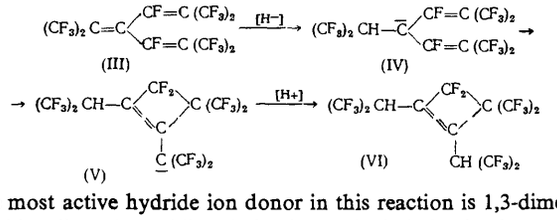
The tendency to form bipolar ions in which the hydride activity of hydrogen atoms is low may possibly also account for the fact that perfluoroisobutylene is not reduced by aliphatic or aliphatic-aromatic tertiary amines and only with Hantzsch ester does it give small quantities of dihydride at 120 °C:[63]



Perfluoroisobutylene reacts as a dehydrofluorinating agent with α,α-difluorotrimethylamine, converting it to the aminocarbene (I); the latter, on reacting with a further molecule of perfluoroisobutylene, is inserted into a C–F bond and gives amine (II):[64]

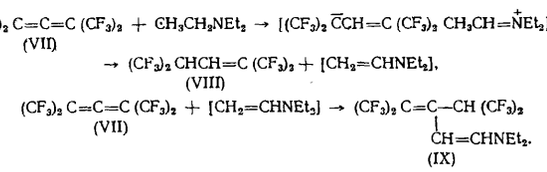
$$HCF_2NMe_2 \xrightarrow[-(CF_3)_3CH]{(CF_3)_2C=CF_2} [\ddot{C}FNMe_2] \xrightarrow{(CF_3)_2C=CF_2} (CF_3)_2C{=}CFCF_2NMe_2$$
(I) (II)

Introduction of two bulky perfluoroisobutenyl groups into the perfluoroisobutylene molecule inhibits the formation of a bipolar ion with a tertiary amine, at the same time not reducing the electrophilicity of the fluoroolefin. Therefore, the cross-conjugated perfluorotriene (III) readily removes a hydride ion from tertiary amines even at room temperature to form carbanion (IV). This linear carbanion then isomerises to the cyclic carbanion (V), and protonation of the latter gives the substituted cyclobutene (VI):[65]



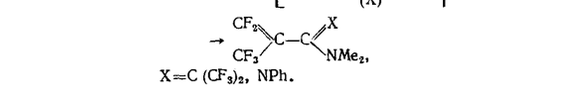
The most active hydride ion donor in this reaction is 1,3-dimethylbenzimidazoline; benzyldimethylamine and triethylamine have comparable activity.

Tertiary amines also reduce the cumulated C=C bond in tetrakis(trifluoromethyl)allene (VII).[66] Reaction with triethylamine at 65 °C results in the formation of the dihydroolefin (VIII) and dienamine (IX). The latter is evidently a product from the condensation of the initial allene (VII) and the intermediate diethylvinylamine:



With 1,3-dimethylbenzimidazoline, allene (VII) gives dihydroolefin (VIII) even at room temperature. Triphenylmethane and phenylacetylene have been used as proton donors in this reaction.[50]

Bis(dimethylamino)methane must have a greater hydride activity than triethylamine. However, when it is reacted with tetrakis(trifluoromethyl)allene or *N*-phenyl-bis(trifluoromethyl)ketenimine, reduction does not occur and there is an "allylic" substitution of a fluorine atom by a dimethylamino group [probably with formation of the intermediate betaine (X)], and the cumulated system of double bonds is converted to a 1,3-diene (or heterodiene) system:[67]

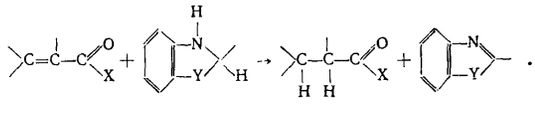


This type of cleavage on treatment with electrophilic reagents to form a dimethylaminomethyl cation which bonds with the anionic part of the electrophile is generally typical for bis(dimethylamino)methane.[68,69]

Thus, out of the fluoroolefins and related compounds studied only perfluorotriene (III) and allene (VII) undergo nucleophilic ionic hydrogenation (compare the results of three studies[6,50,65]) when treated with tertiary aliphatic and aliphatic-aromatic amines.

2. α,β-Unsaturated carbonyl compounds and their analogues

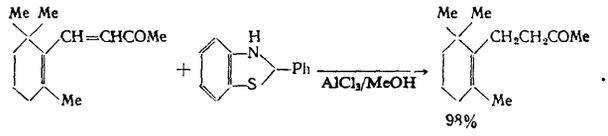
By using nitrogen-containing dihydroheteroaromatic compounds as reducing agents it has been possible in recent years to develop preparative methods for the hydrogenation of the C=C bond without affecting functional groups:



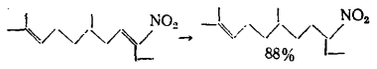
The reduction of a large number of activated olefins $RR^1C{=}CXY$ showed that the ease of reduction of the C=C bond decreases in the series of X, Y: CN, CN > CN, COOR > NO_2, H > COOR, COOR.[57] Replacement of R and R^1 by cyano groups increases the activity of the olefin even further, so that tetracyanoethylene is reduced not only by dihydroheteroaromatic but also by dihydroaromatic compounds such as 1,2-dihydronaphthalene.[70,71]

α,β-Unsaturated carboxylate esters and α,β-unsaturated ketones are reduced by dihydroheteroaromatic compounds only in the presence of Lewis acids.[56] In conjugated dienones it is possible to

reduce selectively just the α,β-C=C bond:[55]



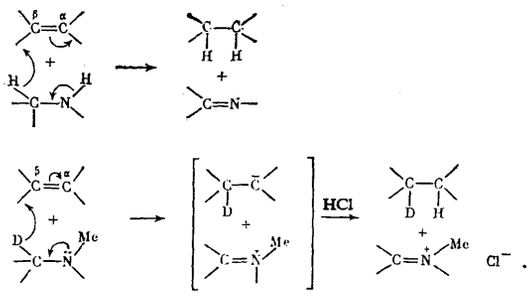
α,β-Unsaturated nitrocompounds and ketones are reduced with Hantzsch ester or 2-phenylbenzimidazoline in the presence of silica gel,[72–74] for example:



The increased hydride activity in 2-phenylbenzthiazolines from the introduction of electron-donating substituents into the *para*-position of the phenyl ring increases the rate of hydrogenation. This indicates that transfer of a hydride ion is the rate-determining stage of the reaction.[55] The use of benzthiazolines and benzimidazolines that were deuterated at the 2- and 3-positions showed that a hydrogen atom was transferred from the 2-position to the β-position and the hydrogen atom at the 3-position was transferred to the α-position of the compound undergoing hydrogenation.[55,57] In the reduction with 1,3-dimethyl-2-phenylbenzimidazoline, the hydrogen atom at the α-position relative to the functional group of the compound being reduced is derived from the solvent.[56]

In the reaction of (*Z*)-1,2-dibenzoyl-1,2-diphenylethylene with 2-phenylbenzthiazoline only *meso*-1,2-dibenzoyl-1,2-diphenylethane is formed stereospecifically. *cis*-Hydrogenation also takes place in the reduction of ethyl phenylpropiolate.[55]

When these results are combined it can be seen that in hydrogenation with benzthiazolines and benzimidazolines that have an unsubstituted nitrogen atom, transfer of the two hydrogen atoms to the C=C bond being reduced takes place simultaneously or almost simultaneously, while in hydrogenation with 1,3-dimethyl-2-benzimidazoline transfer of a hydride ion occurs [or correspondingly an electron and then a hydrogen atom (see Scheme 1)] followed by addition of a proton from the medium:[55–57]



Cyclic α,β-unsaturated carbonyl compounds such as halogenated quinones are some of the strongest electron acceptors. Their reactions with tertiary amines are examined in Section III.

If the C=C bond in the unsaturated compound is activated only by aryl substituents, this is insufficient for nucleophilic ionic hydrogenation by amines. Olefins such as styrene and stilbene react with tertiary amines only on irradiation, forming products from addition, hydrogenation, hydrodimerisation, etc.[36,39,40,75,76]

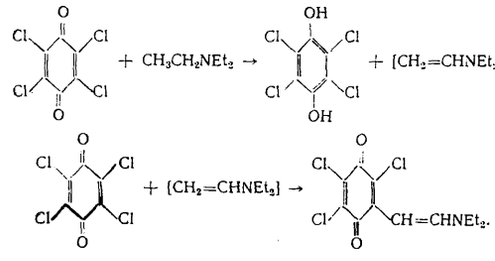
III. Reduction of a C=O bond

Although carbonyl compounds exhibit more marked electrophilic properties than do olefins, in the absence of electron-withdrawing substituents their activity is usually still insufficient for reduction by amines. Only on irradiation are benzophenone, acetophenone, and similar compounds reduced by amines since electron-transfer reactions are typical for the photochemically excited carbonyl group.[15] However, the presence of strong electron-withdrawing substituents in a carbonyl compound enables a hydride ion to be transferred to the unexcited C=O group. In this case reduction via decomposition of a betaine cannot be excluded (see Section I).

1. Haloquinones

Chloranil forms a CTC with tetramethyl-*p*-phenylenediamine[23] or 1,4-diazabicyclo[2.2.2]octane[29] and partially or completely (in polar solvents) isolated radical ion pairs.

When chloranil reacts with triethylamine, it is reduced to tetrachlorohydroquinone, and the resulting diethylvinylamine reacts with a further molecule of choranil, giving a compound with a blue colour—*N*, *N*-diethylaminovinyltrichlorobenzoquinone:[23,77]

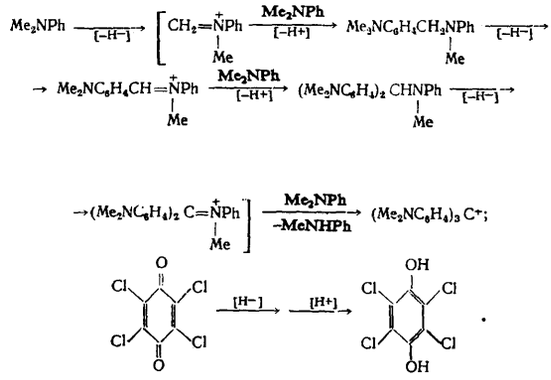


Other chlorinated quinones and also bromanil react in a similar manner to chloranil; iodanil does not react with triethylamine.[77,78]

Diethylcyclohexylamine, *N*-ethylpiperidine, diethylaniline, tetramethylethylenediamine, tribenzylamine, benzyldimethylamine, trimethylamine, tributylamine, and dimethylisobutylamine also have reducing properties in relation to chloranil. In the latter case the resulting enamine $Me_2C=CHNMe_2$ has been determined as isobutanal 2,4-dinitrophenylhydrazone.[77]

Replacement of the chlorine atoms in chloranil by methoxy groups leads to a weakening in oxidising properties; dichlorodimethoxybenzoquinones do not oxidise tertiary amines.

The formation of Crystal Violet when dimethylaniline is treated with chloranil under mild conditions may be due to the successive alternation of a hydride ion transfer to chloranil and electrophilic attack by the intermediate iminium cation at the *para*-position of a dimethylaniline molecule:[23]



2. Aldehydes and ketones

Hexafluoroacetone, which is a strong electrophile,[79] forms a stable iminium salt (XI)[49] with benzyldimethylamine. On hydrolysis of the salt, hexafluoroisopropanol and *N, N'*-dibenzyl-*N, N'*-dimethyldiaminomethane—a product of the condensation of methylbenzylamine with formaldehyde—are isolated. The hydride ion is mainly removed from a methyl group rather than the methylene group, which Gambaryan and Knunyants[49] attribute to steric hindrance:

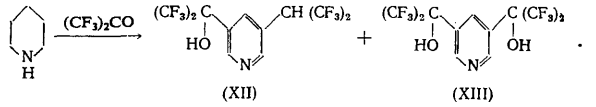
$$(CF_3)_2C{=}O + Me_2NCH_2Ph \rightarrow (CF_3)_2CHO\ CH_2{=}\overset{+}{N}CH_2Ph \xrightarrow{H_2O}$$
$$\rightarrow (CF_3)_2CHOH + PhCH_2\underset{Me}{N}CH_2\underset{Me}{N}CH_2Ph\,.$$
(XI)

Hexafluoroacetone is also reduced to hexafluoroisopropanol when treated with triethylamine,[49] dimethylisopropylamine,[49] and dicyclohexylethylamine[80] (the fate of the respective iminium cations has not been studied). Benzyldiethylamine and tribenzylamine do not react with hexafluoroacetone even on heating to above 100 °C,[49] while a stronger acceptor—the triphenylcarbenium cation—can remove a hydride ion from tribenzylamine.[8]

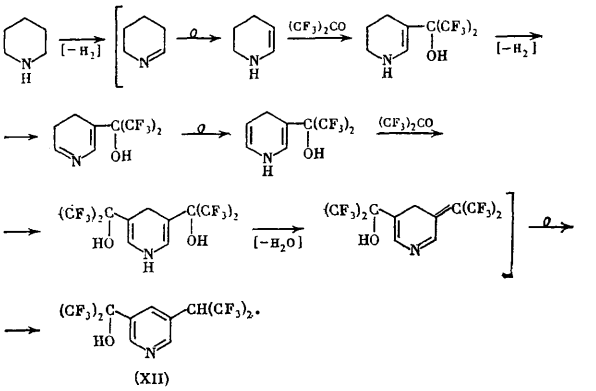
Benzylamine reacts with hexafluoroacetone to give the adduct $(CF_3)_2C(OH)NHCH_2Ph$; heating the adduct to 160 °C followed by hydrolysis yields hexafluoroisopropanol.[49,81]

The $(CF_3)_2CHO^-$ anion has been detected by ^1H NMR spectroscopy in mixtures of hexafluoroacetone and trimethylamine, triethylamine, or diethylmethylamine. When there is excess hexafluoroacetone, there is a signal from the $(CF_3)_2CHOC(CF_3)_2O^-$ anion. Both anions have been isolated as *O*-trimethylsilyl derivatives on addition of trimethylchlorosilane.[82]

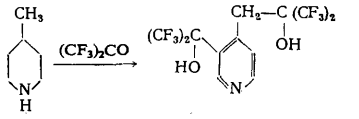
Hexafluoroacetone can also oxidise indoline, piperidine, and tetrahydroquinoline systems¶.[83–86] Thus, in the reaction of piperidine with excess hexafluoroacetone, substituted pyridines (XII) and (XIII) are formed:[83,85]


(XII) (XIII)

In this case aromatisation evidently results from a complex succession of reactions, involving not only the oxidation of amines by hexafluoroacetone but also the hydroxyalkylation of enamines, isomerisation of the intermediates with a double bond displacement, and also the dehydration of hydroxyalkyl-substituted enamines, for example:

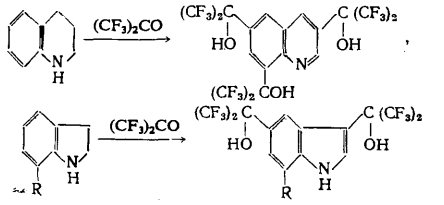

(XII)

In the case of α- and γ-pipecolines and also 2,6-dimethylpiperidine, hydroxyalkylation of both the heterocyclic ring and the methyl group occurs in addition to oxidation:[85]



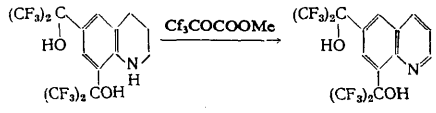
β-Pipecoline is substituted only in the ring.

In condensed systems such as tetrahydroquinoline and indolines, both rings can undergo hydroxyalkylation:[84,86]



It has been shown that in the reactions of piperidines and tetrahydroquinolines substitution takes place until the system is aromatised, as the corresponding aromatic heterocycles do not react with hexafluoroacetone under these conditions.[84,85]

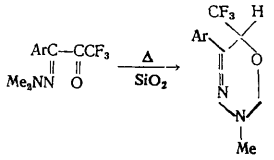
Methyl trifluoropyruvate, in a similar manner to hexafluoroacetone, can oxidise substituted tetrahydroquinoline:[84]



The reaction of hexafluoroacetone with tetramethyl-*p*-phenylenediamine stops at the stage where a CTC is formed.[28] On mixing the reactants the solution at first turns orange ("external complex") and after a few seconds it becomes blue ("internal complex").†

Dimethylaniline is attacked by hexafluoroacetone at the *para*-position,[89] in other words, its potential oxidation to a methyleniminium cation is suppressed by the competing electrophilic substitution in the benzene ring.

Intramolecular oxidation—reduction involving CF_3CO- and $CH_3N<$ groups—takes place on heating 1,1,1-trifluoro-3-arylpropan-2,3-dione phenylhydrazones, giving substituted oxadiazines:[90,91]



Hexachloroacetone, like hexafluoroacetone, proves to be sufficiently electrophilic to remove a hydride ion from triethylamine. However, the reaction does not stop when an iminium salt is formed. The iminium cation is deprotonated and the intermediate vinylamine is attacked by a second hexachloroacetone molecule with simultaneous haloform decomposition to give the aminovinylketone (XIV):[44]

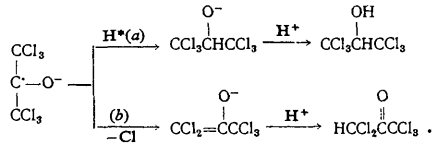
$$(CCl_3)_2CO + CH_3CH_2NEt_2 \rightarrow (CCl_3)_2CHOH + [CH_2{=}CHNEt_2],$$
$$(CCl_3)_2CO + [CH_2{=}CHNEt_2] \rightarrow CCl_3COCH{=}CHNEt_2 + CHCl_3.$$
(XIV)

¶Secondary heterocyclic amines are also oxidised by nitrobenzene (in the presence of transition metal salts).[87,88]

† Charge-transfer complexes and their corresponding terminology have been covered in three reviews.[23–25]

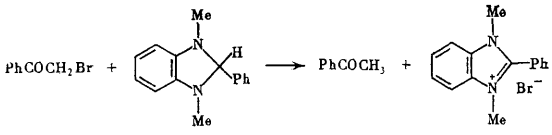
Diisopropylethylamine reacts in a similar manner, with only the ethyl group being oxidised.

When hexachloroacetone is treated with tri-n-propylamine, the product derived from replacing a chlorine atom by hydrogen—pentachloroacetone—is formed in addition to hexachloroisopropanol.[44] Talley[44] suggests that in this case hexachloroacetone acts as a chlorinating agent towards the enamine (compare the results of Laskovics and Schulman[92,93]). It cannot be excluded that both products are formed from a single intermediate—the hexachloroacetone radical anion—by the competing reactions of addition of a hydrogen atom (*a*) and elimination of a halogen atom (*b*):



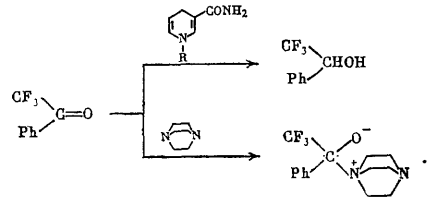
Tetramethyl-*p*-phenylenediamine forms a blue complex with hexachloroacetone;[28] pentachloroacetone and tetrachloroacetone are isolated from the reaction mixture.

An effective reagent for the reduction of α-halocarbonyl compounds which does not affect the carbonyl group is 1,3-dimethyl-2-phenylbenzimidazoline,[58] for example:

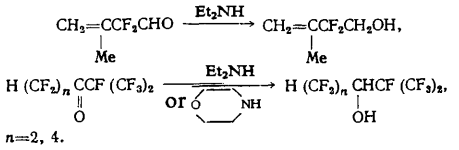


It is assumed that direct hydride transfer occurs in this case.

Trifluoroacetophenone, which is less active than hexafluoroacetone, is readily reduced by 1,4-dihydropyridine derivatives[26,27] but with triethylamine, quinuclidine and 1,4-diazabicyclo[2.2.2]octane it forms only betaines:[20]

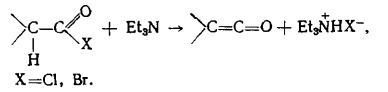


Cases are known where fluorine-containing carbonyl compounds are reduced by diethylamine. Thus, 2,2-difluoro-3-methyl-3-butenal[94] and polyfluoroalkyl heptafluoroisopropyl ketones[95] are converted to the corresponding alcohols:

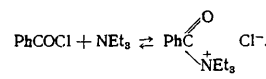


3. Anhydrides and halides of carboxylic acids

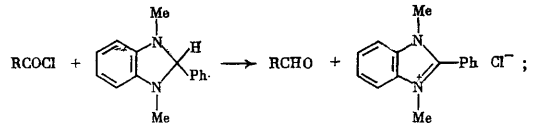
As has already been mentioned above, reactions of hydride transfer from tertiary amines compete with the direct addition of an electrophile to the amine, leading to ammonium salts. This has a particularly clear effect on the reactions of triethylamine with carboxylic acid halides. Thus, if the acid halide contains α-hydrogen atoms, dehydrohalogenation occurs, in other words, the amine acts as a base:[96]



With phosgene[97] and with carboxylic acid chlorides not containing α-hydrogen atoms[98–100] tertiary amines usually form acylammonium complexes, for example:



However, the very strong hydride ion donor—1,3-dimethyl-2-phenylbenzimidazoline—can reduce carboxylic acid chlorides to aldehydes:[58]



R = Ph, *p*-$O_2NC_6H_4$, *p*-$MeOC_6H_4$, n-C_7H_{15}, C_6H_{11}.

In addition, polyhalocarboxylic acid derivatives such as anhydrides,[101–103] acid chlorides,[46,102–105] and acid fluorides[104,105] contain a sufficiently electrophilic carbonyl carbon atom in their molecules that it can remove a hydride ion also from triethylamine.

Thus, acid halides are converted to aldehydes and the resulting diethylvinylamine is acylated by a second molecule of reactant to give aminovinyl ketones:

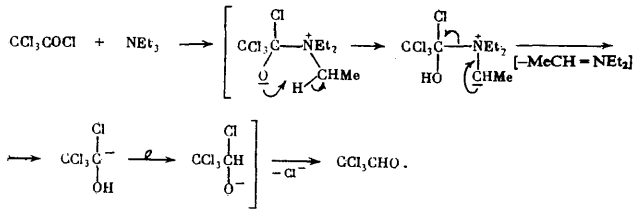
$$RCOX + NEt_3 \rightarrow RCHO + [CH_2{=}CHNEt_2],$$
$$RCOX + [CH_2{=}CHNEt_2] \rightarrow RCOCH{=}CHNEt_2,$$

R = CCl_3, CF_3, n-C_3F_7, iso-Pr; X = Cl, F.

The reaction is a convenient method for synthesising dialkylaminovinyl ketones, the yields of which are 30–90%. The aldehydes formed are usually not isolated since they are unstable under the reaction conditions. However, chloral is obtained in about 60% yield from trichloroacetyl chloride and perfluorobutyraldehyde is obtained (as its 2,4-dinitrophenylhydrazone) in 16% yield from perfluorobutyryl chloride.[104,105]

The reactions of carboxylic acid halides with tertiary amines most probably involve a single-electron transfer to form a CTC. Evidence in favour of this is the detection of characteristic absorption bands on mixing tetramethyl-*p*-phenylenediamine with trichloroacetyl chloride and also the coloration when diethylaniline, tributylamine, and other tertiary amines are added to trichloroacetyl chloride.[104,105]

Fraser and Swingle[46] suggest that the reduction of trichloroacetyl chloride with triethylamine involves the formation of an intermediate betaine:



They assume that the isolation of small quantities of ethylene and trichloroacetic acid diethylamide results from attack by the *O*-anion site in the betaine on to the β-hydrogen atom rather than the

α-hydrogen atom. However, these by-products could also be formed by decomposition of an acylammonium salt:[104]

$$RCONEt_3^+Cl^- \begin{cases} \longrightarrow RCONEt_2 + EtCl \\ \longrightarrow RCONEt_2 + CH_2{=}CH_2 + HCl\,. \end{cases}$$

The formation of an acylammonium salt should not in principle inhibit reduction of the carbonyl group provided that there is an excess of amine reducing agent, since the electrophilicity of the carbonyl carbon atom in an acylammonium cation should be even higher than in the initial acid halide. In fact, when trichloroacetyl chloride is gradually added to an excess of triethylamine, an aminovinyl ketone is formed in about 90% yield. With the reverse order of mixing reactants, only trace amounts of the aminovinyl ketone are isolated and products derived from decomposition of the fairly unstable acylammonium salt—triethylamine hydrochloride, trichloroacetic acid diethylamide, and a considerable amount of tar—are mainly obtained:

$$CCl_3COCl + NEt_3 \begin{cases} \longrightarrow CCl_3COCH{=}CHNEt_2 \\ \longrightarrow CCl_3C^+(Cl)NEt_3Cl \rightarrow CCl_3CONEt_2 + EtCl + CH_2{=}CH_2 + NEt_3 \cdot HCl. \end{cases}$$

Acid fluorides do not form acylammonium complexes (as a result of the high strength of the C–F bond) and the result of the reaction is virtually independent of the order of mixing the reactants.[104]

In the reaction of perfluoropivaloyl fluoride, carbon monoxide and monohydroperfluoroisobutane, which are products derived from the decomposition of the intermediate perfluoropivalaldehyde, are produced:[104,105]

$$(CF_3)_3CCOF \xrightarrow{NEt_3} [(CF_3)_3CCHO] + (CF_3)_3COCH{=}CHNEt_2 \begin{cases} \\ \longrightarrow (CF_3)_3CH + CO\,. \end{cases}$$

α-Chlorohexafluoroisobutyryl fluoride reacts to form an aminovinyl ketone and a product in which the chlorine atom is replaced by hydrogen:[104,105]

$$(CF_3)_2CClCOF + NEt_3 \rightarrow (CF_3)_2CHCOF + (CF_3)_2ClCOCH{=}CHNEt_2.$$

A similar replacement of the bromine atom by hydrogen on treatment with triethylamine is known for bromides CF_3CXYBr (X, Y = CF_3, COOR).[106]

Tributylamine reacts with trichloroacetyl chloride in a similar manner to triethylamine:[104]

$$CCl_3COCl + EtCH_2CH_2NBu_2 \rightarrow CCl_3CHO + CCl_3COC(Et){=}CHNBu_2.$$

When trichloroacetyl chloride is reacted with trimethylamine, only products from the decomposition of the acylammonium salt are found.[104,105]

In the case of diethylaniline small quantities of aminovinyl ketone are formed, but the main reaction route, as also for dimethylaniline, proved to be acylation at the *para*-position of the benzene ring:[104,105]

$$CCl_3COCl + C_6H_4(NR_2) \begin{cases} \xrightarrow{R=Et} CCl_3COCH{=}CHN(Et)C_6H_4 \quad 7\% \\ \xrightarrow{R=Me,\,Et} CCl_3CO\,C_6H_4(NR_2)\,. \quad \sim 60\% \end{cases}$$

Perfluorobutyryl chloride also acylates diethylaniline at the *para*-position. Moreover, in both cases trace amounts of the corresponding triarylmethane dye—Ethyl Violet or Crystal Violet—are formed (see III.1).

Sources of perfluoroacyl fluorides in reactions with triethylamine can be provided by perfluoroolefin oxides,[104,105] which are known[107] to isomerise readily in the presence of catalytic quantities of tertiary amines

$$(CF_3)_2C(O)CF_2 \xrightarrow{NEt_3} (CF_3)_2CFCOF \xrightarrow{NEt_3} (CF_3)_2CFCOCH{=}CHNEt_2.$$

In a similar manner to perhalocarboxylic acid halides, trifluoromethanesulphenyl chloride can also oxidise triethylamine and undergo condensation with the resulting diethylvinylamine:[108]

$$CF_3SCl + CH_3CH_2NEt_2 \rightarrow (CF_3S)_2C{=}CHNEt_2.$$

In the presence of transition metal compounds as catalysts, perfluoroalkyl iodides also undergo a similar reaction.[109,110] Hydrolysis of the resulting amine (XV) gives an aminovinyl ketone or saturated and unsaturated fluorine-containing aldehydes:

$$R_FCF_2I + (RCH_2CH_2)_3N \xrightarrow{(Ph_3P)_4Pd} \rightarrow R_FCF_2C(R){=}CHN(CH_2CH_2R)_2 + R_FCF_2H + (RCH_2CH_2)_3N \cdot HI,$$

(XV)

$$(XV) \xrightarrow{H_2O} \begin{cases} \xrightarrow{(R=H)} R_FCOCH{=}CHNEt_2 \\ \longrightarrow R_FCF_2CH(R)CHO \xrightarrow{-HF} R_FCF{=}CCHO\,(R). \end{cases}$$

Zhou and Huang[109,110] propose a free-radical mechanism for this reaction as it is suppressed when *p*-dinitrobenzene and *p*-benzoquinone are added.

The photochemical reduction of various polyhaloalkanes with triethylamine also occurs by a free-radical mechanism.[111–113]

Trifluoroacetyl bromide phenylhydrazone (XVI) is reduced by triethylamine, with trifluoroacetaldehyde phenylhydrazone and diethylvinylamine being formed. The usual dehydrohalogenation to a nitrilimine occurs together with this; the latter undergoes a [3 + 2]-cycloaddition reaction with the vinylamine, and the subsequent elimination of diethylamine leads to a substituted pyrazole:[114]

$$CF_3C(Br){=}NNHPh \text{ (XVI)} \xrightarrow{NEt_3} \begin{cases} \longrightarrow CF_3CH{=}NNHPh + [CH_2{=}CHNEt_2] \\ \longrightarrow [CF_3C{\equiv}\overset{+}{N}\overline{N}Ph] + Et_3N \cdot HBr \end{cases}$$

$$[CF_3C{\equiv}\overset{+}{N}\overline{N}Ph] + [CH_2{=}CHNEt_2] \rightarrow \left[\text{pyrazolidine intermediate}\right] \xrightarrow{-Et_2NH} \text{1-phenyl-3-trifluoromethylpyrazole}.$$

When bromide (XVI) is reacted with *N*-methylpyrrolidine, only a quaternary salt is formed and reduction is not found to occur:[114]

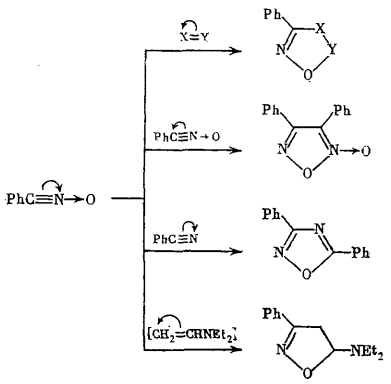
$$CF_3C(Br){=}NNHPh \text{ (XVI)} \xrightarrow{MeN} CF_3C(=NNHPh)\,[Me{-}\overset{+}{N}\,Br^-]$$

The oxidation of triethylamine to diethylvinylamine also occurs in the reaction with benzhydroxamoyl chloride (XVII).[115] The oxidising agent in this case is probably not acid chloride (XVII) but its dehydrochlorination product, a nitrile oxide, which is reduced to a nitrile. Thus, there are two dipolarophiles in the mixture—nitrile and enamine—which can compete for cycloaddition to the nitrile

oxide both with the separate addition of an "external" dipolarophile reagent and with the nitrile oxide itself:

$$PhC(Cl)=NOH + NEt_3 \rightarrow [PhC\equiv N \rightarrow O],$$
(XVII)

$$[PhC\equiv N \rightarrow O] + NEt_3 \rightarrow PhCN + [CH_2=CHNEt_2]$$



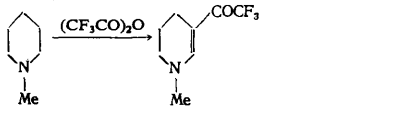
The ratio of products depends on the activity of the "external" dipolarophile, the quantity of trimethylamine, and the nature of the solvent.

In addition to acid chlorides, polyhalocarboxylic anhydrides are also readily reduced by tertiary amines, which is shown in the case of trifluoroacetic anhydride.[101,102] The resulting trifluoroacetaldehyde is isolated as acylal (XVIII). The intermediate enamine undergoes acylation, and in contrast to the reactions with acid chlorides, one[101] or both[102] hydrogen atoms can be replaced:

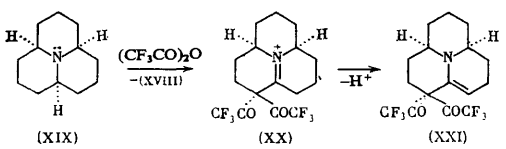
$$(CF_3CO)_2O + Et_3N \rightarrow \underset{\text{(XVIII)}}{(CF_3CO)_2C=CHNEt_2} + CF_3CH(OCOCF_3)_2 + CF_3COO^-\overset{+}{H}NEt_3.$$

Diisopropylethylamine reacts in a similar manner, with only the ethyl group being oxidised. In the case of methylpiperidine the heterocycle is oxidised:[102]

$$CH_3CH_2N(Pr\text{-}iso)_2 \xrightarrow{(CF_3CO)_2O} (CF_3CO)_2C=CHN(Pr(iso)_2 + CF_3COCH=CHN(Pr\text{-}iso)_2,$$



Diisopropylmethylamine is also oxidised by trifluoroacetic anhydride; in this case acylal (XVIII) is isolated but the product from conversion of the amine has not been studied. Treatment of the tricyclic amine (XIX) with trifluoroacetic anhydride gives acylal (XVIII) and the iminium salt (XX), which after treatment with base is isolated as enamine (XXI):[102]



(XIX) (XX) (XXI)

Schreiber[102] suggests various schemes for the mechanism of oxidation, including those that involve single-electron transfer. As the α-hydrogen atoms and unshared electron pair in amine (XIX) lie in different directions from the molecular plane, a mechanism via a cyclic transition state involving a betaine (see Section I) is impossible. However, elimination of a proton could occur on treatment with another amine molecule. Direct hydride transfer also cannot be excluded.

IV. Compounds containing other double bonds

1. Acylimines of fluoroketones

Acylimines of fluoroketones have clearly defined electrophilic activity. Moreover, cycloaddition reactions are typical for these compounds.[116] These properties are exhibited in reactions with tertiary amines.

Hexafluoroacetone benzoylimine readily reacts with triethylamine, oxidising it to diethylvinylamine.[117] When this intermediate reacts with the initial imine, a [4 + 2]-cycloaddition product is formed together with a linear product from addition to the C=N bond:

$$(CF_3)_2C=NCOPh + NEt_3 \rightarrow (CF_3)_2CHNHCOPh + [CH_2=CHNEt_2]$$

$$(CF_3)_2C=NCOPh + [CH_2=CHNEt_2] \rightarrow (CF_3)_2C\langle \text{CH}_2\text{—CH}(\text{NEt}_2)\text{—O—C(Ph)=N} \rangle + (CF_3)_2C(\text{NHCOPh})\text{CH=CHNEt}_2.$$

Hexafluoroacetone carbethoxyimine reacts with greater difficulty, forming only linear products:[117]

$$(CF_3)_2C=NCOOEt + NEt_3 \rightarrow (CF_3)_2CHNHCOOEt + (CF_3)_2C(\text{NHCOOEt})\text{CH=CHNEt}_2.$$

Benzyldimethylamine contains no β-hydrogen atoms in the molecule and the iminium cation that is formed at the first stage of the reaction is deprotonated to an aminocarbene which traps a second hexafluoroacetone benzoylimine molecule to form a [4 + 1]-cycloaddition product:[118]

$$(CF_3)_2C=NCOPh + Me_2NCH_2Ph \rightarrow (CF_3)_2CH\bar{N}COPh\ \overset{CH_2}{Me}\!\!\diagdown\!\!\overset{+}{N}\!\!\diagup\!\!CH_2Ph \rightarrow$$
(XXII)

$$\rightarrow (CF_3)_2CHNHCOPh + \left[\begin{matrix}\ddot{C}H\\ Me\end{matrix}\!\!\diagdown\!\!\diagup\!\!NCH_2Ph\right],$$
(XXIII)

$$(CF_3)_2C=NCOPh + \left[\begin{matrix}\ddot{C}H\\ Me\end{matrix}\!\!\diagdown\!\!\diagup\!\!NCH_2Ph\right] \rightarrow (CF_3)_2C\langle \text{N=C(Ph)—O—CH(Me—N—CH}_2\text{Ph)} \rangle.$$

Exposure to visible light assists the formation of the aminocarbene (the oxidation stage—formation of the iminium salt—does not require light exposure, so this reaction cannot be classed as a photochemical oxidation). The addition of pyridine also accelerates the reaction.‡ The iminium salt (XXII) can be preserved in the dark for a long time but on heating it is converted to the reduction product (XXIII). The products derived from conversion of the amine have not been established in this case.

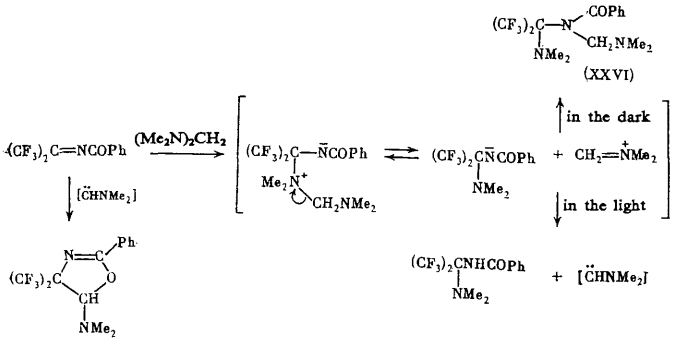
When hexafluoroacetone benzoylimine is reacted with bis-(dimethylamino)methane,[122] elimination of a dimethylaminomethyl group as a cationoid species also occurs together with hydride transfer (see II.1). As a result of hydride transfer, there is the formation of iminium salt (XXIV), which has been identified by

‡ For the generation of aminocarbenes by deprotonation of iminium cations, see the studies of Böhme et al.[7,119,121] Another route for the formation of an aminocarbene from a tertiary amine is dehydrofluorination of α,α-difluorotrimethylamine (see also II.1). The carbene Me_2NCF: undergoes cycloaddition with two moles of hexafluoroacetone to form a substituted dioxolane.[64]

NMR spectroscopy. When this salt is treated with an alcohol it is converted to *N*-benzoylhexafluoroisopropylamine (XXV):

$$(CF_3)_2C{=}NCOPh + (Me_2N)_2CH_2 \rightarrow$$
$$\rightarrow (CF_3)_2CH\bar{N}COPh\ \overset{+}{C}H(NMe_2)_2 \xrightarrow{ROH} (CF_3)_2CHNHCOPh\ .$$
(XXIV) (XXV)

The second reaction route is formation of a betaine followed by dissociation to an anion and the dimethylaminomethyl cation. Subsequently addition occurs in the dark with the formation of triamine (XXVI) while in the light the dimethylaminomethyl cation is deprotonated to dimethylaminocarbene, which traps a second molecule of hexafluoroacetone benzoylimine and a [4 + 1]-cycloaddition product is obtained as a result:



Thus in this reaction bis(dimethylamino)methane serves as the source of a hydride ion, dimethylaminomethyl cation, and dimethylamiocarbene.

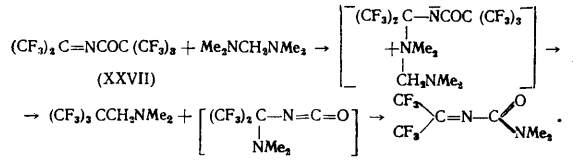
The molecule of hexafluoroacetone perfluoropivaloylimine (XXVII) contains a perfluoro-t-butyl group which is readily eliminated as an anion.[16] This property, as a rule, determines the course of the reactions of imine (XXVII).

Benzyldimethylamine donates a hydride ion to imine (XXVII), the resulting iminium salt having been identified by ^{19}F NMR spectroscopy. The cation of the iminium salt then combines with the perfluoro-t-butyl anion being eliminated, as a result of which amine (XXVIII) and monohydroperfluoroisopropyl isocyanate (XXIX) are obtained:[123]

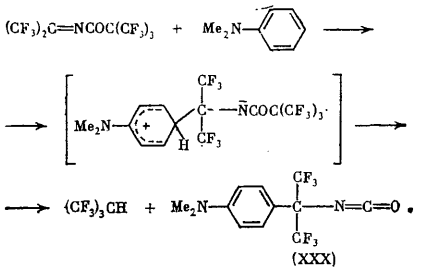
$$(CF_3)_2C{=}NCOC(CF_3)_3 + Me_2NCH_2Ph \rightarrow (CF_3)_2CH\bar{N}COC(CF_3)_3 \rightarrow$$
(XXVII)
$$\rightarrow (CF_3)_2CHN{=}C{=}O + (CF_3)_3CCH_2NCH_2Ph$$
(XXIX) (XXVIII)

Triethylamine also reacts as a hydride ion source with imine (XXVII); in this case isocyanate (XXIX) and monohydroperfluoroisobutane $(CF_3)_3CH$ are isolated.

When bis(dimethylamino)methane reacts with imine (XXVII) it acts only as a source of the dimethylaminomethyl cation; hydride transfer was not found to occur:[122]



Dimethylaniline is attacked by imine (XXVII) at the *para*-position of the benzene ring; elimination of monohydroperfluoroisobutane yields isocyanate (XXX):[123]



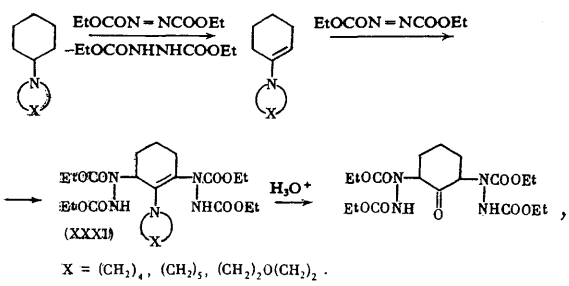
2. Azo compounds

Reactions of tertiary amines with dibenzoyldiimide and diethyl azodicarboxylate resemble the corresponding reactions with hexafluoroacetone benzoylimine. Azo compounds give the reduction products—dibenzoylhydrazine and diethyl hydrazodicarboxylate—in high yield, and the intermediate enamine reacts with the initial azo compound to give either vinyl substitution products of [2 + 4]-cycloaddition products.

Thus, diethyl azodicarboxylate reacts with triethylamine to form a product derived from double substitution in the intermediate enamine:[124]

$$EtOCON{=}NCOOEt + NEt_3 \rightarrow EtOCONHNHCOOEt + [CH_2{=}CHNEt_2],$$
$$EtOCON{=}NCOOEt + [CH_2{=}CHNEt_2] \rightarrow (EtOCONH)_2C{=}CHNEt_2.$$

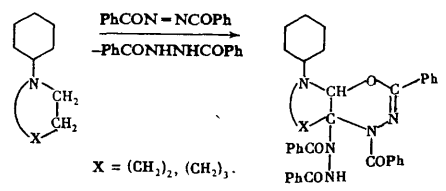
The cyclohexane ring is oxidised in *N*-cyclohexyl-substituted pyrrolidine, piperidine, and morpholine.[124] The azo compound attacks the intermediate enamine to form bis-hydrazines (XXXI):



X = $(CH_2)_4$, $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$.

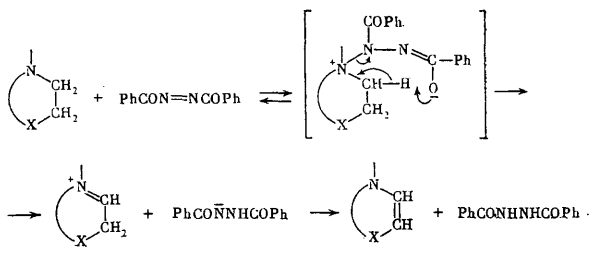
Acid hydrolysis gives a 2,6-disubstituted cyclohexanone. The formation of 2,6-disubstituted compounds (XXXI) is due to the known[125] migration of the double bond in enamines of this type.

Treatment with benzoyldiimide, on the other hand, leads to oxidation of the heterocycle rather than the carbocycle.[45] The resulting enamine reacts with two molecules of initial azo compound to give a product which corresponds to two reaction routes occurring at the same time—replacement of a vinyl hydrogen atom and cycloaddition:

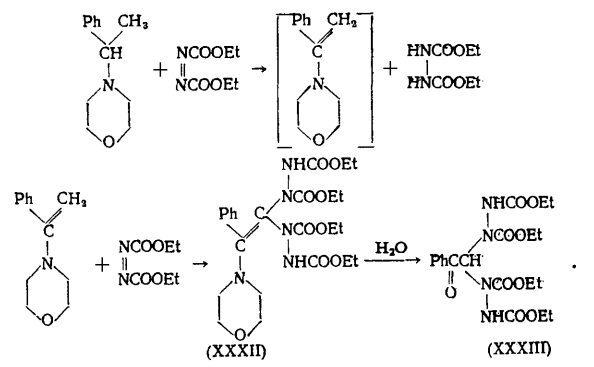


X = $(CH_2)_2$, $(CH_2)_3$.

The variation in oxidation route is attributed to the different mechanisms of these reactions.[45] For diethyl azodicarboxylate a mechanism via the formation of an intermediate CTC and free radicals (styrene added to the reaction mixture undergoes 20% conversion to polystyrene) has been suggested, while for dibenzoyldiimide a mechanism via a betaine has been proposed:

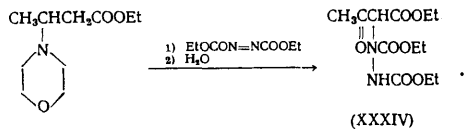


Marchetti[45] considers this to be the explanation for the different behaviour of *N*-cyclohexylmorpholine. Dibenzoyldiimide, in contrast to diethyl azodicarboxylate, does not react with this amine. This appears natural as the basicity of morpholine is less than the basicity of pyrrolidine and piperidine by a factor of 10^3, so the formation of a betaine is inhibited. *N*-(α-Methylbenzyl)morpholine also does not react with dibenzoyldiimide but reacts with diethyl azodicarboxylate.[124] As a result, adduct (XXXII) is formed, and after hydrolysis ketone (XXXIII) is obtained:



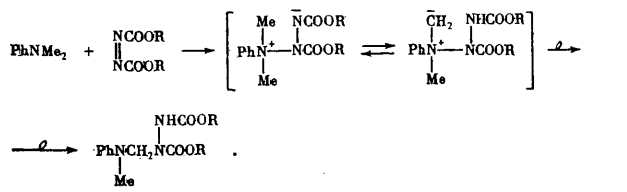
The same product is obtained when starting from a known sample of α-morpholinostyrene.

The hydrazine-substituted ethyl acetoacetate (XXXIV) is obtained in a similar manner from ethyl β-morpholinobutyrate:[124]



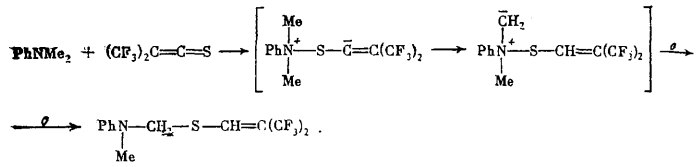
N-Ethylpiperidine, *N*-methylcyclohexylamine, and *N,N*-diethylaniline also reduce diethyl azodicarboxylate.[124] The products derived from dehydrogenation of the amines were not isolated, but after acid hydrolysis piperidine was found in the reaction mixture in the case of *N*-ethylpiperidine and *N*-ethylaniline was found in the case of *N,N*-diethylaniline.

Dimethylaniline adds on to azodicarboxylate esters with cleavage of a C–H bond in a methyl group. An ionic mechanism via a betaine and ylide rearrangement has been proposed:[126]



This reaction can also be interpreted as a hydride transfer followed by addition of the iminium cation to the aza anion.

Dimethylaniline adds on to bis(trifluoromethyl)thioketene in a similar manner:[127]



The mechanism of this reaction is evidently ionic; it is not suppressed by the addition of diphenylpicrylhydrazyl and is retarded by the introduction of electron-withdrawing substituents into the benzene ring of the amine. A similar addition of ethers to bis(trifluoromethyl)thioketene is sensitive to the addition of peroxides, so the reaction with ethers is possibly a free-radical reaction.[127] Thus, the mechanism of these reactions can vary fundamentally with small changes in the nature of the reactants.

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It is clear from the material presented here that the reduction of unsaturated electrophilic compounds by amines (usually tertiary) occurs quite widely in organic chemistry. In certain cases such reactions are of importance synthetically, and further progress is to be expected in this direction. The study of reactions of this type is increasingly important because they are proving to be undesirable as they can compete with "normal" reactions in which amines are used, for example, as basic catalysts. The authors hope that the present review will to some extent stimulate research in this field.

References

1. N C Deno *Contemporary Problems in Physical Organic Chemistry* (Translated into Russian), Izd. Mir, Moscow, 1967, p. 393
2. G Belluci, G Berti, R Bianchini, L Orsini *Tetrahedron Lett.*, 1982, **23** 3635
3. G Belluci, R Bianchini, R Ambrosetti *J. Chem. Soc., Perkin Trans. 2*, 1987, 39
4. H Volz *Kontakte (Darmstadt)*, 1986, (1) 12
5. Z N Parnes, D N Kursanov, Yu I Lakhovetskii *Zh. Vses. Khim. Obshch. im D I Mendeleeva*, 1974, **19** 324
6. D N Kursanov, Z N Parnes, M I Kalinkin, N M Loim *Ionnoe Gidrirovanie* (Ionic Hydrogenation), Izd. Khimiya, Moscow, 1979
7. H Böhme, M Haake *Iminium Salts in Organic Chemistry* (Edited by H Böhme, et al.), Wiley, New York, 1976, Part 1, p. 107
8. R Damico, C D Broaddus *J. Org. Chem.*, 1966, **31** 1607
9. H Völtz, H H Kiltz *Tetrahedron Lett.*, 1970, 1917

10. H Völtz, H H Kiltz *Liebigs Ann. Chem.*, 1971, **752** 86
11. P Yu Ivanov, N N Bychkov, B I Stepanov *Zh. Org. Khim.*, 1982, **18** 391
12. N N Bychkov, V V Milakov, D V Lavrov, B I Stepanov *Zh. Org. Khim.*, 1987, **23** 1516
13. V V Milakov, N N Bychkov, D V Lavrov, B I Stepanov *Zh. Org. Khim.*, 1987, **23** 664
14. T Shono *Tetrahedron*, 1984, **40** 811
15. S G Cohen, A Parolla, G H Parson *Chem. Rev.*, 1973, **73** 141
16. Yu V Zeifman, E G Ter-Gabrielyan, N P Gambaryan, I L Knunyants *Usp. Khim.*, 1984, **53**(3) 431 [English translation in *Russ. Chem. Rev.*, 1984(3)]
17. D J Burton, R D Howelles, P D Vander Valk *J. Am. Chem. Soc.*, 1977, **99** 4830
18. A Le Berre, A Delacroix *Bull. Soc. Chim Fr.*, 1973, 640
19. E N Zil'berman, V N Salov, V L Krasnov, S Yu Atopshev *Izv. Vuzov. Khim. i Khim. Tekhnolog.*, 1986, **29**(4) 22
20. M L Manion Schilling, H D Roth *J. Am. Chem. Soc.*, 1980, **102** 4271
21. Yu V Zeifman, L A Simonyan, Z V Safronov, N P Gambaryan *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1367
22. N P Gambaryan, E M Rokhlin *Usp. Khim.*, 1986, **55**(6) 902 [English translation in *Russ. Chem. Rev.*, 1986, **55**(6)]
23. E M Kossover *New Problems in Physical Organic Chemistry* (Translated into Russian), Izd. Mir, Moscow, 1969, p. 36
24. M A Khidekel', E V Todres *Zh. Vses. Obshch. im. D I Mendeleeva*, 1978, **23** 483
25. B P Bespalov, E V Getmanova, K M Dyumaev *Zh. Vses. Obshch. im. D I Mendeleeva*, 1978, **23** 548
26. J J Steffens, D M Chipman *J. Am. Chem. Soc.*, 1971, **93** 6694
27. A Ohno, H Yamamoto, S Oka *J. Am. Chem. Soc.*, 1981, **103** 2041
28. D C Dittmer, A Lombardo, F H Batzold, C S Greene *J. Org. Chem.*, 1976, **41** 2976
29. F Sěršeň, S Koščal, P Bañacký, L Krasnec *Collect. Czech. Chem. Commun.*, 1977, **42** 2173
30. T Laird *General Organic Chemistry* (Translated into Russian), Izd. Mir, Moscow, 1982, Vol. 2, p. 802
31. Y L Chow, W C Danen, S F Nelsen, D H Rosenblatt *Chem. Rev.*, 1978, **78** 243
32. H D Roth, M L Manion *J. Am. Chem. Soc.*, 1975, **97** 6886
33. M V Serdobov, A V Shapiro, A M Belostotskii *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2707
34. A M Belostotskii, L M Kostochka, A P Skoldinov *Khim. Geterotsikl. Soedin.*, 1982, 1657
35. F D Lewis, T-I Ho *J. Am. Chem. Soc.*, 1977, **99** 7991
36. F D Lewis, T-I Ho *J. Am. Chem. Soc.*, 1980, **102** 1751
37. F D Lewis, T-I Ho, J T Simpson *J. Org. Chem.*, 1981, 1077
38. I H Leaver, G C Ramsey *Tetrahedron*, 1969, **25** 5669
39. F D Lewis, J T Simpson *J. Am. Chem. Soc.*, 1980, **102** 7593
40. F D Lewis, T-I Ho, J T Simpson *J. Am. Chem. Soc.*, 1982, **104** 1924
41. S F Nelsen, J T Ippoliti *J. Am. Chem. Soc.*, 1986, **108** 4879
42. Z V Todres *Ion-Radikaly v Organicheskom Sinteze* (Radical Ions in Organic Synthesis), Izd. Khimiya, Moscow, 1986, p. 31
43. A Ohno, T Schio, H Yamamoto, S Oka *J. Am. Chem. Soc.*, 1981, **103** 2045
44. J J Talley *Tetrahedron Lett.*, 1981, **22** 823
45. L Marchetti *J. Chem. Soc., Perkin Trans. 2*, 1977, 1977
46. R R Fraser, R B Swingle *Tetrahedron*, 1969, **25** 3469
47. A Leninger *Biochemistry* (Translated into Russian), Izd. Mir, Moscow, 1974
48. A A Yasnikov *Zh. Vses. Khim. Obshch. im D I Mendeleeva*, 1978, **23** 579
49. N P Gambaryan, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1965, 722
50. Zh E Ioepero, Thesis, Lensovet Leningrad Technological Institute, Leningrad, 1969
51. D C Dittmer, L J Steffa, J R Potoski, R A Fouty *Tetrahedron Lett.*, 1961, 827
52. D C Dittmer, R A Fouty *J. Am. Chem. Soc.*, 1964, **86** 91
53. R H Abeles, R F Hutton, F H Westheimer *J. Am. Chem. Soc.*, 1957, **79** 712
54. S Singh, V K Sharma, S Gill, R I K Sahota *J. Chem. Soc., Perkin Trans. 1*, 1985, 437
55. H Chikashita, M Miyazaki, K Itoh *J. Chem. Soc., Perkin Trans., 1*, 1987, 699
56. H Chikashita, K Itoh *Bull. Chem. Soc. Jpn.*, 1986, **59** 1747
57. H Chikashita, S Nishida, M Miyazaki, et al. *Bull. Chem. Soc., Jpn.*, 1987, **60** 737
58. H Chikashita, H Ide, K Itoh *J. Org. Chem.*, 1986, **51** 5400
59. Yu A Panshin, S G Malkevich, T S Dunaevskaya *Ftoroplasty* (Fluoroplastics), Izd. Khimiya, Leningrad, 1978, p. 7
60. A T Podkhalyuzin *Zh. Obshch. Khim.*, 1980, **50** 2359
61. R G Kostyanovskii, Z E Samoilova, I I Chervin *Dokl. Akad. Nauk SSSR*, 1969, **186** 835
62. Yu V Zeifman, L T Lantseva, A A Kadyrov, E M Rokhlin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 1116
63. I L Knunyants, M P Krasuskaya, N P Gambaryan *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1965, 723
64. I L Knunyants, N I Delyagina, S M Igumnov *Izv. Akad. Nauk SSSR*, Ser. Khim., 1981, 860
65. E G Ter-Gabrielyan, Z N Parnes, N P Gambaryan, L A Simonyan *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 1656
66. Yu E Aronov, Yu A Cheburkov, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1967, 1758
67. N P Gambaryan, D P Del'tsova, V A Livshits, E G Ter-Gabrielyan *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2344
68. M V Urushadze, E G Abduganiev, Z E Samoilova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, 176
69. H Böhme, B Hilp *Chem. Ber.*, 1970, **103** 104
70. A J Fatiadi *Synthesis*, 1986, 249
71. A Heesing, W Müllers *Chem. Ber.*, 1980, **113** 24
72. K Nakamura, M Fujii, S Oka, A Ohno *Chem. Lett.*, 1985, 523
73. K Nakamura, M Fujii, A Ohno, S Oka *Tetrahedron Lett.*, 1984, **25** 3983
74. G M Burrett, G G Graboski *Chem. Rev.*, 1986, **86** 751
75. F D Lewis *Acc. Chem. Res.*, 1979, **12** 152
76. F D Lewis, T I Ho, J T Simpson *J. Org. Chem.*, 1981, **46** 1077
77. D Buckley, S Dunstan, H B Henbest *J. Chem. Soc.*, 1957, 4880
78. D Buckley, S Dunstan, H B Henbest *J. Chem. Soc.*, 1957, 4901
79. J Middleton *Kirk-Othmer Encyclopedia of Chemical Technology*, 1980, Vol. 10, p. 882
80. W Steglich, K Burger, M Dürr, E Burgis *Chem. Ber.*, 1974, **107** 1488
81. N P Gambaryan, Doctorate Thesis in Chemical Sciences, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1965
82. A F Janzen, C J Willis *Inorg. Chem.*, 1967, **6** 1900

83. V D Sviridov, N D Chkanikov, A F Kolomiets, A V Fokin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1915
84. A E Zelenin, N D Chkanikov, A M Umnov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2074
85. V D Sviridov, N D Chkanikov, M V Galakhov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 1652
86. A E Zelenin, N D Chkanikov, A F Kolomiets, A V Fokin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 121
87. H Imai, T Nishiguchi, K Fukuzumi *J. Org. Chem.*, 1977, **42** 431
88. E N Izakovich, M L Khidekel *Usp. Khim.*, 1988, **57**(5) 753 [English translation in *Russ. Chem. Rev.*, 1988(5)]
89. I L Knunyants, N P Gambaryan, Tsin-Yun Chen, E M Rokhlin *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1962, 684
90. Y Kamitori, M Hojo, R Masuda, et al. *J. Org. Chem.*, 1988, **53** 129
91. Y Kamitori, M Hojo, R Masuda, et al. *Synthesis*, 1988, **208**
92. F M Laskovics, E M Schulman *Tetrahedron Lett.*, 1977, 759
93. F M Laskovics, E M Schulman *J. Am. Chem. Soc.*, 1977, **99** 6672
94. I Vesely, V Dedek *Collect. Czech. Chem. Commun.*, 1985, **50** 2730
95. Yu Ya Sud'enkov, T P Poltanova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1978, 477
96. R S Ward *The Chemistry of Ketenes, Allenes and Related Compounds* (Edited by S Patai), Wiley, Chichester, 1980, Part 1, p. 223
97. H Babad, A G Leiber *Chem. Rev.*, 1973, **73** 75
98. P Leduc, P Chabrier *Bull. Soc. Chim. Fr.*, 1963, 2271
99. V A Vasnev, Doctorate Thesis in Chemical Sciences, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1975
100. D P N Satchel, P S Satchel *The Chemistry of Acyl Halides* (Edited by S Patai), Interscience, London, 1972, p. 103
101. A M Krzhizhevskii, N S Mirzabekyants, Yu A Cheburkov, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 2513
102. S L Schreiber *Tetrahedron Lett.*, 1980, **21** 1027
103. US P. 4 322 537; *Chem. Abst.*, 1982, **97** 55296
104. A M Platoshkin, Doctorate Thesis in Chemical Sciences, Institute of Organoelemental Compounds, USSR Academy of Sciences, 1970
105. A M Platoshkin, Yu A Cheburkov, I L Knunyants *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, 112
106. S T Kocharyan, E M Rokhlin, I L Kunyants *Zh. Khim. Obshch. im. D I Mendeleeva*, 1966, **11** 709
107. H Millauer, W Schwertfeger, G Siegemund *Angew. Chem.*, 1985, **97** 164
108. M R C Gerstenberger, A Haas *J. Fluorine Chem.*, 1983, **22** 81
109. Q-L Zhou, Y-Z Huang *J. Fluorine Chem.*, 1988, **39** 323
110. Y Z Huang, Q Zhou *Tetrahedron Lett.*, 1986, **27** 2397
111. S A Markarian, H Fischer *J. Chem. Soc., Chem. Commun.*, 1979, 1055
112. Sh A Markaryan *Zh. Org. Khim.*, 1983, **19** 1553
113. Sh A Markaryan, N M Beilaryan *Arm. Khim. Zh.*, 1984, **37** 51
114. K Tanaka, S Maeno, K Mitsuhashi *Bull. Chem. Soc. Jpn.*, 1985, **58** 1841
115. P Caramella, A Corsaro, Compagnini, F M Albini *Tetrahedron Lett.*, 1983, **24** 4377
116. A V Fokin, A F Kolomiets, N V Vasil'ev *Usp. Khim.*, 1984, **53**(3) 398 [English translation in *Russ. Chem. Rev.*, 1984(3)]
117. Z V Safronova, L A Simonyan, N P Gambaryan *Arm. Khim. Zh.*, 1979, **32** 315
118. N P Gambaryan, G S Kaitmazova, E M Kagramanova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 1102
119. H Böhme, P Sutoyo *Tetrahedron Lett.*, 1981, **22** 1671
120. H Gross, J Gloede, D Kunath *Tetrahedron Lett.*, 1967, **8** 4089
121. F Knoll, U Krumm *Chem. Ber.*, 1971, **104** 31
122. N P Gambaryan, D P Deltsova, Z V Safranova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1814
123. N P Gambaryan, D P Del'tsova, Z V Safronova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 2022
124. M Colonna, L Marchetti *Gazz. Chim. Ital.*, 1969, **99** 14
125. P W Hickmott *Tetrahedron*, 1982, **38** 1975
126. R Huisgen, F Jacob *Liebigs Ann. Chem.*, 1954, **590** 37
127. M S Raasch *J. Org. Chem.*, 1972, **37** 1347

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Binuclear molybdenum(III) complexes

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ABSTRACT. The methods of synthesis, properties, structure, and electronic structure of binuclear molybdenum(III) complexes are reviewed. Dimers without monatomic bridges and dimers with oxygen, sulphur, and halogen bridging atoms are described. The effect of the bridging ligands on the nature of the M–M bond and the dependence of the distance between the metal atoms in dimeric halomolybdates(III) on the nature of the internal and external coordination spheres are discussed.

The bibliography includes 132 references.

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I. Introduction

Molybdenum has gained a firm reputation as the element which holds the record for the range of cluster systems and compounds with an M–M (metal–metal) bond, including a quadruple bond,[1] formed by it.

A large number of polynuclear complexes in which the M–M bonds differ markedly in length and energy are known for trivalent molybdenum. The diversity of the chemistry of molybdenum(III) clusters is an indication that even for a single electronic configuration, the degree of interaction between metal atoms can vary over wide limits as a function of the ligand environment. In the present review we shall examine binuclear molybdenum(III) complexes, which are the simplest systems in which the Mo–Mo bond can occur.

Dimeric molybdenum(III) complexes can be divided into two groups: 1) complexes whose stability is mainly determined by the Mo–Mo interaction; 2) compounds in which both the Mo–Mo interaction and the ligand bridges make a specific contribution to their stabilisation. To the first group belong dimers without bridging ligands and also complexes which in addition to a strong Mo–Mo bond have bidentate ligands that form polyatomic bridges. The presence of such ligands does not cause any significant change in the structure of the complexes compared to bridgeless dimers. To the second group belong complexes in which the metal atoms are connected by monatomic bridges. The properties and structure of such compounds depend to a considerable extent on the nature of the bridging ligand.

II. Binuclear complexes without monatomic bridges

Molybdenum(III) is capable of forming strong M≡M triple bonds. Such bonds occur in dimers of the type Mo_2L_6 (L = OR^-, R^-, NR_2^-) and their derivatives. A feature of these compounds is the presence of bulky terminal ligands which contain, as a rule, atoms with strong donor properties.[2–7]

Amide, trimethylsilylmethyl, and thiophenol derivatives of the type Mo_2L_6 are obtained by reaction of molybdenum chlorides with LiL. The remaining complexes are synthesised by exchange or addition of ligands or by the insertion of unsaturated molecules into the Mo–L bond in initial Mo_2L_6 dimers in hydrocarbon solvents.[1,5,8–28]

The most commonly occurring structures of the dimers are shown in Fig. 1. Information about the synthesis of the complexes and data on the Mo–Mo interatomic distances are given in Table 1.

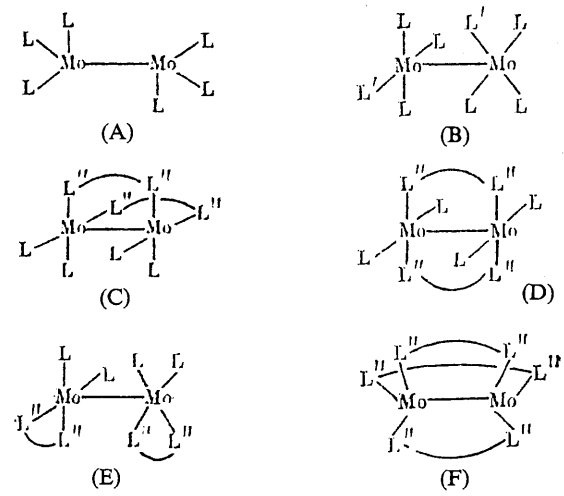


Figure 1. Structures of dimers without monatomic bridges.

Mo_2L_6 molecules have an ethane-like conformation (A). When two ligands are replaced, 1,2-isomers having an *anti* or *gauche* conformation are usually obtained, although 1,1-isomers have also been detected using NMR.[25] For products obtained from the addition of Lewis bases (L′) to Mo_2L_6, a "staggered" configuration of the ligands with an almost planar MoL_3L' square is typical (B). Chelating ligands (L″) can be coordinated in bidentate manner

Table 1. Information on the synthesis and structure of dimers without monatomic bridges.

Initial reactants*	Products*	R_{M-M}, Å	Structural type (Fig.1)	Refs.
$MoCl_5 + LiCH_2SiMe_3$	$Mo_2(CH_2SiMe_3)_6$	2.167	(A)	[1, p.237]
$Mo_2(iso\text{-}OPr)_6 + Mg(CH_2Ph)_2$	$Mo_2(CH_2Ph)_6$	2.175	(A)	[8]
$MoCl_3 + LiNMe_2$	$Mo_2(NMe_2)_6$	2.214	(A)	[1, p.238]
$Mo_2(NMe_2)_6 + HOCH_2Bu\text{-}t$	$Mo_2(OCH_2Bu\text{-}t)$	2.222	(A)	[5]
$Mo_2(t\text{-}BuS)_2(NMe_2)_4 + HSC_6H_2Me_3$**	$Mo_2(SC_6H_2Me_3)_6$	2.239	(A)	[9]
$MoCl_4 + Na + HSC_6H_2(iso\text{-}Pr)_3$	$Mo_2(SC_6H_2(iso\text{-}Pr)_3)_6$	2.228	(A)	[10]
$Mo_2(NMe_2)_6 + Me_3SiCl$	$Mo_2Cl_3(NMe_2)_4$	2.201	(A)	[11]
$Mo_2Cl_3(NMe_2)_4 + LiMe$	$Mo_2Me_3(NMe_2)_4$	2.201	(A)	[12]
$Mo_2Cl_2(NMe_2)_4 + LiP(t\text{-}Bu)_2$	$Mo_2(P(t\text{-}Bu)_2)_2(NMe_2)_4$	2.214	(A)	[13]
$Mo_2Br_3(CH_2SiMe_3)_4 + LiOC_6H_3Me_2$	$Mo_2(OC_6H_3Me_2)_3(CH_2SiMe_3)_4$	2.218	(A)	[14]
$Mo_2(NMe_2)_6 + HOC_6H_3(t\text{-}Bu)Me$	$Mo_2(OC_6H_3(t\text{-}Bu)Me)_2(NMe_2)_4$	2.220	(A)	[15]
$Mo_2(NMe_2)_6 + HOC_6H_3Me_2$	$Mo_2(OC_6H_3Me_2)_4(NMe_2)_2$	2.227	(A)	[16]
$Mo_2(iso\text{-}OPr)_6 + HSC_6H_2Me_3$	$Mo_2(iso\text{-}OPr)_2(SC_6H_2Me_3)_4$	2.230	(A)	[17]
$Mo_2Cl_2(NMe_2)_4 + LiLut$	$Mo_2(NMe_2)_4(Lut)_2$	2.204	(A)	[18]
$Mo_2(NMe_2)_6 + HOSiMe_3$	$Mo_2(OSiMe_3)_6(NHMe_2)_2$	2.241	(B)	[19]
$Mo_4F_4(t\text{-}OBu)_8 + PMe_3$	$Mo_2F_2(t\text{-}OBu)_4(PMe_3)_2$	2.27	(B)	[20]
$Mo_2(t\text{-}OBu)_6 + CO_2$	$Mo_2(t\text{-}OBu)_4(O_2COBu)_2$	2.241	(C)	[5]
$Mo_2(iso\text{-}OPr)_6 + MhpH$	$Mo_2(iso\text{-}OPr)_4(Mhp)_2$	2.206	(C)	[21]
$Mo_2Me_2(NMe_2)_4 + DttaH$	$Mo_2Me_2(NMe_2)_2(Dtta)_2$	2.174	(D)	[22]
$Mo_2(NMe_2)_6 + DttaH$	$Mo_2(NMe_2)_4(Dtta)_2$	2.212	(E)	[23]
$Mo_2(OCH_2Bu\text{-}t)_6 + AcacH$	$Mo_2(OCH_2Bu\text{-}t)_4(Acac)_2$	2.237	(E)	[24]
$Mo_2Cl_2(NMe_2)_4 + LiMeNC_2H_4NHMe$	$Mo_2(MeNC_2H_4NMe)_3$	2.214	(F)	[1, p.251]

*Abbreviations adopted: LutH = 2,6-lutidine; DttaH = ditolyltriazine; MhpH = 2-hydroxy-6-methylpyridine; AcacH = acetylacetone.
**Disubstituted phenols and thiophenols contain substituents at the 2- and 6-positions; trisubstituted products have substituents at the 2-, 4-, and 6-positions.

either with a single molybdenum atom [structure (E)] or they form bridges [structures (C), (D), (F)]. The conformation of complexes with bridging ligands is close to eclipsed.

The compounds listed in Table 1 are solid, diamagnetic products which are fairly volatile under vacuum; they have colours ranging from yellow to red and are very sensitive to the effect of atmospheric oxygen and moisture.

The lengths of the Mo−Mo bonds in the dimers are about 2.2 Å, which corresponds to the length of an Mo≡Mo triple bond. From a qualitative examination of the orbitals of the metal ions it must be assumed that there is overlap of the d_{z^2} orbitals of the molybdenum atoms to form a σ-bond and overlap of the d_{xz} and d_{yz} orbitals to form two π-bonds. This assumption is confirmed by calculations using the self-consistent field of X_α-scattered waves (SCF-X_α-SW) method (see Ref. 1, p. 443).

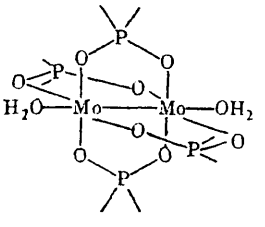


Figure 2. Structure of the $[Mo_2(HPO_4)_4(H_2O)_2]^{2-}$ ion.

The following chemical reactions are typical for complexes of the type Mo_2L_6: a) partial or complete replacement of ligands ($Mo_2L_6^1 \rightarrow Mo_2L_6^2$); b) addition of Lewis bases [$Mo_2(OR)_6 \rightarrow Mo_2(OR)_6L_2'$]; c) insertion of unsaturated molecules into Mo−L bonds; d) reductive elimination [$Mo_2R_2(NMe)_4 + CO_2 \rightarrow CO_2 \rightarrow Mo_2^{4+}$ + alkene + alkane]; e) oxidative addition [$Mo_2(OR)_6$ + ROOR → $Mo_2.(OR)_8$]; f) reactions with NO and CO, accompanied by reduction in the bond order of Mo−Mo; g) formation of polynuclear complexes, oligomerisation of $Mo_2(OR)_6$, and replacement of OR^- groups in $Mo_2(OR)_6$ by halide ions to form tetranuclear products.[2,4,6]

Apart from the compounds considered above, a molybdenum(III) phosphate complex—$[Mo_2(HPO_4)_4]^{2-}$—is also known; it was obtained by dissolving $K_4Mo_2Cl_8.2H_2O$ in 2 M H_3PO_4 in air.[29,30] The salts $(PyH)_3[Mo_2(HPO_4)_4Cl]$ and $Cs_2[Mo_2(HPO_4)_4(H_2O)_2]$, which are stable to air, have been synthesised (Fig. 2).[29,30]

III. Binuclear complexes with bridging oxygen atoms

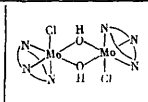
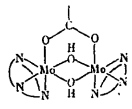
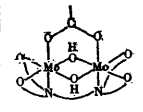
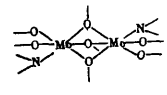
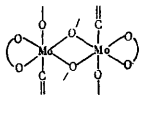
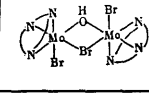
Molybdenum atoms in dimers can be connected by bridging oxygen atoms forming part of hydroxo, alkoxo, or phenoxo groups.

The green ion $[(H_2O)_4Mo(\mu\text{-}OH)_2Mo(H_2O)_4]^{4+}$ occurs in aqueous solutions of Mo(III) in the presence of noncomplexing acids.[31] Reduction of a hydrochloric acid solution of MoO_3 with zinc followed by addition of bis(diphenylphosphino)ethane (DPPE) in 8 M HCl results in the formation of the sky-blue complex $[DPPEH_2]_2[Mo_2(OH)_2Cl_8]$.[32] On hydrolysis of $MoCl_3(C_6H_{15}N_3)$ ($C_6H_{15}N_3$ = triazacyclononane) in the presence of $MeCOO^-$ or HCO_3^-, the green dimers $[Mo_2(OH)_2(MeCOO)(C_6H_{15}N_3)_2]I_3.H_2O$ and $[Mo_2(OH)_2(CO_3)(C_6H_{15}N_3)_2]I_2.H_2O$ are isolated. When the latter is reacted with $MeSO_3H$, HCOOH, and HCl in aqueous solution, $[Mo_2(OH)_2(C_6H_{15}N_3)_2(H_2O)_2]I_4$, $[Mo_2(OH)_2(HCOO)(C_6H_{15}N_3)_2].I_3.2H_2O$, and $[Mo_2(OH)_2(C_6H_{15}N_3)_2Cl_2]I_2$ are synthesised.[33] On reduction of the dimeric molybdenum(V) oxo-complex, $[Mo_2O_4.(C_9H_{21}N_3)_2].[ClO_4]_2.2H_2O$ ($C_9H_{21}N_3$ = 1,5,9-triazacyclododecane), with zinc amalgam in aqueous solutions of HBF_4, RCOOH, HCl followed by the introduction of I^- or ClO_4^-, the complexes [Mo_2.

$.(OH)_2(C_9H_{21}N_3)_2(H_2O)_2]I_4.2H_2O$, $[Mo_2(OH)_2(RCOO)(C_9H_{21}N_3)_2]I_3$, and $[Mo_2(OH)_2(C_9H_{21}N_3)_2Cl_2][ClO_4]_2$ are obtained respectively.[34] Reduction of the ethylenediaminetetraacetate complex $[Mo_2(V).O_4(EDTA)]^{2-}$ in an acetic acid solution gives the di-μ-hydroxo dimers $[Mo_2(OH)_2(Me_3COO)(EDTA)]^-$, $[Mo_2(OH)_2(EDTA)(H_2O)_2]$, and $[Mo_2(OH)_2(EDTA)(SCN)_2]^{2-}$.[35,36] When an aqueous solution of $KMoOCl_2$ and $(NH_4)_2C_2O_4$ is evaporated, $[Mo_2(OH)_2(C_2O_4)_2].6H_2O$ is obtained.[37]

Structural studies of dimers that contain 1,4,7-triazacyclononane or EDTA have shown that geometrically the complexes are distorted octahedra formed by ligand atoms with a common edge of $(\mu\text{-}OH)_2$ (Table 2).[33,35,38] The M—M distances in them are 0.2—0.3 Å longer than in dimers without bridging atoms. A bridging carboxylate ion to all appearances has little effect on the length of the Mo—Mo bond and the weakening of this bond is most probably due to the presence of bridging hydroxo groups.

Table 2. Structure of dimers containing bridging oxygen atoms.

Compound	R_{M-M}, Å	Structure	Refs.
$[Mo_2(OH)_2(C_6H_{15}N_3)_2Cl_2]I_2$	2.501		[33]
$[Mo_2(OH)_2(CH_3COO)(C_6H_{15}N_3)_2]I_3\cdot H_2O$	2.471		[33]
$K[Mo_2(OH)_2(EDTA)(CH_3COO)]$	2.430		[35.38]
$(Me_2NH_2)[Mo_2(OC_6H_4Me)_7(HNMe_2)_2]\cdot C_6H_{14}$	2.601		[39]
$Mo_2(OCH_2Bu\text{-}t)_4(CNBu\text{-}t)_2(Me_2C_3HO_2)_2$	2.508		[40]
$[Mo_2(OH)Br(C_6H_{15}N_3)Br_2]$	2 558		[40]

The formal bond order in di-μ-hydroxo dimers is equal to 3 ($\sigma^2\pi^2\delta^2$).[33] However, the greater M—M distances compared with those in dimers with bridges are due to the lower contribution of a π-interaction.

Dimeric complexes containing EDTA[36] and 1,5,9-triazacyclododecane[34] are diamagnetic. The complex $[Mo_2(OH)_2(C_2O_4)_2].6H_2O$ is characterised by a small paramagnetism, which indicates the weakening of the bond between the metal atoms.[37]

Reaction of $Mo_2(NMe_2)_6$ with 4-methylphenol in hexane gives a dimer with three bridging phenolate ions $(Me_2NH_2)[Mo_2(OC_6H_4Me)_7.(HNMe_2)_2].C_6H_{14}$ (Table 2) in which the overlying paramagnetic states become thermally populated as a result of the increase in the Mo—Mo distance to 2.601 Å.[39]

Dimeric Mo complexes with two alcoxide bridges containing μ-OH and μ-Br ligands are known (Table 2).[40]

The oxychloride $Mo_2O_2Cl_2(H_2O)_6$ has been isolated from a hydrochloric acid solution of molybdenum(III) and acetone;[41–43] its dimeric structure and the oxo bridges present in it have been established hypothetically from an analysis of its magnetic properties and IR spectra. A number of derivatives of this dimer with acetylacetone, carboxylic acids, and *S*-donor ligands (LH) of the type $Mo_2OL_4(H_2O)_x$ and Mo_2OClL_3 have been obtained.[41–44] Reaction of $Mo(OH)_3$ with oxalic acid in an aqueous acetone solution gives $Mo_2O(C_2O_4)_2.6H_2O$.[45] $Mo_2OF_4(H_2O)_6$, which hypothetically contains an Mo—O—Mo fragment, is synthesised by electrolysis of a solution of molybdenum(VI) in 1 M HF.[46]

IV. Binuclear complexes with bridging sulphur atoms

Structural data on dimers containing bridging sulphur atoms are given in Table 3. The Mo—Mo distance in them is even greater than in complexes with bridging oxygen atoms.

Reaction of $(NH_4)_5Mo_2Cl_9.H_2O$ with RSSR in the presence of dithiaoctane (DTO), dithiadecane (DTD), and bis(dimethylphosphino)ethane (DMPE) (LL) results in formation of the dimer $Mo_2(SR)_2Cl_4(LL)_2$.[47] Cotton et al[48] studied the magnetic properties of such dimers and carried out calculations of the electronic structures of hypothetical molecules using the Fenske—Hall and

Table 3. Structure of dimers containing bridging sulphur atoms.

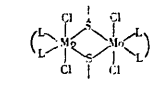
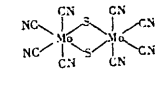
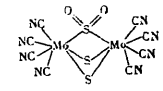
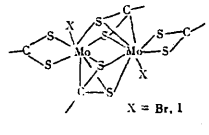
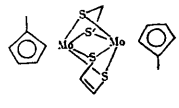
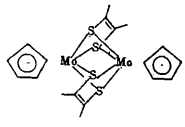
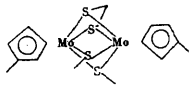
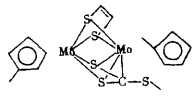
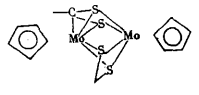
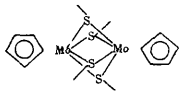
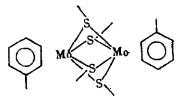
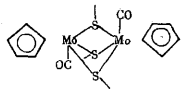
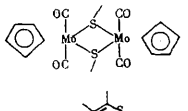
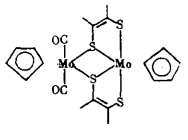
Compound	R_{M-M}, Å	Structure*	Refs.
$Mo_2(SEt)_2Cl_4(DTO)_2$ $Mo_2(SEt)_2Cl_4(DMFE)_2$	2.682 2.712		[47. 48]
$Ba_3[Mo_2S_2(CN)_8]$	2.644		[49—51]
$(Ph_4P)_4[Mo_2S_2(SO_2)(CN)_8]$ $K_4[Mo_2S_2(SO_2)(CN)_8]$	2.730 2.691		[52] [53]
$Mo_2(EtOCS_2)_4Br_2$ $Mo_2(EtOCS_2)_4I_2$	2.723 2.717	 X = Br, I	[54]
$Cp'_2Mo_2(S_2CH_2)(SC_2H_5S)$	2.604		[55]

Table 3 (contd.)

Compound	R_{M-M}, Å	Structure*	Refs.
$Cp_2Mo_2[S_2C_2(CF_3)_2]_2$	2.584		[56]
$Cp'_2Mo_2(S_2CH_2)(SMe)_2$	2.596		[55]
$[Cp'_2Mo_2(SC_2H_2S)(S_2CSMe)]I$	2.623		[57]
$[Cp_2Mo_2(S_2CH_2)(S_2CMe)]Br\cdot{}^1/_2EtOH$	2.635		[58]
$Cp_2Mo_2(SMe)_4$	2.603		[59]
$[(PhMe)_2Mo_2(SMe)_4][BPh_4]_2$	2.614		[60]
$[Cp_2Mo_2(SMe)_2(CO)_2]Br\cdot H_2O$	2.785		[61]
$[Cp_2Mo_2(SBu\text{-}t)_2(CO)_4]\cdot[BF_4]_2$	3.008		[62]
$Cp_2Mo_2[S_2C_2(CF_3)_2]_2(CO)_2$	3.256		[56]

*For the sake of simplicity, hydrocarbon substituents are not shown.

Reaction of $Mo_2(MeCOO)_4$ with $K(EtOCS_2)$ in ethanol followed by oxidation of the product with a free halogen in a dichloroethane solution led to the synthesis of the ethyl xanthate complex $Mo_2(EtOCS_2)_4X_2$ (X = Cl, Br), containing four bridging sulphur atoms from two xanthate ions.[54]

A large number of diamagnetic cyclopentadienyl molybdenum(III) dimers with four bridging sulphur atoms have been reported.[55–60,63–65] On reacting $CpMoH(CO)_3$ or $[CpMo(CO_3)_3]_2$ (Cp = cyclopentadienyl) with thioepoxides in tetrahydrofuran, $Cp_2Mo_2(SC_nH_{2n}S)_2$ complexes, where n = 2 or 3, were isolated, from which Cp_2Mo_2.$(SCHRCHRS)_2$ and $Cp_2Mo_2(SCRCRS)_2$ complexes were obtained by reaction with alkenes and alkynes.[64] As a result of treating $[CpMo(CO)_3]_2$ with dimethyl disulphide, $Cp_2Mo_2(SMe)_4$ was isolated.[59] Reaction of $Cp'_2Mo_2S_2(S_2CR_2)$ (Cp′ = methylcyclopentadienyl) with the same alkenes and alkynes results in the formation of the dithiol and dithiolene derivatives Cp'_2Mo_2.$(S_2CR_2)(SC_2H_4S)$ and $Cp'_2Mo_2(S_2CR_2)(SC_2H_2S)$, while with LiMe the complex $Cp'_2Mo_2(S_2CH_2)(SMe)_2$ is formed.[55] The dimers $Cp'_2Mo_2(SC_2H_2S)(S_2CS)$, $[Cp'_2Mo_2SC_2H_2S)(S_2CSMe)]I$,[57] $[Cp_2Mo_2(S_2CH_2)(S_2CMe)]Br.\frac{1}{2}EtOH$,[58] $Cp_2Mo_2(S_2CNR)_2$, and $[Cp_2Mo_2(S_2CNRR')_2]X_2$ have also been synthesised.[63]

On reacting $[(PhR)MoPy_3][PF_6]$ (R = H, Me) with an excess of an aqueous solution of MeSH and MeOH followed by extraction with HPF_6 in acetone, orange complexes $[(PhR)_2Mo_2(SMe)_4][PF_6]_2$ were isolated; as a result of anion exchange $[(PhMe)_2Mo_2(SMe)_4]$.$[BPh_4]_2$ was obtained.[60] Reduction of these compounds with zinc amalgam in the presence of 1-methylimidazole (MeIM) in acetonitrile, oxidation with oxygen, and extraction with HPF_6 in acetone gives the green paramagnetic (μ_{eff} = 1.45 B.M.) complex $[Mo_2(SMe)_3(MeIm)_6][PF_6]_3$ in which there are hypothetically three bridging thiolate ligands.

In dimers with four bridging sulphur atoms the Mo–Mo distance varies from 2.60 to 2.72 Å (Table 3). Calculation using the extended Hückel method (EHM) gives the electronic configuration a_{1g} (σ-Mo–Mo), b_{1u} (δ*-Mo–Mo), b_{2g}(δ-Mo–Mo) or $\sigma^2\delta^{*2}\delta^2$, which virtually corresponds to a single Mo–Mo bond.

Carbonyl-containing molybdenum dimers with μ-*S*-ligands are known: $Cp_2Mo_2[S_2C_2(CF_3)_2]_2(CO)_2$,[56] $[Cp_2Mo_2(SMe)_3(CO)_2]$.$Br.H_2O$,[61] and $[Cp_2Mo_2(SBu\text{-}t)_2(CO)_4][BF_4]_2$.[62] In the first of these the molybdenum atoms are at a distance of 3.256 Å and there is apparently no Mo–Mo bond.

The synthesis of dimeric complexes with N-, O-, and S-containing thiols of the type $Mo_2Cl_6L_m$, m = 2, 3, has been reported.[66] The values of the effective magnetic moments of these complexes is lower than the pure spin values. The existence of sulphide bridges in these complexes has been proposed.

SCF-X_α-SW methods. The effective multiplicity of the Mo–Mo bond proved to be close to 2 ($\sigma^2\pi^2$), while the δ-interaction was very weak. On the assumption that $^1A_{1g}$ ($\sigma^2\pi^2\delta^2$) is the ground state of the dimers, the energies of the thermally populated states $^3B_{1u}$, $^1B_{1u}$, and $^1A^*_{1g}$, corresponding to filling with electrons from the δ^* orbital, were calculated from magnetic data.

The complexes $K_6[Mo_2S_2(CN)_8]$ and $Ba_3[Mo_2S_2(CN)_8]$, each containing two sulphide bridges, have been obtained.[49–51] Oxidation of the complex anion $[Mo_2S_2(CN)_8]^{6-}$ with atmospheric oxygen results in the formation of $[Mo_2S_2(SO_2)(CN)_8]^{4-}$, in which the molybdenum atoms are connected by a disulphide ion and an SO_2 molecule coordinated via its sulphur atom.[52,53]

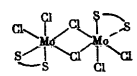
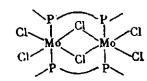
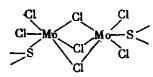
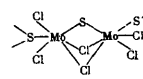
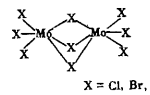
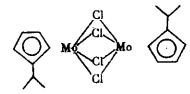
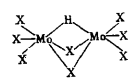
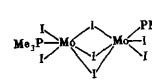
V. Binuclear complexes with halide bridges

In dimeric molybdenum(III) complexes with halide bridges (Cl, Br, I) the Mo–Mo bonds are of approximately the same length as in dimers containing bridging sulphur atoms (Table 4).

When a dichloromethane solution of $Mo_2Cl_4(DTO)_2$ is kept under a layer of hexane, crystals of $Mo_2Cl_6(DTO)_2$ are formed. The $Mo_2Cl_6(DTO)_2$ complex consists of two octahedra connected by a Cl–Cl edge.[67] $Mo_2Cl_6(Ph_2PCH_2PPh_2)_2$, obtained by the reaction of $K_2Mo_2Cl_8$ with $HC(PPh_2)_3$, has a similar structure.

Reduction of $MoCl_4(Me_2S)_2$ using EtSiH in dichloromethane leads to the synthesis of $Mo_2Cl_6(Me_2S)_3$, from which the complex $Ph_4P[Mo_2Cl_7(Me_2S)_2$ is obtained by exchanging an Me_2S group for Cl^-.[68] The NMR data indicate that there is thermal population of the electronic states of the latter complex with spins $S \neq 0$. A similar structure (with three halide bridges) occurs for $Mo_2X_9^{3-}$ ions (X = Cl, Br, I), which will be examined in Section VI.

Table 4. Structure of dimers with halide bridges.

Compound	R_{M-M}, Å	Structure*	Refs.
$Mo_2Cl_6(DTO)_2$	2.735		[67]
$Mo_2Cl_6(Ph_2PCH_2PPh_2)_2$	2.789		[40]
$(Ph_4P)[Mo_2Cl_7(Me_2S)_2]$	2.746		[68]
$Mo_2Cl_6(Me_2S)_3$	2.462		[68]
$Cs_3Mo_2Cl_9$ $Cs_3Mo_2Br_9$ $Cs_3Mo_2I_9$	2.655 2.616 3.07*	 X = Cl, Br, I	[69] [69] [70]
$Mo_2[C_5H_4(iso\text{-}Pr)]_2Cl_4$	2.607		[71]
$Rb_3Mo_2Cl_8H$ $(PyH)_3Mo_2Cl_8H$ $(Me_4N)_3Mo_2Cl_8H$ $(Et_4N)_2(H_3O_2)Mo_2Cl_8H$ $(Et_4N)_3(H_3O_2)[Mo_2Cl_8H][MoOCl_4(H_2O)]$ $(Me_4N)_2(H_7O_3)Mo_2Br_8H$ $(Et_4N)_2(H_7O_3)Mo_2I_8H$	2.38 2.371 2.374 2.384 2.375 2.384 2.408		[72] [73] [74] [75] [76] [77] [77]
$[PHMe_3][Mo_2I_7(PMe_3)_2]$ $[AsPh_4][Mo_2I_7(PMe_3)_2]$	3.021 3.022		[78] [78]

*According to X-ray powder diffraction analysis.

Molybdenum(III) complexes of the type $Mo_2(C_5H_4-R)_2Cl_4$ (R = iso-Pr), which contain four bridging chlorine atoms, have been obtained by treatment of $Mo(C_6H_6)(C_5H_4-R)$ with hydrogen chloride in toluene.[71]

The complexes $[PHMe_3][Mo_2I_7(PMe_3)_2]$ and $[AsPh_4][Mo_2I_7.(PMe_3)_2]$, each containing three iodide bridges, have been synthesised by reaction of $MoI_3(THF)_3$ with PMe_3, NMe_4I and $AsPh_4I$.[78]

Association of $MoCl_3(THF)_3$ in CH_2Cl_2 solution results in the formation of the dimeric $Mo_2Cl_6(THF)_3$, and reaction of $MoCl_5$ with MeCN gives $Mo_2Cl_6(MeCN)_3$.[79] By replacing the organic ligands in such complexes with tertiary phosphines, pyridine, and nitriles, products of the type $Mo_2Cl_6L_3$ can be obtained.[79,80] Thermolysis of monomeric halomolybdates(III) results in the formation of compounds that contain $Mo_2Cl_{10}^{4-}$ ions.[81] Thermal decomposition of $(oxineH_2)_3Mo_2Cl_9.3H_2O$ gives $Mo_2Cl_6(oxineH)_3$ (oxineH = 8-hydroxyquinoline).[82] Similar tri-μ-chloride complexes with thiourea[83] and bis(diphenylphosphino)ethane[84] derivatives are known.

Diamagnetic halogen-hydrido bridge complexes of the type $A_3Mo_2X_8H$ (X = Cl, Br, I; A is a single-charged cation) have been studied in detail (Table 4). They were synthesised by dissolving $Mo_2(MeCOO)_4$ in a concentrated acid HX at 60 °C and precipitating out the resulting $Mo_2X_8H^{3-}$ with a suitable cation.[72–77,85] Complexes of this type are readily converted to Mo(III) ($Mo_2X_9^{3-}$, MoX_3Py_3) or Mo(II) ($Mo_2Cl_4Py_4$) compounds.[86] Introduction of the hydride bridge reduces the Mo–Mo distance by ~0.4 Å compared to that in purely chloride-bridged dimers. This is due to the small size of the hydride ion compared to halide ions, which prevent the molybdenum atoms converging.[85] As can be seen from Table 4, the ligand environment has little effect on the length of the Mo–Mo bond in the $Mo_2X_8H^{3-}$ ion, which is an indication of the high rigidity of the Mo(μ-H)(μ-X_2)Mo group, the geometry of which is determined to a large extent by the presence of the hydride ion.

VI. Nonahalodimolybdates(III)

$Mo_2X_9^{3-}$ anions (X = Cl, Br) are of considerable interest as interaction between the *d* electrons of the two molybdenum atoms results in the formation of a relatively weak Mo–Mo, with the result that the ligand environment and even the outer coordination sphere of the complex appreciably affect the bonding of the molybdenum atoms.

A single iodide complex $Cs_3Mo_2I_9$ is known. Its IR spectra have been studied,[87] and the Mo–Mo distance in the dimer has been determined by X-ray powder photography.[70] Information is also available on the synthesis of $K_3Mo_2F_9.2H_2O$ (see Ref. 88, p. 111).

Nonachloro- and nonabromo-dimolybdates(III) can be obtained by the following methods: a) disproportionation of MoX_6^{2-} in liquid ammonia;[89] b) oxidation of Mo(II) and Mo(II, III)[90–92] dimers or electrolytic oxidation of the $Mo_2X_8H^{3-}$ ion in concentrated HX;[72] c) fusing metal halides ($2MoX_3 + 3CsX$) are 800 °C;[93] d) coproportionating Mo(0) and Mo(II) carbonyl complexes with Mo(IV) and Mo(V) halides;[94–96] e) precipitation of Mo(III) with a suitable cation in hydrochloric acid;[97] f) replacement of ligands in Mo(III) dimers by halide ions;[90,98] g) electrolytic reduction of MoO_3 in concentrated hydrochloric acid, evaporation of an Mo(III) solution in concentrated hydrochloric or hydrobromic acid and precipitation of nonahalomolybdate(III) with a suitable cation.[82,99–105]

The latter synthetic method is the most convenient. It is based on the reaction between MoX_6^{3-} and $[MoX_5(H_2O)]^{2-}$ ions that occurs when the concentration of molybdenum(III) in hydrohalic acid is increased, leading to the formation of the $Mo_2X_9^{3-}$ ion.[99,104] If the Mo(III) solution is evaporated in a mixture of HCl and HBr, the mixed-ligand anions $Mo_2Cl_3Br_6^{3-}$ and $Mo_2Cl_6Br_3^{3-}$ can be obtained.[102]

The dimerisation of halomolybdate(III) ions takes place according to the following scheme:

$$2\,MoX_6^{3-} + 3\,H_3O^+ \rightarrow Mo_2X_9^{3-} + 3H_2O\uparrow + 3HX\uparrow.$$

A similar reaction takes place on thermolysis of the "acid" halomolybdates(III) $(PimH_2)(H_5O_2)MoX_6$ (Pim = 2-amino-4,6-dihydroxypyrimidine) and $(oxineH_2)_2H[MoBr_6].3H_2O$, from which $(PimH)_3Mo_2X_9$ and $(oxineH_2)_3Mo_2Br_9$ are obtained by isothermal decomposition.[82,105]

The monoethanolammonium (MeaH) salts $(MeaH)_3Mo_2X_9$, which are readily soluble in HX, have proved to be convenient reagents for the synthesis of nonachloro- and nonabromo-dimolybdates(III) with organic cations. A number of compounds, including both cation and anion mixed salts, have been synthesised from these reagents by cation exchange.[106–108]

The chloro- and bromo-complexes are solid compounds, red and brown in colour. They are more or less stable towards atmospheric oxygen and moisture; in solution they are slowly oxidised by air. In hydrohalic acid solutions a slow decomposition of the $Mo_2X_9^{3-}$ dimer occurs, giving MoX_6^{3-} and $[MoX_5(H_2O)]^{2-}$ ions (at room temperature over a period of several hours).[102,109] However, in the presence of 4,4′-dipyridyl in a mixture of concentrated HCl and ethanol, $Mo_2Cl_9^{3-}$ very rapidly decomposes to monomeric complexes.[108] Reaction of $Cs_3Mo_2X_9$ with pyridine at 200 °C results in the formation of *trans*-MoX_3Py_3.[86] In contrast to monomeric halomolybdates(III), the $Mo_2Cl_9^{3-}$ ion is readily reduced by zinc amalgam to Mo(II) dimers.[110]

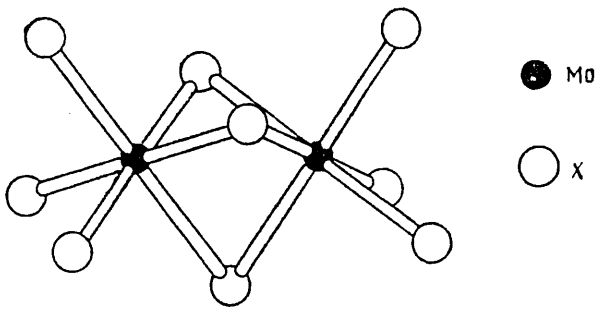


Figure 3. Structure of the $Mo_2X_9^{3-}$ ion (X = Cl, Br).[69]

The complete X-ray diffraction analysis of $Cs_3Mo_2Cl_9$ and $Cs_3Mo_2Br_9$ which was carried out for the first time by Saillant et al[69] made it possible to establish the structure of the anion, which is shown in Fig. 3. By comparing the geometric characteristics of $M_2X_9^{3-}$ ions, where M = Cr, Mo, W; X = Cl, Br (Table 5) it was possible to identify interesting structural features of molybdenum dimers. In $Cr_2X_9^{3-}$ ions the Cr atoms are displaced from the octahedral centres towards the outer halogen atoms and there is no Cr–Cr bond. This is confirmed by the presence of three unpaired electrons in each Cr^{3+} ion according to the results of magnetic measurements.[111] In the $W_2Cl_9^{3-}$ ion the W–W distance is ~0.7 Å shorter than the Cr–Cr distance in $Cr_2Cl_9^{3-}$. The tungsten atoms are very considerably displaced from the octahedral centres towards each other, forming a W–W bond. As a result of this, $K_3W_2Cl_9$ has only a temperature-independent paramagnetism. In $Mo_2X_9^{3-}$ the Mo atoms are displaced from the octahedral centres towards each other to a lesser degree than in $W_2Cl_9^{3-}$. The Mo–Mo bond is weaker than the W–W bond, so compounds $A_3Mo_2X_9$ display a weak paramagnetism, the temperature dependence of which indicates that there is a considerable antiferromagnetic coupling between the molybdenum atoms in such dimers. In systems where direct exchange takes place between the molybdenum atoms, the antiferromagnetic interaction energy can characterise the strength of the Mo–Mo bond (see Ref. 113, p. 125).

Table 5. Structural characteristics of $M_2X_9^{3-}$ ions (M = Cr, Mo, W).[69]

Compound	R_{M-M}, Å	Angle of X_B-M-X_B, deg.*
$Cs_3Cr_2Cl_9$	3.12	85.8
$Cs_3Cr_2Br_9$	3.31	83.0
$Cs_3Mo_2Cl_9$	2.66	94.2
$Cs_3Mo_2Br_9$	2.82	93.9
$K_3W_2Cl_9$	2.41	98.4

*X_B is bridging halogen atom.

As long ago as the late 1960's it was found that the magnitude of the antiferromagnetic exchange coupling in the nonahalodimolybdate(III) ion depended to a considerable extent on the nature of the cation, and at the time attempts were made to relate this phenomenon to the change in Mo–Mo distance in the dimer.[103,104,114]

Grey and Smith[114] studied the dependence of the exchange integral on the Mo–Mo distance in a number of nonachlorodimolybdates with different cations. However, these distances were known only for the compounds $K_3Mo_2Cl_9$ and $Cs_3Mo_2Cl_9$, and as it subsequently transpired, the correlation found proved to be incorrect. A relationship between the stretching vibrational frequencies of the bridging chloride atoms and the size of the cation was established by Grey and Smith.[103] By making a combined analysis of the IR spectra and structural characteristics of $Cs_3Cr_2Cl_9$ and $Cs_3Mo_2Cl_9$ it could be assumed that on increasing the $Cl_B-Mo-Cl_B$ angle (Cl_B is bridging chlorine atom), namely, by axial compression of the dimer, the difference between the vibrational frequencies of a_2'' and e' of the $Mo-Cl_B$ bond will also increase. The $Cl_B-Mo-Cl_B$ angle increases on going from $K_3Mo_2Cl_9$ to $Cs_3Mo_2Cl_9$, but the $Cl_T-Mo-Cl_T$ angle (Cl_T is terminal chlorine atom) changes only slightly.[69,103] Consequently, the difference between the vibrational frequencies of a_2'' and e' of the $Mo-Cl_T$ bond will be small, but it will be considerable for the $Mo-Cl_B$ bond. This assumption is also confirmed by IR spectroscopic analysis.[103] What is more, as the size of the cation increases the difference between the frequencies of a_2'' and e' of the $Mo-Cl_B$ bond decreases, in other words, the $Cl_B-Mo-Cl_B$ angle decreases, hence (if the change in distance of $Mo-Cl_B$ is ignored) in the cation series K^+, NH_4^+, Cs^+, Me_4N^+, Et_4N^+ the dimer becomes more and more "extended" axially.[103]

The dependence of the chemical shift (ΔE) of the L_{α_1,α_2} line in the X-ray emission spectra of $K_3Mo_2Cl_9$, $Cs_3Mo_2Cl_9$, $MoCl_3$, K_3MoCl_6 on the Mo—Mo distance has been studied.[115] As the Mo—Mo distance decreases ΔE increases, which corresponds to an increase in the degree of bonding between the *d* electrons of the molybdenum atoms.

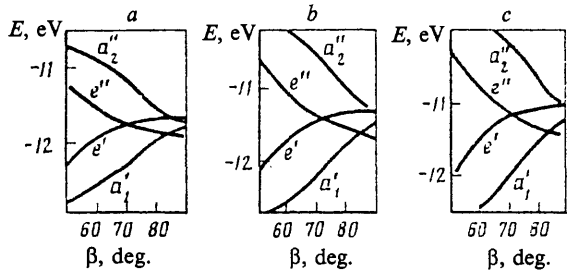


Figure 4. Dependence of the energy of the electron levels in the $M_2Cl_9^{3-}$ ion on the magnitude of the M—Cl_B—M angle, where M = Cr (*a*), Mo (*b*), W (*c*).[118]

The first calculations of the electronic structure of the $Mo_2Cl_9^{3-}$ ion were carried out using the RMK[116] and Fenske—Hall methods. An examination was subsequently made of the dependence of the energies of the orbitals responsible for the M—M bonding on the degree of axial distortion of the dimeric $M_2Cl_9^{3-}$ anion (M = Cr, Mo, W) (Fig. 4).[118] The M—Cl_B—M angle was taken as a parameter for the magnitude of distortion, in accordance with the method suggested by Cotton and Ucko[119] for studying such dimers. As can be seen from Fig. 4, on reducing the M—Cl_B—M angle (this corresponds to a convergence of the metal atoms for a fixed length of the M—Cl_B bond), there is a reduction in energy of the $a_1'(\sigma)$ and $e'(\pi)$ bonding orbitals of M—M and an increase in energy of the $a_2''(\sigma^*)$ and $e''(\pi^*)$ antibonding orbitals. In the series M = Cr, Mo, W, the gap between the bonding and antibonding orbitals in the dimer increases, with the strengthening of the bond between the metal atoms assisting the compression of the dioctahedron despite the repulsion between the terminal and bridging chlorine atoms and the rigidity of the M—Cl_B—M angle.[118]

More rigorous calculations of the electronic structure of the $Mo_2Cl_9^{3-}$ ion in the salts $Cs_3Mo_2Cl_9$ and $K_3Mo_2Cl_9$ were carried out by Ginsberg[120] using the SCF-X_α-SW method. The energies of the antiferromagnetic exchange coupling were determined theoretically and correlated with the experimental data. The data on the structure of the upper molecular orbitals of $Cs_2Mo_2Cl_9$ salt are given in Table 6. The successively grouped $21a_1'$, $22e'$, $17e''$, and $18a_2''$ orbitals retain the nature of 4*d* orbitals of Mo to the extent of 64—81% and constitute respectively the following orbitals of the Mo—Mo bond: σ, $2(1/3\pi + 2/3\delta)$, $2(1/3\pi^* + 2/3\delta^*)$, and σ^*. The electronic configuration of the ground state $\sigma^2(1/3\pi + 2/3\delta)^4$ formally corresponds to the formation of an Mo≡Mo triple bond. However, whereas the $\sigma-\sigma^*$ separation is quite large (~2 eV), the difference between the energy of the $22e'$ and $17e''$ orbitals is ten times less, in other words, the bond between the molybdenum atoms is essentially a single bond.

In order to determine the contribution of superexchange interactions through the bridging chlorine atoms to the total exchange coupling, the electronic structure of the dimeric anion in $K_3Mo_2Cl_9$ was calculated when the Mo—Cl_B distance was reduced by 0.06 Å.[120] The change in the magnitude of exchange integral in this case was less than 1%. Such a result was to be expected since the Mo—Mo bonding orbitals, although overlapping with the orbitals of the bridging chlorine atoms, are nonbonding in relation to them and hence they do not make a substantial contribution to the Mo—Mo coupling.[120]

In the electronic spectra of $Mo_2X_9^{3-}$ ions there are usually four absorption bands.[91,93–95,99–101,121] The appearance of bands at ~13000 and ~15000 cm^{-1} is due to the formation of the Mo—Mo bond.[91] By studying the absorption spectra, circular dichroism, and

Table 6. Energy levels of the $Mo_2Cl_9^{3-}$ ion in $Cs_3Mo_2Cl_9$. (Calculation using the SCF—X_α—SW method[120]).

Energy level	Energy, a.u.	Charge distribution, %					Spherical harmonics	Description
		2Mo	$6Cl_T$	$3Cl_B$	int	out		
$22a_1'$	—0.124	1	3	3	59	35	—	—
$23e'$	—0.180	54	8	16	17	5	d_{xz}, d_{yz}	Mo—Cl antibonding
$18e''$	—0.209	68	12	8	10	2	$d_{x^2-y^2}$, d_{xy}	Mo—Cl antibonding
$18a_2''$	—0.278	78	2	10	10	0	d_{z^2}	σ^*-Mo-Mo; Mo, Cl nonbonding
$17e''$	—0.384	81	2	7	10	0	d_{xz}, d_{yz}	$(\pi+\delta)^*$-Mo-Mo; Mo, Cl nonbonding
$22e'$	—0.403	64	0	21	14	0	$d_{x^2-y^2}$, d_{xy}	$(\pi+\delta)$-Mo—Mo; Mo, Cl nonbonding
$21a_1'$	—0.485	69	7	13	11	0	d_{z^2}	σ-Mo—Mo; Mo, Cl nonbonding

Table 7. Average geometric parameters of $Mo_2Cl_9^{3-}$ ions.[123]

Compound	Chemical formula	Geometric parameters					
		Mo—Mo, Å	Mo—Cl_B, Å	Mo—Cl_T, Å	Mo—Cl_B—Mo, deg.	Cl_B—Mo—Cl_B, deg.	Cl_T—Mo—Cl_T, deg.
(I)	$(Bu_4N)_4[Mo_2^{III}Cl_9][Mo^{V}OCl_4(H_2O)]$	2.815 (3)	2.465 (6)	2.418 (7)	69.7 (2)	90.6 (2)	91.0 (2)
(II)	$(Et_4N)_2(H_7O_3)Mo_2Cl_9$	2.743 (3)	2.459 (6)	2.415 (6)	67.8 (1)	91.9 (2)	90.2 (2)
(III)	$(PipeH)_3Mo_2Cl_9$	2.734 (1)	2.447 (2)	2.409 (2)	67.9 (1)	91.8 (1)	89.3 (1)
(IV)	β-$(4\text{-MePyH})_3Mo_2Cl_9$	2.719 (5)	2.45 (1)	2.41 (1)	67.3 (3)	92.2 (4)	90.0 (4)
(V)	$(PyH)_3Mo_2Cl_9$	2.685 (1)	2.460 (1)	2.409 (1)	66.15 (5)	93.0 (1)	90.1 (1)
(VI)	$Cs_3Mo_2Cl_9$	2.655 (11)	2.487 (12)	2.384 (6)	64.5 (1)	94.2 (1)	91.0 (3)
(VII)	α-$(4\text{-MePyH})_3Mo_2Cl_9$	2.634 (2)	2.465 (3)	2.411 (4)	64.6 (1)	94.1 (1)	91.6 (1)
(VIII)	$(4,4'\text{-DipyH}_2)(MeaH)Mo_2Cl_9$	2.619 (1)	2.470 (2)	2.417 (2)	64.03 (5)	94.5 (1)	91.5 (1)
(IX)	$(4\text{-}NH_3PyH)(MeaH)Mo_2Cl_9$	2.610 (2)	2.465 (5)	2.410 (5)	63.9 (1)	94.6 (2)	91.0 (2)
(X)	$(EnH_2)_2[Mo_2Cl_9]Cl$	2.585 (3)	2.460 (7)	2.404 (8)	63.4 (2)	94.9 (3)	90.7 (3)
(XI)	$(NH_4)_3Mo_2Cl_9$	2.569 (4)	2.462 (6)	2.397 (6)	62.9 (1)	95.3 (2)	90.5 (2)

Zeeman splitting for $Cs_3Mo_2Cl_9$ monocrystals,[122] it was possible to detect and interpret the fine structure of the absorption bands due to the Mo—Mo interaction. The absorption bands were attributed to the following transitions: $^1A_1' \rightarrow {}^3E$ (7800 cm^{-1}), $^1A_1' \rightarrow {}^3A_1''$ (~11600 cm^{-1}), $^1A_1' \rightarrow {}^1A_1'$, $^1A_1''$ (12600 → 14000 cm^{-1}), $^1A_1' \rightarrow {}^1E'$ (~15300 cm^{-1}). On the basis of the theoretical calculations it was concluded that there was a very weak Mo—Mo π-interaction when the strength of the Mo—Mo σ-bond was high.

The geometry and magnetic properties of the $Mo_2Cl_9^{3-}$ ion in relation to the crystal environment were studied in detail and the structures of ten nonachlorodimolybdates(III) with different organic cations and ammonia were determined.[109,123–127] In the crystal lattice of each compound this ion undergoes low-symmetry distortions. The average geometric parameters determined when it was assumed that the dimeric anion has D_{3h} symmetry are given in Table 7.

The $Mo_2Cl_9^{3-}$ anion has the following characteristics. The Mo—Cl_B—Mo angle in all cases is less than 70.5° (for a true dioctahedron) and the molybdenum atoms have converged as a result of Mo—Mo bonding. The dimeric anion is slightly distorted along the Mo—Mo axis from the effect of the crystal environment. The distance between the metal atoms in the dimer varies from 2.815 Å in the tetrabutylammonium salt (I) to 2.569 Å in the simple ammonium salt (XI). As the Mo—Mo distance decreases, the Mo—Cl_B—Mo angle also decreases, but the lengths of the Mo—Cl_B and Mo—Cl_T bonds and the Cl_T—Mo—Cl_T angle show little variation. It follows from this that in essence only the bridging $Mo(Cl_B)_3Mo$ fragment is distorted.

The geometry of the dimeric anion is determined by two forces acting in opposition: 1) the mutual attraction of the molybdenum atoms, leading to compression of the dimer; and 2) the effect of "pushing apart" from the bridging chlorine atoms, which is due to the increase in overlap of atomic orbitals in the system Mo—Cl_B—Mo and at the same time the mutual repulsion of the bridging and terminal chlorine atoms. The balance of forces probably leads to the energy curve near the minimum on the z coordinate (the axis passes along the Mo—Mo bond) having a small bend, and hence even with a significant change in Mo—Mo distance the energy of the $Mo_2Cl_9^{3-}$ ion varies only slightly.

In an $Mo_2Cl_9^{3-}$ ion free from external effects the repulsion between the chlorine atoms assists the extension of the dimer along the Mo—Mo axis. In the crystal lattice the interligand repulsion is weakened by the effect of the positive charges of the cations; this together with the Mo—Mo interaction leads to compression of the $Mo(Cl_B)_3Mo$ fragment and a reduction in Mo—Mo distance.

Cations that form hydrogen bonds have the most marked effect. Thus, in $(Bu_4N)_4[Mo_2(III)Cl_9][Mo(V)OCl_4(H_2O)]$ the positive cation centres are at a considerable distance from the chlorine atoms, the effect of the cations is small, and the Mo—Mo distance is the greatest (see Table 7). In the structure of $(Et_4N)_2(H_7O_3)Mo_2Cl_9$ only one of the cations, namely, the hydrated proton, has any appreciable effect on the geometry of the dimer as a result of the formation of hydrogen bonds; the Mo—Mo distance is 2.743 Å. In the crystal lattices of compounds (III)—(VI) all cations have their positive centres directed towards the chlorine atoms, so N—H...Cl hydrogen bonds are formed and the Mo—Mo distance is reduced. In the structures of nonachlorodimolybdates(III) containing doubly charged cations, a further compression of the bridging group occurs. These structures display a trimeric network of hydrogen bonds joining all cations and anions. The ammonium cation has the maximum effect on the Mo—Mo distance; it is lowest in $(NH_4)_3Mo_2Cl_9$. It is worth noting that in compounds (VII)—(X) (Table 7), which contain organic cations that are much larger than in $Cs_3Mo_2Cl_9$, the length of the Mo—Mo bond is less than in the caesium salt. This demonstrates the strong effect of hydrogen bonding on the geometry of the dimeric group.

It may be assumed that the minimum effect of the cations and correspondingly the maximum Mo—Mo distance in the $Mo_2Cl_9^{3-}$ ion in the crystal lattice will occur when there are bulky low-polarity cations present. If cations, even those of large volume, can form strong hydrogen bonds with the anion, the Mo—Mo distance in nonahalodimolybdates(III) will be relatively short.

The values of the exchange integrals for structurally determined nonachlorodimolybdates(III) have been calculated from magnetic susceptibility data [for compounds (I)—(V) and (VII)—(XI), see the study by Kazin;[109] for $Cs_3Mo_2Cl_9$ and $Cs_3Mo_2Br_9$, see the study by Grey and Smith.[104]]

To all appearances a direct Mo—Mo exchange coupling mainly occurs in $Mo_2Cl_9^{3-}$ ions.[120] The dependence of the exchange integral ($-2J$) on the Mo—Mo distance in a dimer is shown in Fig. 5. As the relative change in parameters is low, this dependence approximates to a linear function.[109] The tendency for the exchange coupling to increase as the Mo—Mo distance decreases is apparent, but deviations from a linear dependence are considerable.

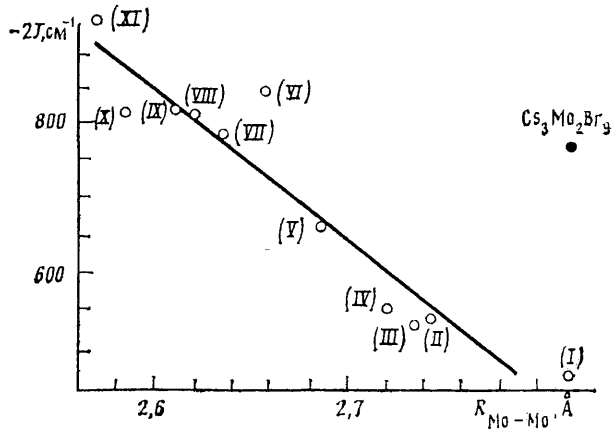


Figure 5. Dependence of the exchange integrals on the Mo—Mo distance in $Mo_2Cl_9^{3-}$ ions.[109] For the numbering of the compounds, see Table 7.

For a more accurate representation of the exchange interaction, the values of the exchange integrals were expressed as a two-parameter function of R and α (the geometry of the bridging fragment $Mo(Cl_B)_3Mo$ in D_{3h} symmetry is determined by these two parameters).[109] The derived dependences of the antiferromagnetic interaction energy on the geometric parameters of the $Mo_2Cl_9^{3-}$ ion can prove useful for predicting the structure of similar dimers from their magnetic properties.

The value of $-2J$ for the structurally determined compound $Cs_3Mo_2Br_9$ is substantially higher than that which should occur if the linear dependence of $-2J$ on R_{Mo-Mo} obtained for $Mo_2Cl_9^{3-}$ ions were applied to it (Fig. 5). The most probable reason for the increase in the exchange coupling is the lesser electronegativity of bromine compared to chlorine. Consequently, the effective positive charge on the molybdenum atoms in the bromide complex is less, giving rise to a greater diffuseness of the $4d$ orbitals of the metal atoms and correspondingly a greater overlap of the orbitals in the direction of the Mo—Mo bond than in the chloride dimer at the same distance between the molybdenum atoms.

For isomorphous nonabromodimolybdates(III) the values of $-2J$ are usually less than their chloride analogues.[104,109] Evidently the decrease in exchange resulting from the increase in Mo—Mo distance in bromo-complexes exceeds the increase caused by the greater diffuseness of the $4d$ orbitals of the molybdenum atoms.

Reaction of $(Bu_4N)_3Mo_2Cl_8H$ with I_2 in dichloroethane solution followed by addition of diethyl ether led to the synthesis of $(Bu_4N)_3$. Mo_2Cl_8I, and $(NH_4)_3Mo_2Cl_8I$ was isolated by exchanging cations in methanol. The dimeric anions contain bridging iodine atoms in addition to chlorine atoms.[128] The values of $-2J$, calculated from the magnetic susceptibility of the ammonium and tetrabutylammonium salts differ substantially. The nature of the cation probably has a similar strong effect on the geometry of the $Mo_2Cl_8I^{3-}$ ion as on the structure of nonachloro- and nonabromodimolybdate(III) ions.

Compounds containing $[Mo_2Cl_8.(H_2O)]^{2-}$ and $Mo_2X_8^{2-}$ (X = Cl, Br) ions have been obtained by thermal decomposition of "acidic" nonahalodimolybdates(III) in the solid state.[129–132] A study of the temperature dependence of magnetic susceptibility showed that exchange couplings in such compounds are localised within the dimers.[109] To all appearances the bridging $Mo(X_B)_3Mo$ group is preserved in the crystal lattice.

The values of the exchange integrals for an $(Et_4N)_3Mo_2X_9$ complex, the initial "acidic" tetraethylammonium salts, and their thermolysis products are given below.

Compound	$-2J$, cm^{-1}	Compound	$-2J$, cm^{-1}
$(Et_4N)_3Mo_2Cl_9$	480±13	$(Et_4N)_3Mo_2Br_9$	430±10
$(Et_4N)_2(H_9O_4)Mo_2Cl_9$	540±15	$(Et_4N)_2(H_9O_4)Mo_2Br_9$	490±15
$(Et_4N)_2(H_5O_2)Mo_2Cl_9$	600±15	$(Et_4N)_2(H_5O_2)Mo_2Br_9$	555±15
$(Et_4N)_2[Mo_2Cl_8(H_2O)]$	580±15	$(Et_4N)_2Mo_2Br_8$	515±15
$(Et_4N)_2Mo_2Cl_8$	575±15		

On replacing a single Et_4N^+ cation in $(Et_4N)_3Mo_2Cl_9$ by the proton tetrahydrate $H_9O_4^+$ cation in $(Et_4N)_3Mo_2Cl_9$ by the proton tetrahydrate $H_9O_4^+$, which forms hydrogen bonds with anions and thus assists in compressing the dimer, the exchange coupling increases. In the complex $(Et_4N)_2(H_5O_2)Mo_2Cl_9$, which contains a proton dihydrate, a further increase in the exchange coupling occurs, which may be due to the strengthening of the hydrogen bonds between the hydroxonium ion and the complex anion. The values of $-2J$ for $(Et_4N)_2[Mo_2Cl_8(H_2O)]$ and $(Et_4N)_2Mo_2Cl_8$ occur within the limits of the exchange integral values for the previous two compounds. The same pattern occurs for tetraethylammonium bromo-complexes. Consequently, replacement of the terminal ligands in the $Mo_2X_9^{3-}$ ion leads to a change in exchange coupling to about the same extent as replacing one of the cations; and the effect of the ligand environment on the magnetic properties and geometry of the $Mo(X_B)_3Mo$ fragment is comparable with the effect of exterior cations.

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An analysis of the literature data shows that molybdenum(III) in binuclear complexes can form strong Mo≡Mo triple bonds. However, such a situation occurs only in dimers without bridges and in complexes containing polyatomic bridges. The occurrence of monatomic bridges results in a considerable weakening of the Mo—Mo bond. What are the main reasons for this?

Calculations of the electronic structure of dimers without bridges indicate that the Mo—Mo bond is formed by being filled with electrons in σ and 2π orbitals. The dimers with monatomic bridges have the following electronic configuration: with two bridges—$\sigma^2\pi^2\delta^2$; with three bridges—$\sigma^2(1/3\pi + 2/3\delta)^4$; with four bridges—$\sigma^2\delta^{*2}\delta^2$. Thus, the bridging ligands use some of the $4d$ orbitals of the metal atoms to form Mo—L—Mo bonds. In this case the Mo—Mo σ bond remains unchanged while as the number of bridges increases the Mo—Mo π bonds are gradually replaced by the much less effective δ bonds. At the same time the Mo—Mo bond order decreases, so that in a four-bridged dimer it reduces to 1. However, as follows from Tables 2—4, there are no clear correlations between the length of the Mo—Mo bond and the number of monatomic bridges, but on the other hand the dimensions of the

bridging atoms have a marked effect. The literature data on the Mo—Mo distances in molybdenum(III) dimers are correlated in Table 8.

Table 8. Mo—Mo distances in molybdenum(III) dimers with different bridging ligands.

Bridging fragment	Range of Mo—Mo distances, Å	Number of known compounds	Refs.
Without bridging ligands	2.17—2.27	16	[4,7—20, 23, 24]
Polyatomic bridges	2.17—2.24	4	[4,7, 21, 22]
Monatomic bridges			
(μ-H) + 2(μ-X), X = Cl, Br, I	2.37—2.41	7	[72—77]
2(μ-O), 3(μ-O)	2.43—2.60	4	[33, 35, 38, 39]
(μ-S) + 2(μ-Cl)	2.46	1	[68]
2(μ-S), 3(μ-S), 4(μ-S)	2.60—2.79 3.01; 3.26	15	[47—62]
2(μ-Cl), 3(μ-Cl), 4(μ-Cl)	2.57—2.82	16	[67—71, 123]
3(μ-Br)	2.82	1	[69]
3(μ-I)	3.02—3.07	3	[70, 78]

Mo—Mo bonds are shortest in length in dimers without bridges and in complexes with polyatomic bridges. In $Mo_2X_8H^{3-}$ complexes, whose geometry is determined by the hydride ion, the Mo—Mo distances are 0.2 Å greater on average than in dimers without bridges. In binuclear complexes with oxygen bridges the lengths of the Mo—Mo bonds are slightly greater than in complexes with hydride bridges. A further increase in Mo—Mo distance is characteristic of dimers that have bridging sulphur or chlorine atoms.

In $Cs_3Mo_2Br_9$ the Mo—Mo distance is at the upper limit of the range of these distances for chloride-bridged dimer. If the lengths of the Mo—Mo bonds in the isomorphous salts $Cs_3Mo_2Cl_9$ and $Cs_3Mo_2Br_9$ (2.655 and 2.815 Å respectively) are compared, it may be assumed that the Mo—Mo distance in bromide dimers will on average be 0.15 Å greater.

In complexes with iodide bridges the Mo—Mo distances exceed 3 Å, which results form the large size of the iodide ion.

Thus, although monatomic bridges weaken the Mo—Mo interaction in dimers by involving the 4*d* orbitals of the molybdenum atoms in the formation of the Mo—L bond, in all probability the main result of their presence in the molecule is their influence on the geometric structure of the dimers, resulting in a considerable extension of the Mo—Mo bond. The weakening of this bond in turn is accompanied by a decrease in the rigidity of the bridging group. In this case, as studies on dimeric halomolybdates(III) have shown, the effect of the internal and external coordination spheres on the characteristics of Mo—Mo bonds must be considered in totality.

References

1. F A Cotton, R Walton *Metal—Metal Multiple Bonds* (Translated into Russian), Izd. Mir, Moscow, 1985, p. 535
2. M H Chisholm *Angew. Chem., Int. Ed. Engl.*, 1986, **25** 21
3. M H Chisholm *Trans. Metal. Chem.*, 1978, **3** 321
4. M H Chisholm, F A Cotton *Acc. Chem. Res.*, 1978, **11** 356
5. M H Chisholm *Polyhedron*, 1983, **2** 681
6. M H Chisholm *Adv. Chem. Ser.*, 1979, **173** 396
7. M H Chisholm *Faraday Symp. Chem. Soc.*, 1980, (14) 194
8. S M Beshouri, J P Rothwell, K Folting, et al. *Polyhedron*, 1986, **5** 1191
9. P J Blower, J R Dilworth, J Zubieta *Inorg. Chem.*, 1985, **24** 2866
10. M H Chisholm, J F Corning, J C Huffman *J. Am. Chem. Soc.*, 1983, **105** 5924
11. M Akiyama, M H Chisholm, F A Cotton, et al. *Inorg. Chem.*, 1977, **16** 2407
12. M H Chisholm, F A Cotton, M W Extine, C A Murillo *Inorg. Chem.*, 1978, **17** 2338
13. W E Buhro, M H Chisholm, K Folting, J C Huffman *J. Am. Chem. Soc.*, 1987, **109** 905
14. T W Coffindaffer, I P Rothwell, J C Huffman *J. Chem. Soc., Chem. Commun.*, 1983, 1249
15. T W Coffindaffer, I P Rothwell, J C Huffman *Inorg. Chem.*, 1985, **24** 1643
16. T W Coffindaffer, I P Rothwell, J C Huffman *Inorg. Chem.*, 1984, **23** 1433
17. M H Chisholm, J F Corniry, J C Huffman *Inorg. Chem.*, 1984, **23** 784
18. M H Chisholm, K Folting, J C Hoffman, I P Rothwell *Inorg. Chem.*, 1981, **20** 1496
19. M H Chisholm, F A Cotton, M W Extine, W W Reicchert *J. Am. Chem. Soc.*, 1978, **100** 153
20. M H Chisholm, L C David, J C Huffman *Polyhedron*, 1985, **4** 1203
21. M H Chisholm, K Folting, J C Huffman, I P Rothwell *Inorg. Chem.*, 1981, **20** 2215
22. M H Chisholm, D A Haitko, J C Huffman, K Folting *Inorg. Chem.*, 1981, **20** 2211
23. M H Chisholm, D A Haitko, J C Huffman, K Folting *Inorg. Chem.*, 1981, **20** 171
24. M H Chisholm, K Folting, J C Huffman, A L Ratermann *Inorg. Chem.*, 1984, **23** 613
25. M H Chisholm, I P Rothwell *J. Am. Chem. Soc.*, 1980, **102** 5950
26. K J Ahmed, M H Chisholm, K Folting, J C Huffman *Inorg. Chem.*, 1985, **24** 4039
27. W S Harwood, S M Kennedy, F E Lytle, et al. *Inorg. Chem.*, 1987, **26** 1784
28. P R Sharp, M T Rankin *Inorg. Chem.*, 1986, **25** 1508
29. A Bino, F A Cotton *Inorg. Chem.*, 1979, **18** 3562
30. M D Hopkins, V M Miaskowski, H B Gray *J. Am. Chem. Soc.*, 1986, **108** 959
31. M Ardon, A Pernick *Inorg. Chem.*, 1974, **13** 2275
32. A Herbowski, J M Sobezak, J J Ziolkowski *Polyhedron*, 1986, **5** 399
33. K Wieghardt, M Hahn, W Swiridoff, J Weiss *Inorg. Chem.*, 1984, **23** 94
34. K Wieghardt, M Guttmann, P Chaudhuri, W Gebert *Inorg. Chem.*, 1985, **24** 3151
35. G G Kneale, A J Geddes, Y Sasaki, et al. *J. Chem. Soc., Chem. Commn.*, 1975, 356
36. T Shibahara, A G Sykes *J. Chem. Soc., Dalton Trans.*, 1978, (2) 95
37. S Wajda, E Bezak *Bull. Pol. Acad. Sci., Chem.*, 1977, **25** 109

38. G G Kneale, A J Geddes *Acta Crystallogr., Sect. B*, 1975, **31** 1233
39. T W Coffindaffer, G P Niccolai, D Powell, et al. *J. Am. Chem. Soc.*, 1985, **107** 3572
40. F A Cotton *Polyhedron*, 1987, **6** 667
41. W Wardlaw, R L Wormell *J. Chem. Soc. (London)*, 1927, 130
42. E Bezak, S Wajda *Wiad. Chem.*, 1977, **31**(3) 163
43. P C H Mitchell, R D Scarle *J. Chem. Soc., Dalton Trans.*, 1972, (16) 1809
44. P C H Mitchell, R D Scarle *J. Chem. Soc., Dalton Trans.*, 1975, (2) 110
45. S Wajda, E Bezak *Bull. Pol. Acad. Sci., Chem.*, 1977, **25** 45
46. M Lamache *Compt. Rend.*, 1976, **282** 1081
47. F A Cotton, G L Powell *J. Am. Chem. Soc.*, 1984, **106** 3371
48. F A Cotton, M P Diebold, C J O'Connor, G L Powell *J. Am. Chem. Soc.*, 1985, **107** 7438
49. M G B Drew, P C H Mitchell, C F Pygall *Angew. Chem.*, 1976, **88** 855
50. A Müller, R Jostos, W Eltzner, et al. *Inorg. Chem.*, 1985, **24** 2872
51. C D Garner *Coord. Chem. Rev.*, 1981, **37** 117
52. C Potvin, J M Brègeault, J M Manoli *J. Chem. Soc. Chem. Commun.*, 1980, 664
53. J M Manoli, J M Brègeault, C Potvin *Inorg. Chim. Acta*, 1984, **88** 75
54. F A Cotton, M W Extine, R H Niswander *Inorg. Chim. Acta*, 1978, **17** 692
55. M McKenna, L L Wright, D J Miller, et al. *J. Am. Chem. Soc.*, 1983, **105** 5329
56. K Rosselet, K E Doan, S D Johnsen, et al. *Organometallics*, 1987, **6** 480
57. L L Wright, R C Haltiwanger, J Noordik, R M DuBois *J. Am. Chem. Soc.*, 1987, **109** 282
58. D E Coons, J C V Laurie, R C Haltiwanger, R M DuBois *J. Am. Chem. Soc.*, 1987, **109** 283
59. N G Connelly, L F Dahl *J. Am. Chem. Soc.*, 1970, **92** 7470
60. W E Silverthorn, C Coudwell, K Prout *J. Chem. Soc., Chem. Commun.*, 1978, 1009
61. M B G De Lima, J E Guerchais, R Mercier, F Y Petillion *Organometallics*, 1986, **5** 1952
62. M Gueguen, J E Guerchais, F Y Petillion, J Talarmin *J. Chem. Soc., Chem. Commun.*, 1987, 557
63. D J Miller, R M DuBois *J. Am. Chem. Soc.*, 1980, **102** 4925
64. R M DuBois, R C Haltiwanger, D J Miller, G Glatzmaier *J. Am. Chem. Soc.*, 1979, **101** 5245
65. D L DuBois, W K Miller, R M DuBois *J. Am. Chem. Soc.*, 1981, **103** 3429
66. L F Lindoy, S E Livingstone, T H Lockyer *Aust. J. Chem.*, 1965, **18** 1549
67. F A Cotton, P E Fanwick, J W Fitch *Inorg. Chem.*, 1978, **17** 3254
68. P M Boorman, K J Moynihan, R T Oakley *J. Chem. Soc., Chem. Commun.*, 1982, 899
69. R Saillant, R B Jacrson, W E Streib, et al. *Inorg. Chem.*, 1971, **10** 1453
70. R Stranger, I E Grey, I C Madsen, P W Smith *J. Solid State Chem.*, 1987, **69** 162
71. P D Grebenik, M L H Green, A Izquerdo, et al. *J. Chem. Soc., Dalton Trans.*, 1987, 9
72. M I Bennet, J V Brencic, F A Cotton *Inorg. Chem.*, 1969, **8** 1060
73. A Bino, F A Cotton *Angew. Chem.*, 1979, **91** 356
74. F A Cotton, P C W Leung, W J Poth, et al. *J. Am. Chem. Soc.*, 1984, **106** 117
75. A Bino, B Burstein, F A Cotton, A Foung *Inorg. Chem.*, 1982, **21** 3775
76. A Bino, F A Cotton *J. Am. Chem. Soc.*, 1979, **101** 4150
77. A Bino, S Luski *Inorg. Chim. Acta*, 1984, **86** L35
78. F A Cotton, R Pole *Inorg. Chem.*, 1987, **26** 3310
79. C Miniscloux, G Martino, L Sajus *Bull. Soc. Chim. Fr.*, 1973, 2179
80. M W Anker, J Chatt, G J Leigh, A G Wedd *J. Chem. Soc., Dalton Trans*, 1975, 2639
81. V I Spitsyn, S V Mozgin, N A Subbotina, M G Felin *Dokl. Akad. Nauk SSSR*, 1983, **272** 423
82. V I Spitsyn, P E Kazin, N A Subbotina, et al. *Zh. Neorg. Khim.*, 1984, **29**(12) 3053 [English translation in *Russ. J. Inorg. Chem.*, 1984(12)]
83. V B Evdokimov, V V Zelentsov, I D Kolli, et al. *Dokl. Akad. Nauk SSSR*, 1962, **145** 1282
84. A Herbowski, J O Dzielewski *Chem. Scr.*, 1984, **24** 41
85. F A Cotton, B J Kalbacher *Inorg. Chem.*, 1976, **15** 522
86. F J San, M A S King *Inorg. Chem.*, 1976, **15** 1228
87. P W Smith, R Stranger *Aust. J. Chem.*, 1986, **39** 1269
88. A A Opalovskii, I I Tychinskaya, Z M Kuznetsova, P P Samoilov *Galogenidy Molibdena* (Molybdenum Halides), Izd. Nauka, Novosibirsk, p. 256
89. A J Edwards, R D Peacock, A Said *J. Chem. Soc.*, 1962, 4643
90. A Bino *Inorg. Chem.*, 1981, **20** 623
91. H D Glicksman, A D Hamer, T J Smith, R A Walton *Inorg. Chem.*, 1976, **15** 2205
92. S A Best, T J Smith, R A Walton *Inorg. Chem.*, 1978, **17** 99
93. R Saillant, R A D Wentworth *Inorg. Chem.*, 1969, **8** 1226
94. W H Delphin, R A D Wentworth, M S Matson *Inorg. Chem.*, 1974, **13** 2552
95. W H Delphin, R A D Wentworth *J. Am. Chem. Soc.*, 1973, **95** 7920
96. W H Delphin, R A D Wentworth *Inorg. Chem.*, 1974, **13** 2037
97. A Herbowski, T Lis *Polyhedron*, 1985, **4** 127
98. E Hey, F Weller, B Simon, et al. *Z. Anorg. Allg. Chem.*, 1983, **501** 61
99. J Lewis, R S Nyholm, P W Smith *J. Chem. Soc., Ser. A*, 1969, 57
100. P W Smith, A G Wedd *J. Chem. Soc., Ser. A*, 1970, 2447
101. N Kh Chi, V V Zelentsov, N A Subbotina, et al. *Zh. Neorg. Khim.*, 1972, **17**(12) 3260 [English translation in *Russ. J. Inorg. Chem.*, 1972(12)]
102. N Kh Chi, Candidate's Thesis in Chemical Sciences, Moscow State University, Moscow, 1974, p. 148
103. I E Grey, P W Smith *Aust. J. Chem.*, 1969, **22** 1627
104. I E Grey, P W Smith *Aust. J. Chem.*, 1969, **22** 121
105. V I Spitsyn, P E Kazin, N A Subbotina, et al. *Zh. Neorg. Khim.*, 1985, **30**(10) 2554 [English translation in *Russ. J. Inorg. Chem.*, 1985(10)]
106. V I Spitsyn, P E Kazin, N A Subbotina, et al. *Zh. Neorg. Khim.*, 1987, **32**(1) 71 [English translation in *Russ. J. Inorg. Chem.*, 1987(1)]
107. V I Spitsyn, P E Kazin, M G Felin, et al. *Zh. Neorg. Khim.*, 1987, **32**(5) 1262 [English translation in *Russ. J. Inorg. Chem.*, 1987(5)]
108. P E Kazin, V I Spitsyn, N A Subbotina, et al. *Zh. Neorg. Khim.*, 1987, **32**(2) 377 [English translation in *Russ. J. Inorg. Chem.*, 1987(2)]

109. P E Kazin, Candidate's Thesis in Chemical Sciences, Moscow State University, Moscow, p. 178
110. A Bino, D Gibson *J. Am. Chem. Soc.*, 1980, **102** 4277
111. R Saillant, R A D Wentworth *Inorg. Chem.*, 1968, **7** 1606
112. V V Zelentsov, N Kh Chi, A T Fal'kengof, et al. *Zh. Neorg. Khim.*, 1973, **18**(11) 2790 [English translation in *Russ. J. Inorg. Chem.*, 1973(11)]
113. Yu V Rakitin *Stroenie Molekul i Khimicheskaya Svyaz'* (The Structure of Molecules and the Chemical Bond), VINITI, Moscow, 1986, Vol. 10 (Results in Science and Technology), p. 125
114. I E Grey, P W Smith *Aust. J. Chem.*, 1971, **24** 73
115. G P Kostikova, M P Morozova, Yu P Kostikov, D V Korol'kov *Teor. Eksp. Khim.*, 1974, **10** 69
116. D V Korol'kov, Kh Missner *Teor. Eksp. Khim.*, 1973, **9** 336
117. L Natkaniec *Bull. Pol. Acad. Sci., Chem.*, 1978, **26** 633
118. R H Summerville, R Hoffman *J. Am. Chem. Soc.*, 1979, **101** 3821
119. F A Cotton, D A Ucko *Inorg. Chim. Acta*, 1972, **6** 161
120. A P Ginsberg *J. Am. Chem. Soc.*, 1980, **102** 111
121. W C Trogler *Inorg. Chem.*, 1980, **19** 697
122. L Dubicki, E Krausz, R Stranger, et al. *Inorg. Chem.*, 1987, **26** 2247
123. M Yu Subbotin, Candidate's Thesis in Chemical Sciences, Moscow State University, Moscow, 1985, p. 185
124. V I Spitsyn, P E Kazin, M Yu Subbotin, et al. *Dokl. Akad. Nauk SSSR*, 1986, **287** 134
125. M Yu Subbotin, P E Kazin, L A Aslanov, V V Zelentsov *Koord. Khim.*, 1985, **11** 1568
126. M Yu Subbotin, P E Kazin, L A Aslanov, V V Zelentsov *XV Vsesoyuznoe Chugaevskoe Soveshchanie po Khimii Kompleksnykh Soedinenii: Tezisy Dokladov* (Abstracts of Reports at the XVth All-Union Chugaev Conference on the Chemistry of Complex Compounds), Kiev, 1985, Part 1, p. 146
127. N A Subbotina, P E Kazin, M Ju Subbotin, *Proceedings of the XXIVth International Conference on Coordination Chemistry*, Athens, 1986, p. 292
128. A M Mityukov, V V Zelentsov, P E Kazin, et al. *Zh. Neorg. Khim.*, 1987, **32**(12) 2939 [English translation in *Russ. J. Inorg. Chem.*, 1987(12)]
129. P E Kazin, N A Subbotina, M G Felin, et al. *Dokl. Akad. Nauk SSSR*, 1987, **296** 1383
130. V I Spitsyn, P E Kazin, M Yu Subbotin, et al. *Koord. Khim.*, 1986, **12** 1563
131. V I Spitsyn, P E Kazin, M Yu Subbotin, et al. *XV Vsesoyuznoe Chugaevskoe Soveshchanie po Khimii Kompleksnykh Soedinenii: Tezisy Dokladov* (Abstracts of Reports at the XVth All-Union Chugaev Conference on the Chemistry of Complex Compounds), Kiev, 1985, Part 2, p. 518
132. P E Kazin *Materialy Konferentsii Molodykh Uchenykh Khimicheskogo Fakul'teta MGU* (Information from the Conference of Young Scientists of the Chemistry Department at Moscow State University), 1985, No. 2, p. 318. Article Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 5.12.85, No.8374-V

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Electron-transfer reactions in polymer matrices

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ABSTRACT. This paper discusses the dark reactions and photoreactions that occur with transfer of an electron from a donor to an acceptor in polymer matrices under electron tunnelling conditions and when forming change-transfer complexes. The main emphasis is on an analysis of the factors that determine the rate of electron transfer, which, in accordance with the advanced theory of electron transfer, are the magnitude of the exchange interaction, the free energy of the process, and the reorganisation energies of the medium and the reacting donor and acceptor molecules.

The existing models for the movement of charge carriers between single-type transport sites are discussed. The limits of applicability of the different models have been determined. The reorganisation energy of a polymer matrix is shown to have a considerable effect on the rate of movement of charge carriers on introduced transport molecules. The effect of the dielectric properties and free volume of polymer matrices on the characteristics of electron phototransfer in donor-acceptor complexes is discussed.

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I. Introduction

With the production of polymeric materials for electrophotography and films for photochemical recording of optical information, and with the development of solar energy converters and the synthesis of conductive and semiconductive polymers, electron-transfer reactions in polymer matrices have started to stimulate an increasing interest among research workers in recent years.[1–13] Moreover, polymer matrices with transport sites constitute an effective model system for the study of charge transfer in disordered media.

In the present study we shall restrict ourselves to an examination of dark and photolytic electron-transfer processes in systems involving a polymer matrix as the dielectric medium and donor (D) and acceptor (A) components distributed in it.

In this case D and A components can be chemically bonded to polymer chains. An analysis of the factors that determine the rate of electron transfer in polymer donor-acceptor systems is given below together with the quantum yield of products of electron phototransfer and the effect of temperature, the concentration of the transport sites, electric field, and characteristics of the polymer matrix on the mobility of the charge carriers (electrons or holes) in polymers.

An examination will be made of systems in which the distance between the components (R) is greater than the sum of the van der Waals radii of the molecules (the notation D ... A is given for such systems) and electron transfer is due to a quantum effect— tunnelling,[14,15] and also of composites based on charge-transfer complexes (CTC, denoted as D·A) in which the value of R as a result of efficient packing can be less than the van der Waals radii of the components.[16]

A common feature of these systems is the fact that electron transfer in them under dark conditions and with photoexcitation is due to overlap of the wave functions of the states without electron transfer— ψ_0(D, A)—and the states that correspond to complete electron transfer from D to A—$\psi_1(D^+, A^-)$.[16–19]

$$\psi_i(DA) = \psi_0(D, A) + \lambda\psi_1(D^+, A^-), \quad (1)$$

$$\psi_{f,ex}(D^+A^-) = \psi_1(D^+A^-) - \lambda\psi_0(D, A), \quad (2)$$

Here ψ_i(DA) and $\psi_f(D^+, A^-)$ are the wave functions of the initial and final states of the system with thermal electron transfer; ψ_i(DA) and $\psi_{ex}(D^+, A^-)$ represent the ground and excited state of the system with electron phototransfer; $\lambda = V_{01}/\Delta G$, where V_{01} is the energy of the exchange interaction; ΔG is the free energy of electron transfer.

$$\Delta G = E_0 - E_1, \quad (3)$$

where E_0 and E_1 are the energies of the states without bonding and with complete electron transfer respectively:

$$E_0 = \int\psi_0^*(D, A)H\psi_0(D, A)dv,$$

$$E_1 = \int\psi_1^*(D^+A^-)H\psi_1(D^+A^-)dv,$$

where ψ^*(D, A) and $\psi^*(D^+, A^-)$ are complex associated wave functions, v is a combination of the spatial and spin coordinates of the electron.

The thermal reaction

$$D ... A \rightleftarrows D^+ ... A^- \quad (4)$$

occurs as a result of "horizontal" electron transfer.

The transition between the two equilibrium states D ... A and $D^+ ... A^-$ involves surmounting the potential barrier $G^{\neq}$ (Fig. 1*a*). According to two analyses,[17,18] with values of $V_{01} < 20$ cm^{-1} (i.e., 2.48×10^{-3} eV) electron transfer occurs under nonadiabatic conditions when the D ... A system, existing in the transition state (near the point $q^{\neq}$, see Fig. 1*a*), repeatedly crosses the $q^{\neq}$ point along its own potential curve before undergoing transfer to a lower trajectory corresponding to the $D^+ ... A^-$ state. Adiabatic conditions (Fig. 2), in other words, transfer of the D ... A system to the $D^+ ... A^-$ state at each crossing of the $q^{\neq}$ point, correspond to the values $20 < V_{01} < 400$ cm^{-1} ($\sim$0.05 eV).

The convergence of the components on conversion to D·A complexes gives rise to an exponential increase in V_{01} from 0.05 to 0.5 eV. The rate of electron transfer corresponds to the value $\nu = V_{01}/h \sim 10^{13}$ s^{-1} (h is Planck's constant). In this case we are dealing with the dipole $D^{+\delta}A^{-\delta}$ (D·A $\rightleftharpoons$ ($D^+ \cdot A^-$).[16,19] As a result of mixing the states

without bonding and with complete charge transfer [$\lambda > 0$ in expressions (1) and (2)], an optical transition with charge transfer is possible in both systems

$$D...A \text{ (or } D.A) \xrightarrow{h\nu_{et}} D^{+}...A^{-} \text{ (or } D^{+}A^{-})$$

(Fig. 1*a* or Fig. 2).[16–19]

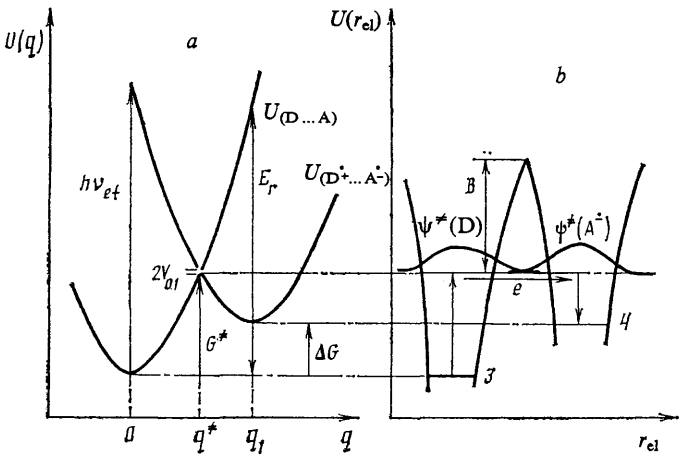


Figure 1. *a*) Dependence of the potential energies $U_{(D...A)}$ and $U_{(D^{+}...A^{-})}$ on the generalised coordinate q. The parameters that determine the rate of thermal reaction (4) and electron phototransfer under non-adiabatic conditions ($V_{01} < 20$ cm^{-1}) are given. *b*) Dependence of the electron energy $U(r_{el})$ on the coordinate r_{el}. The levels cor-respond to: *3*) equilibrium potential $E_{1/2}(^{1}D_0/D^{+})$; *4*) $E_{1/2}(A^{-}/A)$. For further explanation, see text.

II. Thermal electron transfer

The polaron theory of electric conductivity[20] has been developed in relation to ionic semiconductors. According to this theory the movement of an electron can be represented as the successive transfer between lattice points (by a distance R) when there is strong polarisation of the lattice. Polaron theory proposes that the energy barrier for movement of an electron is determined by the change in polarisation of the lattice on transfer of the electron from one transport site to another $M^{+}...M \rightarrow M...M^{+} \rightarrow$ etc. The main conclusions of the polaron theory were used to develop the quantum-chemical theory of thermal electron transfer in liquid media (the model of the dielectric continuum).[17,21–29] The latter model extends the polaron theory by taking into account the expenditure of energy on intramolecular reorganisation in the change from a molecule to a radical ion. This model is becoming more common because it is suitable for a wide range of donor-acceptor systems $D...A \rightarrow D^{+}...A^{-}$ for which the driving force of electron transfer is the free energy of this process.

According to the Marcus–Levich–Dogonadze–Kuznetsov model of the dielectric continuum, the rate of charge transfer is determined by a combination of processes that take place in a "supermolecule" consisting of the D...A system and the neighbouring sphere of the surrounding dielectric continuum (in our case the polymer medium). As a result of thermal motion there is a fluctuation of such parameters as the mutual orientation of the D...A components and the molecules of the medium, the distance between the D...A components, and the internuclear distances in the D and A molecules, and a redistribution of charge occurs in the D...A system and the molecules of the medium, etc. This causes fluctuations in the generalised coordinate q, which characterises the interaction between D...A and the dielectric medium and inside the D...A system.

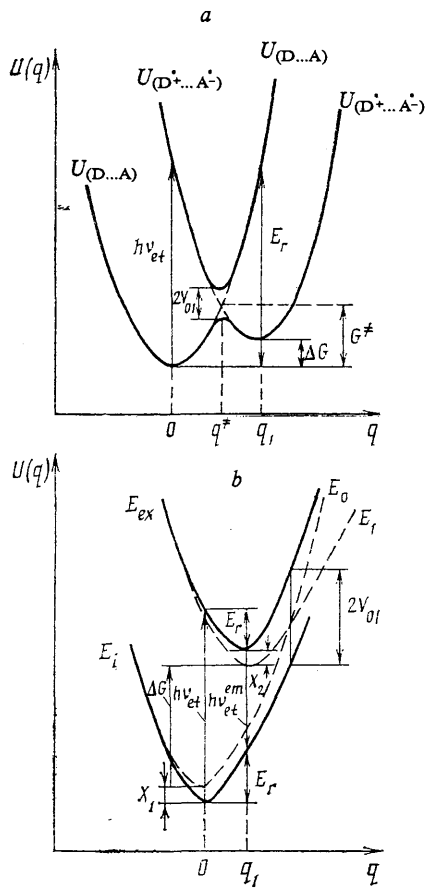


Figure 2. *a*) Dependence of the potential energies $U_{(D...A)}$ and $U_{(D^{+}...A^{-})}$ on the generalised coordinate q. The parameters that determine the rate of thermal reaction (4) and electron phototransfer under adiabatic conditions ($20 < V_{01} < 400$ cm^{-1}) are given. *b*) Relative position of the ground E_i ($\equiv U_{(D.A)}$) and excited E_{ex} ($\equiv U_{(D^{+}.A^{-})}$) levels of the D.A complex. The parameters that determine electron phototransfer are given. For further explanation, see text.

The potential energies of the fluctuating system that occurs in the initial (D...A) and final ($D^{+}...A^{-}$) states are represented as two parabolae (see Fig. 1):

$$U_{(D...A)}(q) = aq^2, \tag{5}$$

$$U_{(D^{+}...A^{-})}(q) = b(q - q_1)^2 + \Delta G, \tag{6}$$

where q_1 is the equilibrium coordinate of the final state. The

coefficient a corresponds to the potential energy value of the initial state at the equilibrium coordinate of the final state ($q = q_1$):

$$U_{(D...A)}(q_1) = aq_1^2 \equiv E_r,$$
$$a = E_r/q_1^2,$$

where E_r is the reorganisation energy of the "supermolecule" brought about by electron transfer in the D ... A system. The coefficient b corresponds to the potential energy of the final state at the equilibrium coordinate of the initial state ($q = 0$):

$$U_{(D^{\cdot+}...A^{\cdot-})}(0) = b(-q_1)^2 + \Delta G = E_r + \Delta G.$$

In reversible reactions $E_r = E_r'$ and correspondingly $a = b$. Thus, for reversible reactions we obtain

$$U_{(D...A)}(q) = E_r(q/q_1)^2, \quad (5a)$$
$$U_{(D^{\cdot+}...A^{\cdot-})}(q) = E_r\left(\frac{q - q_1}{q_1}\right)^2 + \Delta G,$$
$$E_r = E_{in} + E_s, \quad (6a)$$

where E_{in} is the energy expended on the transition from D ... A to $D^{\cdot+}$... $A^{\cdot-}$ ion radicals, resulting from the change in distance between the components of the complex as well as the distances between the nuclei and the bond angles in these same molecules D and A (the "inner-sphere" energy, including intramolecular reorganisation); E_s is the reorganisation energy of the medium (the "outer-sphere" reorganisation).

(a) Rate of electron transfer in condensed media

The rate constant of thermal electron transfer (k_{et}) in the reaction D ... A < $D^{\cdot+}$... $A^{\cdot-}$ under nonadiabatic conditions (na) is determined by the relationship

$$k_{et}(na) = (2\pi/\hbar)|V_{01}|^2 FC, \quad (7)$$

where FC is the Franck–Condon factor.

Necessary conditions for electron transfer in accordance with reaction (4) are: 1) adherence to the Franck–Condon principle; and 2) overlap of the wave functions of the donor and the acceptor radical anion in a Franck–Condon state (see Fig. 1*b*); then

$$V_{01} = \int \psi^{\neq}(D ... A) H \psi^{\neq}(D^{\cdot+} ... A^{\cdot-}) dv > 0. \quad (8)$$

A Franck–Condon state conforms to the isoenergetic condition (Fig. 1*b*):

$$\int \psi^{*\neq}(D ... A) H \psi(D ... A) dv = \int \psi^{*\neq}(D^{\cdot+} ... A^{\cdot-}) H \psi^{\neq}(D^{\cdot+} ... A^{\cdot-}) dv.$$

In accordance with the Franck–Condon principle, electron transfer occurs with an unchanged nuclear configuration as a result of the high rate of the act of electron transfer ($t < 10^{-13}$ s). Only the electronic polarisation of the medium is synchronous to this process whereas the other forms of polarisation, which are related to the movement of nuclei (atomic, configurational) are established much more slowly in $> 10^{-13}$ s and $10^{-12}-10^{-9}$ s respectively.[24] Consequently, electron transfer from molecule D to A will only occur after the "supermolecule" acquires from thermal fluctuations a nonequilibrium configuration (along the $q^{\neq}$ coordinate) in which the potential energies of the initial and final states coincide; i.e., when

$$E_r(q^{\neq}/q_1)^2 = E_r\left(\frac{q^{\neq} - q_1}{q_1}\right)^2 + \Delta G.$$

hence

$$q^{\neq}/q_1 = (E_r + \Delta G)/2E_r.$$

According to equation (5a) the energy of activation for transfer of the D ... A system to the Franck–Condon state ($G^{\neq}$, see Fig. 1) is equal to:

$$U_{(D...A)}(q^{\neq}) \equiv G^{\neq} = (E_r + \Delta G)^2/4E_r. \quad (9)$$

Hence the FC factor in equation (7) is given by

$$FC = A\exp(-G^{\neq}/kT) = A\exp[-(E_r + \Delta G)^2/4E_r kT], \quad (10)$$

where

$$A = (4\pi E_r kT)^{-1/2}.$$

Equation (10) represents the state of the system in the classical approximation, i.e., when $\hbar\omega \ll kT$, where ω is the effective angular frequency of the fluctuations in the "supermolecule" (related to E_r by the relationship $E_r = \hbar\omega q_1^2/2$). The FC factor has a maximum value $FC = A$ when there is a negative free energy $-\Delta G = E_r$.

According to expression (10), in isoenergetic systems (when $\Delta G = 0$) $G^{\neq} \equiv G^{\neq}(0) = E_r/4$.

The free energy of the thermal reaction (4) is equal to

$$\Delta G = E_0 - E_1 = e[E_{1/2}(D/D^{\cdot+}) - E_{1/2}(A^{\cdot-}/A)] + e^2/\varepsilon R, \quad (11)$$

where $E_{1/2}(D/D^{\cdot+})$ and $E_{1/2}(A^{\cdot-}/A)$ are the equilibrium potentials of oxidation of the donor and reduction of the acceptor respectively, $e^2/\varepsilon R$ is the Coulomb attraction energy of the radical ions $D^{\cdot+}$ and $A^{\cdot-}$, having their own solvation shells; ε is the dielectric constant of the medium.

The reorganisation energy of the medium due to electron transfer is calculated from the equation of Marcus:[21,25]

$$E_s = e^2(1/n^2 - 1/\varepsilon) f(r, R), \quad (12)$$

where n is refractive index of the medium, $f(r, R)$ is a function that depends on the radius of the components and on the distance of electron transfer R. For exchange reactions

$$M^{\cdot+} ... M \overset{k_{et}}{\rightleftharpoons} M ... M^{\cdot+}, \quad (13a)$$

$$M^{\cdot-} ... M \overset{k_{et}}{\rightleftharpoons} M ... M^{\cdot-} \quad (13b)$$

function $f(r, R) = (1/r - 1/R)$, which for reaction (4): $f(r, R) = (1/2r_D - 1/2r_A - 1/R)$. Here r, r_D, and r_A are the radii of the transport site M, the donor molecule, and acceptor molecule respectively.

The "inner-sphere" reorganisation energy E_{in}, such as for reaction (13a), can be determined experimentally from the difference in gas-phase ionisation potentials:[30–33]

$$E_{in} = I^V - I, \quad (14)$$

where I^V is the vertical or Franck–Condon ionisation potential, which is equal to that quantum of energy ($I^V = h\nu_{max}$) at which are formed the maximum number of electrons from photodecomposition; I is the adiabatic ionisation potential. In two studies[30,31] I was calculated from the equation $I = h\nu + 0.15$ eV, where $h\nu$ is that quantum of energy at which the number of electron from photodecomposition is 1% of those that are formed at $h\nu_{max}$. The value of E_{in} determined thus for a series of 25 alkylamines is 0.6–0.7 eV.

The complete reorganisation energy of a "supermolecule" is given by the difference

$$E_r = E^V - [eE_{1/2}(M/M^{\cdot+}) + E_0], \quad (15)$$

where E^V is that quantum of energy which corresponds to photoionisation of molecules in the liquid phase when the energy of the electrons emitted into the gas phase is close to zero. $E_{1/2}(M/M^{\cdot+})$ is the equilibrium oxidation potential of the molecule compared to a reference electrode (S.H.E.). E_0 is the energy level of the reference

electrode relative to vacuum [E_0 = 4.43 eV for a standard hydrogen electrode (S.H.E.)].[34] Thus, [$eE_{1/2}(M/M^+)$ + E_0] is the energy of the radical cation M^+ relative to vacuum in a completely relaxed state, namely, after completion of both "inner-sphere" and "outer-sphere" reorganisation. The value of E_r was determined from the experimental values of E^V and $E_{1/2}(M/M^+)$ for a number of alkylamines[32] (Table 1) and for all methyl-substituted benzenes.[32,33] The "intramolecular" reorganisation energy, calculated from the expression $E_{in} = E_r - E_s$, is also given in Table 1.[31] In the calculation of E_s it was suggested that $r = r_{eff} = R/2$. The effective radius r_{eff} of M molecules was determined from the experimentally determined electron polarisation energy, taken as equal to $P_e = [(I^V + I)/2] - E^V$ and related to r_{eff} by the expression $P_e = e^2(1-1/n^2)/2r_{eff}$.[31,32] Thus

$$r_{eff} = e^2(1 - 1/n^2)/(I^V + I - 2E^V).$$

Table 1. Reorganisation energy E_r of a "supermolecule" and the medium E_s for exchange reaction (13a) of a number of alkylamines in acetonitrile calculated from equations (15) and (12) and the intramolecular reorganisation energy $E_{in} = E_r - E_s$.[31]

Compound	E_r, eV*	E_s, eV	E_{in}, eV*
Butylamine	1.67	1.17	0.5
Isobutylamine	1.64	1.23	0.41
t-Butylamine	1.6	1.22	0.38
Dibutylamine	1.3	1.07	0.23
Tributylamine	1.23	0.82	0.41
Tetramethyl-*p*-phenylenediamine			0.365**

*The value of E_0 = 4.5 eV used by Watanabe et al[31] has been replaced by 4.43 eV for a S.H.E.[34]
**Value taken from two studies.[35,36]

It was shown[31] that values of r_{eff} calculated from this expression agree with the values that are calculated from the volume occupied by the molecule: $4\pi r_{eff}^3/3 = MW/dN_A$, if the coefficient 0.5 is used instead of $(3/4\pi)^{1/3}$ (MW is the molecular weight of alkylamine, d is the density of alkylamine, N_A is the Avogadro number).

The most common method for determining E_r, and hence E_{in}, is a determination of the energy of activation $G^{\neq}$ of exchange reactions, for which, as has already been mentioned, $G^{\neq} \equiv G^{\neq}(0) = (E_{in} + E_s)/4$. The energy E_{in} thus obtained for the exchange reaction of *N,N,N',N'*-tetra-methyl-*p*-phenylenediamine (TMPD) in different solvents is given in Table 1. The value of E_{in} was determined by extrapolating the dependence of $4G^{\neq}$ on $(1/n^2 - 1/\varepsilon)$ to $(1/n^2 - 1/\varepsilon) = 0$, i.e., when $E_s = 0$ [see (equation 12)].[35,36] The value of E_{in} obtained for TMPD by this method (0.365 eV, see Table 1) is close to that calculated by the Pariser–Parr–Pople method (0.337 eV). For methyl-substituted benzenes ($C_6H_{6-n}(CH_3)_n$, $n = 1-6$) the experimental value E_{in} = 0.26 eV.[32,33]

It should be mentioned in addition that the total polarisation energy of the medium by a radical cation $M^+(D^+)$ is determined from the adiabatic ionisation potential:

$$p^+ = e^2(1 - 1/\varepsilon)/2r_{eff} = \{I - [eE_{1/2}(M/M^+) + E_0]\}.$$

The energy of the exchange interaction in a Franck–Condon state (8) is given by the equation[37,38]

$$V_{01} \equiv V(R) = V(R_0)\exp[-(R - R_0)/\alpha], \quad (16)$$

where R_0 is the sum of the van der Waals radii of D and A^-, α is the attenuation factor of the wave function in the Franck–Condon state.

$$\alpha = 1/0.511B^{1/2}, \text{ Å}. \quad (17)$$

here B is the height of the barrier or difference between the position of the highest occupied orbital of the donor and the energy of the lowest conducting state of the medium (in eV) (see Fig. 1*b*).

Thus the rate constant of electron transfer under nonadiabatic conditions in accordance with equations (7), (10), and (16) can be written in the general form

$$k_{et}(na) = (2\pi/\hbar)(4\pi E_r kT)^{-1/2} V^2(R_0)\exp[-2(R - R_0)/\alpha] \cdot \exp[-(E_r + \Delta G)^2/4E_r kT]. \quad (18)$$

It is necessary to bear in mind that because of steric hindrance in the formation of molecular conformations with minimum potential energies in polymer matrices, a nonuniform distribution of ionisation potentials and electron affinities (i.e., ΔG), steric variation in the dielectric constant of the medium ε (i.e., E_r), and other factors giving rise to a variation in k_{et} are possible.

In organic systems there is a common situation when the frequency of the "outer-sphere" fluctuations ω_s ($E_s = \hbar\omega_s q^2/2$) conforms with the inequality $\hbar\omega_s \ll kT$, while the distance between the vibrational levels in the donor and acceptor molecules conforms with the inequality $\hbar\omega_{in} \gg kT$. Under these conditions, the lowest vibrational level is occupied in the initial system D ... A, while the final state (D^+... A^-) is represented by a set of parabolae, given by equation (6a), separated from each other on the y-axis by a quantum of vibrational energy $\hbar\omega_{in}$.[17,39] Electron transfer can occur by conversion to different vibrational levels of the acceptor [$n_i\hbar\omega_{in}$, where $v_i = (v + 1/2)$] (v is the vibrational quantum number, equal to 0, 1, 2, 3...). The overall constant results from summation of the rate constants of electron transfer to different vibrational levels and is given by:[39]

$$k_{et} = (2\pi/\hbar)V_{01}^2(4\pi E_r kT)^{-1/2}\sum_{v_i=0}^{\infty}\frac{\exp(-S)S^{v_i}}{v_i!}\times \times\exp\left[-\frac{(\Delta G + v_i\hbar\omega_{in} + E_s)^2}{4E_s kT}\right]. \quad (18a)$$

where $S = E_{in}/\hbar\omega_{in}$. For large negative values of ΔG (when $|\Delta G| > E_s$) the main channel for electron transfer reduces to a vibrational term corresponding to the value $G^{\neq} = 0$, i.e., $v_i = (\Delta G - E_s)/\hbar\omega_{in}$.

At the adiabatic (*a*) limit (Fig. 2*a*)[40,41]

$$k_{et}(a) = \frac{\varepsilon}{\tau_D n^2}\left(\frac{E_s}{4\pi kT}\right)^{1/2}\exp\left[-\frac{G^{\neq} - V_{01}}{kT}\right]. \quad (19)$$

where τ_D is the dielectric relaxation time of the medium after electron transfer. In contrast to nonadiabatic conditions, in which the rate of electron transfer is controlled by the exchange interaction V_{01}^2, under adiabatic conditions k_{et} is mainly determined by the longitudinal relaxation time of the medium $\tau_L : \tau_L = \tau_D n^2/\varepsilon$.

In contrast to liquid media in which an electron transfer reaction mainly occurs after the diffusional approach of components to the distance R_0, equal to the sum of the van der Waals radii, in polymer systems D and A are either fragments of a polymer chain and are separated by a fixed distance or are dissolved in the polymer matrix

and have a random distribution with an interaction radius R. In this case the pattern of electron transfer can be complicated by the effect of the free volume and other polymer effects.

Donor-acceptor compounds with bridging groups (B) constitute a model of dielectric polymer media. Charge transfer along the saturated bonds $-CH_2-$ is caused by hyperconjugation[42,43] (superexchange interaction), namely, by overlap of the π-orbitals of the organic aromatic groups D and A with the atomic $p\sigma$-orbital of an unsaturated $-CH_2-$ fragment. The extent of this overlap depends on the rotation angle of the aromatic rings relative to the bridging group.[42,44] The $-CH_2-Ar-CH_2-$ groups are regarded as bridges (Ar is aromatic fragment).[44,45] The stepwise transfer of an electron via bridging groups can occur with complete reorganisation of the "supermolecule" at each transition step as well as a dynamic transfer when short-lived bridging states participate in electron transfer.[17] The energy of the exchange interaction for bridging systems is determined from the equation:[44,45]

$$V_{01}=\sum_{B} V_{0B}V_{B_i}/(G_1^{\neq}-E_B),$$

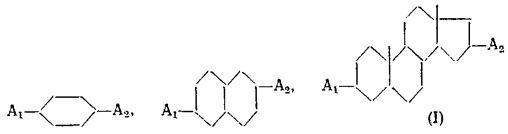
where the index B relates to a bridging group; E_B is the energy at the minimum of the potential curve of the bridging group; $G_1^{\neq}$ is the energy of the initial state of the D...A system at the point of intersection of the initial potential curve of $U_{(D...A)}$ with the potential curve of the bridging fragment; V_{0B} and V_{B1} are the energies of the exchange interaction of the orbitals of D and B^- and B^- and A^- respectively.

Under conditions of superexchange the attenuation factor α in expression (16) takes the form

$$\alpha=\frac{1}{R}\ln\left(\frac{B}{V_{B^-B}}\right),$$

where R and V_{B^-B} (or V_{B^-B}) are respectively the distance and exchange integral between bridging groups on which the movement of a charge occurs.

Electron transfer has been studied[28,46,47] in compounds of the type A_1-B-A_2 such as substituted cyclohexanes, decalins, and steroids:



(I)

where A_1 is biphenyl (electron affinity 2.4 eV), A_2 are aromatic compounds with different values of the equilibrium potential $E_{1/2}(A_2^-/A_2)$ corresponding to a free energy of electron transfer

$$\Delta GT=e[E_{1/2}(A_1^-/A_1)-E_{1/2}(A_1^-/A_2)]=0 \text{ to } -0.25 \text{ eV}.$$

Pulsed radiolysis was used to study the reaction

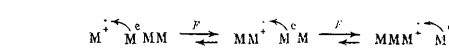
$$A_1-B-A_2 \xrightarrow{e} \begin{cases} \rightarrow A_1^- - B - A_2 \\ \rightarrow A_1 - B - A_2^- \end{cases} \quad (20)$$

The first step in reaction (20) is capture by an A_1-B-A_2 molecule of an electron formed during pulsed irradiation of solvents such as methyltetrahydrofuran (MTHF), tetrahydrofuran, and isooctane at 296 K.

The interconversion of the optical spectra of A_1^- and A_2^- is an indication of electron transfer, in accordance with reaction (20), via saturated $-CH_2-$ (or $>CH-$) bonds. When substituted steroids (I) are used, the dependence of k_{et} on $-\Delta G$ acquires a bell-shaped form. The experimentally determined dependence is in agreement with that calculated from expression (18a) when E_{in} = 0.45 eV, $\hbar\omega_{in}$ = 1500 cm^{-1}, V_{01} = 6.2 cm^{-1}, E_s = 0.75 eV in MTHF and 0.15 eV in isooctane. In the calculation of E_s from equation (12) it is assumed that $r_{A_1}=r_{A_2}$ = 2.95 Å, R = 17.3 Å. The value of the constant k_{et} decreases from 5×10^9 to 10^6 s^{-1} on increasing the number of saturated bonds (n) that separate A_1 and A_2 from 4 to 10. A relationship was established[47] between the energy of the exchange interaction V_{01} and n when $V_0=1.1\times10^3$ cm^{-1}: $2\ln V_{01}=2\ln V_0-1.15(n-1)$.

(b) Electron transfer between single-type transport sites

Electron transfer between single-type transport sites that are situated in a disordered manner in a solid dielectric medium is of particular interest from a theoretical viewpoint and important for practical application. Polymers with a glass transition temperature (T_g) that exceeds the temperature at which the electron transfer measurements are carried out are usually chosen as the medium. An important feature of these systems is the participation of the oxidised (or reduced) form of the neutral transport site (M) in electron transfer and the occurrence of fixed distances between the transport sites [reaction (13a) and (13b)]. When an external electric field F is applied, these reactions determine the flow of hole (or electron) current through the sample:



etc.

The transport of holes is simpler to study experimentally in systems with transport sites that are characterised by low ionisation potentials I_M (or low oxidation potentials of M), while the transport of electrons is simpler to study in systems with high values of electron affinity E_M. This is related to the fact that in polymer matrices there are chemical impurities and structural defects which in the case of electron transport are electron traps if their electron affinity is higher than E_M. Capture of electrons in traps considerably complicates their transport through a sample. The effect of additional traps on the transport of charges has been studied experimentally and theoretically.[48] In the present review this question is not considered as it is possible to select experimental conditions that exclude the effect of additional traps.

In this section four types of systems will be examined: 1) polymers in which the transport sites are substituents in the main chain, for example, the carbazolyl group in polyvinylcarbazole (PVCA), polyepoxypropylcarbazole (PEPCA), etc.; 2) polymers in which the transport sites occur in the main chain, for example, polyimides,[49] polyphenylene sulphides,[50] polyepoxyamino adduct,[51] and others; 3) molecularly doped polymers, namely, inert polymer matrices [polystyrene (PS), polycarbonate (PC), and others] in which are dissolved low-molecular weight transport molecules such as triphenylmethane (TPM) and its derivatives, triphenylamine (TPA), isopropylcarbazole (IPCA), and others; 4) mixed systems, for example, PVCA in which TPA is dissolved, PC containing IPCA and TPA in different proportions, and also the system that has been the most studied—PVCA + trinitrofluorenone (TNF).

The electron transfer reaction in the systems is the simplest of those considered above, it is completely reversible, and the composition of the reaction products is no different from that of the initial reactants. Serious problems in the theoretical treatment arise because the distances between the neighbouring transport sites are fixed but

differ over quite a wide range. The result of this is that the energy of the bond between the electron and the transport site, which depends on the local environment, also varies for specific transport sites, the distribution of energy of the bond reaching a width of several magnitudes of kT.

This electron transfer process determines the electron conductivity of photoconductive organic materials by nonequilibrium charge carriers. These materials are extensively used as electron-transport media in electrophotographic films, high energy transformers, etc. An experimental study of these reactions for the determination of k_{et} and the kinetic mechanisms presents certain difficulties because of the identification of the chemical composition of the reactants and the reaction products, the spin state, and spectroscopic characteristics. However, charge transfer in an external field F has the result that the charge acquires an additional drift rate in the direction of the field, and a current arises in the electric circuit which includes the polymer sample; the charge mobility μ is determined by analysing the current. The rate constant k_{et} and charge mobility μ are related through the diffusion coefficient

$$\mu = De/kT; \quad D = \rho^2 k_{et}$$

by the relationship

$$\mu = \rho^2 k_{et} e/kT, \tag{21}$$

where ρ is the length of electron hop.

In accordance with expression (21) all subsequent treatment of electron mobility in polymer matrices is also fully related to a study of the rate constant of the electron transfer reaction between identical sites. The most informative method for studying electron (hole) transport is the measurement of transit times. A packet of nonequilibrium charge carriers is produced on the surface of a polymer film at the time $t = 0$ (by injection from a catalyst or by direct photoexcitation with strongly absorbed light). If the transport sites are arranged in an ordered manner, the packet of charge carriers will move in the external field through the polymer film to the collector electrode, spreading out through drift but retaining a Gaussian form. In the process the distribution of charge carriers on the coordinate (σ) increases its width according to the principle $\sigma \sim t^{1/2}$. In this case the transport is called Gaussian and the current in the external circuit (i) has a constant value during drift (transit) of the packet through the film and rapidly decreases when it reaches the collector electrode at time t_{tr}. The drift mobility is determined here as $\mu = l/F t_{tr}$ (l is thickness of sample), and the current during drift can be expressed as

$$i = \mu e N \text{ (for } t < t_{tr}), \tag{22}$$

where N is the concentration of drifting charges. If the transport sites are arranged in a disordered manner, the hopping times between neighbouring sites vary over a wide range. Because of this, the packet of charges loses its Gaussian form, the plateau on the $i-t$ curve disappears, and it takes the form of a diminishing curve with a considerably elongated tail. In this case a determination of t_{tr} from the relationship $i = f(t)$ becomes impossible. However, in the logarithmic coordinates $\log i - \log t$ the current curve is converted into two linear sections which correspond to the relationships

$$i(t) \sim t^{-(1-\beta_1)} \text{ when } t < t_{tr},$$

$$i(t) \sim t^{-(1+\beta_2)} \text{ when } t > t_{tr}, \tag{23}$$

where β_1 and β_2 are constants which are independent of t; they have values within the limits $0 \leqslant (\beta_1, \beta_2) \leqslant 1$. The transit time occurs at the point of intersection of the linear segments, but in this case it corresponds to the arrival at the collector electrode (and mobility) of the fastest charges. The prolonged decrease after the break point can only be accounted for if it is assumed that there is a sufficiently large scatter (deviation) of t_{tr} for different groups of drifting charges. Hence charge transfer with the cited anomalous current characteristics is called dispersive. It is possible to determine the value of the current if the average displacement $\bar{x}$ of the packet of charges in relation to t is known. For Gaussian transport, $\bar{x} \sim t$, in accordance with equation (22), we obtain $i \sim d\bar{x}/dt = \text{const}$. If it is assumed that the displacement of the packet does not occur at a constant rate but gradually slows down, so that $\bar{x} \sim t^{\beta_1}$, for the current we obtain the dependence[52] $i(t) \sim d\bar{x}/dt \sim t^{-(1-\beta_1)}$, which is in agreement with equation (23).

It should be mentioned that the rate of movement of the packet $d\bar{x}/dt$ is proportional to the rate constant k_{et}; therefore, if Gaussian transport occurs, k_{et} is independent of t, but if dispersive transport takes place, $k_{et} = At^{-(1-\beta_1)}$, where A is a constant independent of t. A rate constant that varies with time in accordance with this relationship correlates well with a number of experimental results on the fate of captured electrons in vitreous matrices at 77 K.[53]

Relationships (23) were first obtained by Sher and Montroll[54] using the continuous time random walk (CTRW) model. In order to take account of the dispersion of t_{tr} occurring as a result of the dispersion in hopping times between neighbouring transport sites in the CTRW model, a disordered medium is broken down into single units composing a regular lattice. Each unit contains a sufficiently large number of transport sites so that the units have an equivalent concentration of M. The distribution of hopping times for the neighbouring sites in each unit is expressed as a prolonged distribution function for the probability of hops between units [$\psi(t) \sim t^{-(1+\beta)}$], which leads to dependence (23) with $\beta_1 = \beta_2 = \beta$. In Gaussian transport the distribution function decreases exponentially with time and has a single characteristic time τ_0:

$$\psi(t) = (1/\tau_0) \exp(-t/\tau_0).$$

It was originally supposed that the CTRW model represents electron hops between neighbouring sites by a tunnel mechanism. In this case it is clear that the relationship $h' > \rho$ holds true between the linear dimensions of a unit (h') and ρ. Subsequent analysis showed[15,55] that the condition for the CTRW model to be applicable was the inequality with an opposite form: $h' \ll \rho$. This indicates that the transport of electrons occurs in a conduction zone (a zone mechanism) with repeated capture on traps with an energy distribution in a certain range.

Dispersive current with the decreasing curve (23) must occur during nonequilibrium transport of electrons, namely, in the absence of thermal equilibrium between mobile (electrons in the conduction zone) and localised (electrons in localised states) fractions. In this case the time of electron motion in the conduction zone determines the probability of their being trapped, while the dispersive characteristics of transport determine the energy distribution of trap depths. For example, for an exponential distribution of trap depths:

$$g(E) = (N_t/E_0) \exp(-E/E_0),$$

(N_t is trap density), the relationships $\beta_1 = \beta_2 = \beta$ and $\beta = kT/E_0$ are fulfilled.[56]

A condition for nonequilibrium transport is that the relationship $\tau_l(E) > t_{tr}$, where $\tau_l(E)$ is the distribution of charge localisation times in traps of varying depth E, holds for a substantial fraction of the traps. After generation (injection or photoexcitation of the surface

layer of the film sample) the charges are localised in traps according to their concentration and independent of depth. In order to establish thermal equilibrium repeated escape of the charges from the traps into the conduction zone is necessary. If the condition $\tau_l(E) \ll t_{tr}$ is fulfilled for all traps, during the time of drift of a packet through the sample the current has a constant value and on reaching t_{tr} it falls more or less abruptly.

The temperature dependence of μ is determined by trap depth, and by extrapolating the dependence $\mu - T$ in the Arrhenius curve to $T^{-1} \to 0$ it is possible to determine the charge mobility in the conduction zone μ_0. For organic polymer systems (in contrast to, for example, chalcogenide glasses) μ_0 has the value $\mu_0 \sim 1$ cm^2 V^{-1} s^{-1}, and this corresponds to the limiting value that determines the applicability of the zone model, since when $\mu_0 < 1$ cm^2 V^{-1} s^{-1} the length of the electron path becomes comparable with or less than R in the polymer. Therefore, even though direct simulation of the transient current $i(t)$ using Monte Carlo curves for the zone model with repeated capture of charges by traps effectively represents the characteristics of hole transfer in PVCA[57,58] (including the lack of dependence of μ on l, the disappearance of the inflection on the transient current curve when the temperature is decreased, the prolonged decrease of transient current when $t > t_{tr}$, etc.), the suitability of the zone model for representing charge transfer in a polymer matrix is in doubt.

This difficulty can be overcome in the percolation of model of dispersive transport, developed in several studies,[15,55,59,60] which can be used to replace the CTRW approximation when the condition $h' \gg \rho, \rho = R - R_0$, is fulfilled, namely, when tunnel electron transfer occurs between transport sites. The rate of electron transfer between neighbouring sites depends exponentially on R and the height of the energy barrier.

In the percolation model it is considered that in an amorphous solid with a considerable concentration of transport sites it is possible to distinguish "rapid" trajectories of the movement of electrons through sites, the distance between which is less than a given optimum distance R_m, and "slow" trajectories for which $R > R_m$. On increasing the concentration of transport sites to a threshold concentration C_0, the rapid trajectories combine to form an endless cluster on which rapid electron transfer through the sample from electrode to electrode occurs. A further increase in the concentration of transport sites leads to an increase in density of the endless cluster, so that $i = (C - C_0)^\gamma$, where γ is a constant.

If the energy of the bonding between the electrons and the sites is distributed over the range δE and $kT > \delta E$ (quite high temperatures), it may be assumed that the energy of the electron on hopping does not vary and the only variable that determines the rate of transit is R. As a result, as analysis has shown,[15] when $t < t_{tr}$ the current remains constant, but when $t > t_{tr}$ the current displays a prolonged non-exponential decay. If the important role played by the energy scatter of the bond between the electrons and sites when $\delta E > kT$ is taken into account in the percolation model, the current is given by expression (23), $\beta_1 = \beta_2 = \beta$.

Thus, in measurements of electron transfer, the percolation model predicts the possibility when the measurement temperature is increased of changing from a purely dispersive transport to a Gaussian one with a constant current when $t < t_{tr}$. However, such a change is also predicted by the zone model with repeated capture on replacing nonequilibrium transport with quasi-equilibrium (with an increase in temperature), which is due to the decrease of $\tau_l(E)$ so that for all depths $\tau_l(E) < t_{tr}$. Such a change has been observed more than once experimentally, for example, in PVCA it occurs at 424 K,[61] while in poly(*p*-phenylene sulphide) it occurs at 310 K.[62] It should be emphasised that in the initial CTRW model, transport is regarded as dispersive, regardless of the temperature and other factors, which is at variance with the results obtained for these systems.

The percolation model effectively accounts for the kinetic characteristics of electron transfer between transport sites, the dependence of μ on the width of the sample (l), and other phenomena, but it follows from it that

$$i(t, T, F) = (eF\mu/l)\hat{f}(T, t), \tag{24}$$

namely, that the mobility μ is independent of F. This is at variance with the experimental data, according to which the dependence μ on F is almost exponential. A similar situation occurs in the CTRW model.

The discrepancies between the theoretical models and experiment that have been detected are so serious that, in order to simplify the interpretation of the experimental results, in recent years measurements have been conducted on polymer systems in which dispersive transport is absent and i = const when $t < t_{tr}$. In this case the mobility does not depend on the width of the film sample. It is these systems, mainly polymer dielectric matrices (PC, PS) doped with aromatic amines and diamines,[63] which are examined below. In such systems the average distances between the neighbouring sites can readily be varied by changing the concentration of transport sites. In the majority of the experiments carried out the dependence of μ on the three main parameters—R, T, and F—has been studied. All of the experimental results are effectively related by the equation

$$\mu = \frac{eR^2}{kT} \exp[f_1(R)] \exp[f_2(T, R)] \exp[f_3(F, T, R)], \tag{25}$$

when $F \to 0$, $f_3(F, T, R) \to 0$, and the absence of the cofactor $[f_3(F, T, R)]$ in expression (25) gives a zero-field approximation. Attention was drawn for the first time by Gill[65] to the fact that in amorphous polymer systems the mobility μ is related to R by:

$$\mu \sim R^2 \exp[-2(R - R_0)/\alpha]. \tag{26}$$

Hence it follows that $f_1(R) = -2(R - R_0)/\alpha$. Thus, $\exp[f_1(R)]$ in expression (25) is the factor for overlap of wave functions of the neighbouring sites [see equations (8) and (16)]. In the majority of cases an activation dependence of μ on T occurs. On Arrhenius coordinates when measurements are made over a wide temperature range, a reduction in the energy of activation ΔE_a sometimes occurs in the high-temperature region (above 300 K). Furthermore, ΔE_a usually increases with an increase in R, in other words, it may be assumed that $f_2(T, R) = -\Delta E_a(R)/kT$. In all of the experimental and theoretical models[66,67] the cofactor $f_3(F, T, R)$ reflects the reduction in the energy barrier for electron transfer in an electric field and is usually written as $f_3(F, T, R) = e(R - R_0)F/kT$.

As a result, in representing the experimental data use is made of a simple relationship of the form:

$$\mu = \frac{eR^2}{kT} \exp[-(R - R_0)/\alpha] \exp\{-[\Delta E_a - e(R - R_0)F]/kT\}. \tag{27}$$

For a more complete representation of the experimental data it is necessary to find more exact relationships and to select the most realistic models of charge transfer in polymer systems.

The exponential dependence of μ on F in the model of repeated capture on traps in the case of quasi-equilibrium transport is due to the Frenkel–Poole effect; in this case $f_3 = \eta F^{1/2}/kT$, where η is the Frenkel–Poole constant. However, the suitability of this model for polymer systems, as has already been mentioned, raises serious

objections and the Frenkel–Poole effect itself assumes the existence of a large concentration of charged traps in which charges are captured during transport. The latter is not likely for the single-component systems doped with molecules that are commonly studied such as PC + TPA, and also for PVCA and other transport polymers without added components.

Bassler et al.[66,68] used the Monte Carlo method to resolve the problem of electron transfer in a transport system that meets the following conditions:

1) the energy distribution of the bonding of the charges on sites is Gaussian:

$$\varphi(E) = (2\pi\sigma)^{-1/2} \exp(-E^2/2\sigma^2);$$

2) the factor for overlap of wave functions of the neighbouring transport sites is written in the form

$$\exp[f_1(R)] = \exp[-2(R - R_0)/\alpha];$$

3) the probability of a hop from the ith transport site to the jth site when $E_j > E_i$ is taken into account using the Boltzmann constant:

$$W_{ij} = \nu_0 \exp[-2(R - R_0)/\alpha] \exp[-(E_j - E_i)/kT]$$
$$W_{ji} = \nu_0 \exp[-2(R - R_0)/\alpha],$$

i.e.

$$W_{ij} \exp(-E_j/kT) = W_{ji} \exp(-E_i/kT).$$

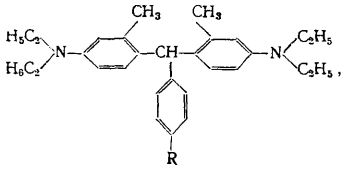
4) the electric field increases the number of transport sites on to which an electron can hop without activation; this occurs when $E_i + e(R - R_0)F > E_j$.

It was shown that the temperature dependence of mobility in such systems does not follow the Arrhenius equation, but in expression (25) $f_2 = -(T_0/T)^2$ and $f_3 = F/F_0$. Here $T_0 = K\sigma$ and

$$F_0 = \frac{T^2 R_0}{2B' eK^2 \sigma},$$

where K and B' are constants.

An analytical solution of this problem [69,70] leads to similar results: in this case K = 7400 Kl eV^{-1}, B' = 0.15. The values of T_0 and F_0 were calculated for different TPM derivatives–PC (TPM concentration of 40 wt.%) from the experimental dependences of μ on T and F determined by Pai et al.[71] and Bassler.[72]



where R = N$(C_2H_5)_2$; H; OH; Br; OCH_3; CN; NO_2.

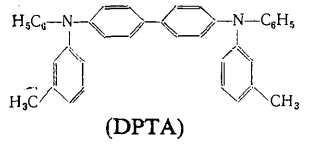
It was found for this series of derivatives that as the electron affinity of substituent R increases, the mobility of the charge carriers decreases by a factor of 10^4. It was suggested[72] that with an increase in electron affinity of substituent R, there is an increase in dopole moment (κ) of the TPM derivative, and consequently an increase in the polarity of the medium (ε).

According to Bassler[72] the spread of distances between neighbouring transport sites M results in a scatter (σ) of interaction energies between a charge on a site and the medium, and σ increases as ε increases, changing the values of F_0 and T_0. Even though the values of T_0 and F_0 vary considerably for the different TPM derivatives, their product remains constant $T_0/F_0 \simeq 310 \pm 4$ mV K cm^{-1} when T = const; this accords with the model under consideration: $T_0F_0 = T^2R_0/(2B'eK)$, and does not depend on σ. We should emphasise that the increase in the slope of the temperature dependences of $T_0 = K\sigma$ with an increase in κ does not unequivocally prove that there is a direct relationship between κ and σ. The slope may also depend on the intramolecular reorganisation energy (E_{in}) of the transport site M during an electron hop. This reorganisation energy naturally depends on the structure of M. Moreover, according to the Bassler model, for different values of F, straight lines on the coordinates of $\log\mu = f(T_0/T)^2$ should intersect at the same point on the y-axis [when $(1/T)^2 \to 0$] in accordance with equation (25). In fact, this characteristic was found for PVCA + TNF (1 : 0.2) systems.[72,73]

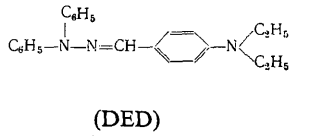
However, this model is not valid for polymers doped with aromatic amines since the relationships between μ, T and F do not hold in this case.

It should be mentioned that the relationship $\log\mu \sim (1/T)^2$ can reflect the temperature change of the energy of activation, which is possible for a Gaussian distribution of energy of the bonding of the charges on the transport sites; at which values of σ it ceases to be observed and what form it takes with other types of distribution is not clear at the present time (further investigation of this problem is required). Moreover, as has been indicated above, deviations from an Arrhenius relationship may be due to a change in the state of the polymer matrix as T increases and thus the relationship $f_2 = -(T_0/T)^2$ may be regarded as a special case of the temperature dependence of μ. A more general case is the Arrhenius dependence of μ on T with ΔE_a = const.

Interesting results were obtained for two systems based on PC doped with di (*N*-phenyl-*N*-*m*-tolyl)-*p*-aminobiphenyl (DPTA)[63] and *p*-diethylaminobenzaldehyde diphenylhydrazone (DED).[64]



(DPTA)



(DED)

It transpired that in DED the energy of activation (ΔE_a) does not depend on the distance R between the dopant molecules on changing R from 8 to 18 Å, while in DPTA it increases from 0.35 to 0.53 on changing R from 10 to 15.5 Å. The distance was determined from the equation $R = 3 \times 10^{27}/(4\pi \times N_A C^{1/3})$ Å, where C is the molar concentration of dopant. Values of μ [extrapolated to $F = 0$ ($f_3 = 0$)] and the energies of activation ΔE_a determined at different concentrations of C were used to calculate $f_1(R)$ from equation (25).[64] The result was that with these limits for varying R in DPTA, f_1 = const, namely, the $\exp(f_1)$ term in equation (25) does not depend on R, while in DED $f_1(R) = -2(R - R_0)/\alpha$ (where α = 1.7 Å). These results may be accounted for using a simple model of activated hops by polarons of small radius,[64,74] for which, as has been mentioned above, $\Delta G = 0$, $E_{in} = 0$, $G^{\neq} = E_s/4$.[20] For a nonadiabatic case in a zero-field approximation the mobility of a polaron of small radius is given by the expression:[64,74]

$$\mu = (eR^2/kT)\nu_0 \exp[-2(R - R_0)/\alpha] \exp(-G^{\neq}/kT). \quad (28)$$

where ν_0 is the frequency of optical phonons (without taking into account dispersion within the simple model), $G^{\neq} = e^2(1/r - 1/R)/4\varepsilon_p$, r is the radius of localisation if the charge, $1/\varepsilon_p = (1/n^2 - 1/\varepsilon)$. On comparing expressions (25) and (28) it is clear that

$$\exp(f_1) = \nu_0 \exp[-2(R - R_0)/\alpha]; \quad f_2 = -G^{\neq}/kT.$$

For small-sized DED molecules, for which $1/R < 1/r$, the effect of R on $G^{\neq}$ is small, which is in line with experiment. For the large DPTA

molecules, at all of the concentrations used R was comparable with $2r$ (i.e., there was contact between the molecules) and adiabatic electron transfer can be assumed. In this case

$$\exp(f_1) \approx \nu_0; \quad f_2 = -(G^{\neq} - V_{01})/kT. \tag{29}$$

Namely, in accordance with experiment f_1 does not depend on R, while the energy of activation in f_2 varies with R. This treatment is qualitative, but we should mention that, in accordance with (21), the rate constant of electron transfer $k_{et} = \exp(f_1)\exp(f_2)$ enters into the equations for μ [(25), (28) and (29)]. Expressions for the rate constant in the model for small-radius polaron hops constitute a special case of relationships (18) and (19) (when $\Delta G = 0$ and $E_{in} = 0$) for the rate constant of electron transfer between donor and acceptor components in a dielectric medium (model of the dielectric continuum).

The possibility of using the Marcus–Levich–Dogonadze–Kuznetsov[17] theory for the elucidation of electron transport in polymer media was demonstrated by Sahyun,[4] and the experimental proof was obtained by Vannikov et al.[75,76] in studying the effect of the polarity of the matrix on charge transport in a TPA + PC system. In this case the polarity was varied not by replacing the substituents in transport sites, as was carried out by Pai et al.,[71] but by the introduction of added components with different κ values that did not participate in transport. The added components were *p*-, *m*-, and *o*-dinitrobenzenes (DNB), which have dipole moments of 0.5, 4, and 6 D respectively. The concentration of TPA was 33 wt.% and that of DNB varied from 0 to 6 wt.%. It can be seen in Fig. 3 that at the same concentrations of DNB, *o*-DNB had the greatest effect on μ and ΔE_a and *p*-DNB had no effect.

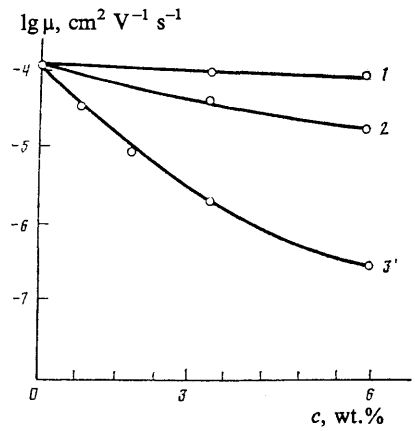


Figure 3. Dependence of the drift mobility of holes μ in the system PS + TPA on the concentration of added quantities of: *1*) *p*-DNB; *2*) *m*-DNB; *3*) *o*-DNB. TPA concentration = 33 wt.%.[75,76]

The ionisation potential of DNB in the gas phase is 10.5 eV, which is considerably higher than the ionisation potential of TPA (6.8 eV), therefore DNB molecules cannot be traps for holes, the transport of which occurs in TPA + PC systems. On increasing the concentrations of *o*-DNB to a value of 6 wt.%, the dielectric constant increases from 2.9 to 4.9 (in this system, $n^2 = 2.4$). The energy of activation for electron transfer may be determined, in accordance with what has been stated above, as

$$\Delta E_a \equiv G^{\neq} = \frac{(E_s + E_{in} + \Delta G)^2}{4(E_s + E_{in})}, \tag{30}$$

where ΔG is given by expression (11), $E_r = (E_s + E_{in})$, and E_s and E_{in} are determined from equations (15), (12), and (14) respectively.

For electron transfer through identical sites in an electric field F we can write $\Delta G = e(R - R_0)F$.

When the concentration of TPA is equal to 33 wt.%, $R = 10$ Å. In electron transfer from a neutral TPA molecule to a TPA^+ radical cation, a change in valence state of the nitrogen atom occurs. In TPA the nitrogen atom has a tetrahedral structure while in TPA^+ it is planar. The "inner-sphere" reorganisation energy E_{in} of the molecule, namely, the energy required for converting TPA to a TPA^+ form in the gas phase is 0.8–1.0 eV.[4] The experimental results of the dependence of μ and ΔE_a on the dielectric constant ε of the polymer matrix are shown in Fig. 4.[75,76] As can be seen, when ε increases from 2.9 to 4.9 μ decreases by a factor of 320 while ΔE_a increases from 0.18 to 0.46 eV. The curve of ΔE_a against ε, calculated from equation (30) [in calculating E_s from equation (12) it was assumed that $R = 25$, $r = 3$ Å, $E_{in} = 0.6$ eV, $F = 3 \times 10^5$ V cm^{-1}), is also given on Fig. 4. This value of E_{in} (less than that calculated in the gas phase) may occur because in the polymer matrix conformations of TPA^+ with different bond angles of the nitrogen atom are frozen,[77] resulting in a reduction in magnitude of E_{in}. On the whole the form of the curve agrees with the experimental results. The value of μ_1/μ_2, calculated from the equation

$$\mu_1/\mu_2 = \left[\exp\left(-\frac{\Delta E_{a1}}{kT}\right) \Big/ \exp\left(-\frac{\Delta E_{a2}}{kT}\right)\right] \simeq 320,$$

agrees with that obtained experimentally. Here the values of ΔE_{a1} and ΔE_{a2} are calculated from equation (30) when $\varepsilon = 2.9$ and 4.9 respectively. The difference between the experimental value of ΔE_a and that calculated for a maximum $\varepsilon = 4.9$ (see Fig. 4) may be due to the above-mentioned effect of the polarity of the medium on the energy spread of the bonding between a hole and M.

It should be mentioned that the models considered above (with the exception of the models of the polaron of small radius and the dielectric continuum) do not take into account the effect of the polarity of the medium on electron transfer in a polymer matrix. The cited experiment that involved a varying polarity of the medium showed that there is a dependence of the mobility of the charge carriers on the dielectric properties of the medium and also on the intramolecular reorganisation energy, which can only be explained on the basis of the dielectric continuum model of Marcus–Levich–Dogonadze–Kuznetsov.

II. Electron phototransfer

1. Tunnel electron phototransfer during exchange interaction in the ground state

The interaction of the wave functions [see (1) and (2)] results in stabilisation of the ground state of the system ($X_1 = E_i - E_0$) and destabilisation of the excited state ($X_2 = E_1 - E_{ex}$) by the amount (see Fig. 2*b*):[16,78–80]

$$X_{1,2} = \mp [\Delta G/2 - (\Delta G^2/4 + V_{01}^2)^{1/2}], \tag{31}$$

where E_i and E_{ex} are the energies of the ground and excited states of the D ... A system respectively (Fig. 2*b*); ΔG is given by equations (3) and (11). When $V_{01} \ll \Delta G/2$, expression (31) frequently reduces to the form:[16,79,80]

$$X_{1,2} = \mp\left\{\frac{\Delta G}{2} - \left[\frac{\Delta G}{2}\left(1 + \frac{4V_{01}^2}{\Delta G^2}\right)^{1/2}\right]\right\} = \pm\frac{V_{01}^2}{\Delta G}. \qquad (32)$$

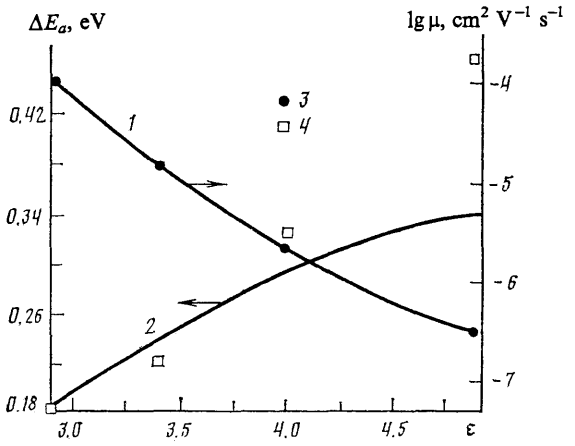


Figure 4. Dependence of the drift mobility of holes μ (curves *1* and *3*) and the energy of activation ΔE_a (curves *2* and *4*) on the dielectric constant of the polymer matrix ε. *1*) Calculation from expression (28); *2*) calculation from expression (30). Curves *3* and *4* are experimental results.[75,76]

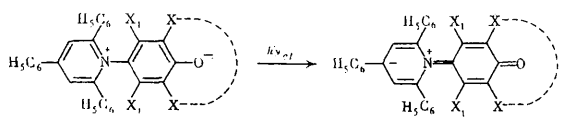
The spectroscopic distribution of the optical density $D(\nu)$ of the charge-transfer band (Fig. 1) is determined by the *FC* factor:[17,18]

$$D(\nu) = D(\nu_{max}) \exp\left[-\frac{(E_r + \Delta G - h\nu_{et})^2}{4E_r kT}\right], \qquad (33)$$

where $D(\nu_{max}) \sim V_{01}^2$ is the optical density at the maximum of the charge-transfer band, namely, when $h\nu_{et}^{max} = E_r + \Delta G$. According to expression (33), the width of the charge-transfer band is given by

$$h\Delta\nu_{1/2} = (2\ln 2)^{1/2}(2E_r kT)^{1/2}. \qquad (34)$$

The dependence of the position and shape of the charge-transfer band on E_r in liquid media has been studied experimentally.[83–86] In aqueous solution containing a high concentration of ferri- and ferrocyanide ions the shape of the electron-transfer band ($\lambda_{max} \sim 800$ nm) is determined by the "outer-sphere" reorganisation, to which the reorganisation energy of the solvent and the reorganisation of the ionic atmosphere make contributions.[83] Kjaer and Ulstrup[84,85] have studied the solvatochromism of intramolecular charge transfer in *N*-substituted 2,4,6-triphenylpyridines (betaines):



The position of the maximum of the charge-transfer band $h\nu_{et}^{max}$ in solutions of the betaines forms the basis for developing a polarity scale of the solvents.

In accordance with their effect on the width of the charge-transfer band, the solvents were divided into three groups: polar aprotic solvents, alcohols, and nonpolar aprotic solvents. In polar aprotic solvents, in accordance with equation (34), the shape of the band is determined by the relationship $E_r = E_s + E_{in}$, where the energy of intramolecular reorganisation results from the change in the C–O, N–C, and C–C bond lengths ($E_{in} = 0.2$ eV) on changing the distribution of charge by exposure to light with energy $h\nu_{et}$. In alcohols the change in vibrational frequencies of the hydrogen bonds formed between an alcohol and betaine makes an additional contribution to E_r. In nonpolar aprotic solvents the width of the charge-transfer band is determined not by E_r but by other forms of electrostatic interaction between the betaines and the solvent (dispersion forces, etc.).

A temperature-dependent ($\sim T^{1/2}$) broadening of the charge-transfer band in a mesitylene–tetracyanoethylene complex in hexane was established by Novikov et al.;[86] this was in complete agreement with expression (34).

According to Hopfield[18] the dipole moment of an optical transition $h\nu_{et}$ is given by

$$\mu_{ex,i} = \int \psi_{ex}^{*}\mu_{0d}\psi_i d\tau \simeq eRV_{0i}/\Delta G,$$

Here μ_{0d} is the dipole moment operator. The molar extinction coefficient of the $h\nu_{et}$ band is proportional to $(\mu_{ex,i})^2$.[16]

$$\varepsilon_{max} \sim \nu_{et}^{max}\mu_{ex,i}^2/\Delta\nu_{1/2}.$$

Where ε_{max} is the extinction coefficient at the charge-transfer band maximum (at ν_{et}^{max}), $\Delta\nu_{1/2}$ is the width of the spectrum or the distance between the points at which $\varepsilon_{1/2} = \varepsilon_{max}/2$. Thus,

$$\varepsilon_{max}^{na} : \varepsilon_{max}^{a} : \varepsilon_{max}^{DA} = (R^{na}V_{01}^{na})^2 : (R^{a}V_{01}^{a})^2 : [R_0V(R_0)]^2.$$

The values of ε_{max}^{na} and ε_{max}^{a} can be determined from the above-mentioned values of V_{01} of ~20 and 400 cm^{-1} respectively for non-adiabatic and adiabatic conditions of charge transfer and also from expression (16) for R, for example, in the approximation $V(R_0) = 1100$ cm^{-1}, $\alpha = 1$ Å, $R_0 = 7.4$ Å.[12] (For D·A complexes $R \simeq R_0$, i.e., $V_{01} \simeq V(R_0)$. After substitution we obtain

$$\varepsilon_{max}^{na} : \varepsilon_{max}^{a} : \varepsilon_{max}^{DA} = (11{,}4^2 \cdot 4 \cdot 10^2) : (8{,}4^2 \cdot 16 \cdot 10^4) : (7{,}4^2 \cdot 1{,}1^2 \cdot 10^6).$$

For D·A complexes $\varepsilon_{max}^{DA} \sim 10^3$ dm^3 mol^{-1} cm^{-1}, hence $\varepsilon_{max}^{a} \simeq 170$ and $\varepsilon_{max}^{na} \simeq 0.78$ dm^3 mol^{-1} cm^{-1}. The latter value agrees with the estimate obtained in two studies,[18,87] in which it is observed that ε usually does not exceed 1 dm^3 mol^{-1} cm^{-1}.

2. Tunnel phototransfer of electrons in the absence of an exchange interaction in the ground state

In the absence of a D·A interaction in the ground state, overlap of the orbitals of the components which gives rise to electron transfer can occur through photoexcitation of one of the components (Fig. 5). In contrast to a liquid, in which electron transfer mainly occurs after diffusion convergence of the components, in a solid (including a polymer) matrix noncontact exciplexes $(D \ldots A)^* \rightarrow (D^{+} \ldots A^{-})$, where $(D \ldots A)^*$ means $(^{1,3}D_1 \ldots {}^1A_0)$ or $(^1D_0 \ldots {}^{1,3}A_1)$, can participate in electron-transfer reactions. The wave functions of the initial excited and ionic state have the form [by analogy with expressions (1) and (2)]:

$$\psi_1(D \ldots A)^* = \psi_0(D \ldots A)^* + \lambda\psi_1(D^{+} \ldots A^{-}),$$

$$\psi_{11}(D^{+} \ldots A^{-}) = \psi_1(D^{+} \ldots A^{-}) - \lambda\psi_0(D \ldots A)^*.$$

The free energy $\Delta G'$ (Fig. 5) and λ are given by expression (3) when E_0 is replaced by $E_{0'}$ and V_{01} is replaced by $V_{01'}$.

$$E_0' = \int \psi_0^*(\mathrm{D}\ldots\mathrm{A})^* H \psi_0(\mathrm{D}\ldots\mathrm{A}) d\tau,$$

$$V_{01}' = \int \psi_0^*(\mathrm{D}\ldots\mathrm{A})^* H \psi_1(\mathrm{D}^{\dot{+}}\ldots\mathrm{A}^{\dot{-}}) d\tau.$$

The transformation of a noncontact exciplex into a contact form when the D and A components are brought closer together, i.e., when V_{01}' is increased, is similar to that shown in Figs. 1 and 2 for donor-acceptor systems interacting in the ground state.

In the present section we shall consider systems in which the distance R between the D ... A components is greater than the van der Waals radii. In these systems when component D or A undergoes photoexcitation in solid matrices, reactions leading to formation of the radical ion pair $^{1,3}[\mathrm{D}^{\dot{+}}\ldots\mathrm{A}^{\dot{-}}]$ can occur:

$$\left.\begin{array}{l} {}^{1,3}\mathrm{D}_1 + {}^1\mathrm{A}_0 \rightarrow {}^{1,3}\mathrm{D}_1 \ldots {}^1\mathrm{A}_0 \\ {}^1\mathrm{D}_0 + {}^{1,3}\mathrm{A}_1 \rightarrow {}^1\mathrm{D}_0 \ldots {}^{1,3}\mathrm{A}_1 \end{array}\right\} \rightarrow {}^{1,3}(\mathrm{D}^{\dot{+}}\ldots\mathrm{A}^{\dot{-}}) \rightarrow \left\{\begin{array}{l} \mathrm{D}^{\dot{+}} + \mathrm{A}^{\dot{-}} \\ \text{products} \\ {}^1\mathrm{D}_0 + {}^1\mathrm{A}_0 \end{array}\right. \quad (35)$$

$$({}^2(\mathrm{D}^{\dot{+}}\ldots{}^2\mathrm{A}^{\dot{-}}))$$

(The equilibrium $^{1,3}[\mathrm{D}^{\dot{+}}\ldots\mathrm{A}^{\dot{-}}] \rightleftharpoons [{}^2\mathrm{D}^{\dot{+}}\ldots{}^2\mathrm{A}^{\dot{-}}]$ corresponds to a weak spin correlation (or its absence) of radical ions that are separated by a distance greater than the van der Waals radii.)

In reactions (35) a photoexcited charge-transfer complex involving a bridging molecule (B) can act as one of the components:

$$\left.\begin{array}{l} {}^{1,3}(\mathrm{D.B})_1 + {}^1\mathrm{A}_0 \rightarrow {}^{1,3}(\mathrm{D.B})_1 \ldots {}^1\mathrm{A}_0 \\ {}^1\mathrm{D}_0 + {}^{1,3}(\mathrm{B.A})_1 \rightarrow {}^1\mathrm{D}_0 \ldots {}^{1,3}(\mathrm{B.A})_1 \end{array}\right\} \rightarrow {}^1\mathrm{B}_0 + \left\{\begin{array}{l} {}^{1,3}[\mathrm{D}^{\dot{+}}\ldots\mathrm{A}^{\dot{-}}] \\ {}^2[\mathrm{D}^{\dot{+}}\ldots\mathrm{A}^{\dot{-}}] \end{array}\right.$$

and subsequently as in reaction (35). Reactions of this type have been studied in detail in a review,[12] in which various classes of dyes that can cause spectroscopic sensitization of electron transfer in donor-acceptor systems are used as a bridging molecule. The free energy of electron transfer according to reaction (35) is given by (Fig. 5):

$$\Delta G' = eE_{1/2}({}^{1,3}\mathrm{D}_1/\mathrm{D}^{\dot{+}}) - eE_{1/2}(\mathrm{A}^{\dot{-}}/{}^1\mathrm{A}_0) + e^2/\varepsilon_s R \quad (36)$$

or

$$\Delta G' = eE_{1/2}({}^1\mathrm{D}_0/\mathrm{D}^{\dot{+}}) - eE_{1/2}(\mathrm{A}^{\dot{-}}/{}^{1,3}\mathrm{A}_1) + e^2/\varepsilon_s R. \quad (36a)$$

Here

$$E_{1/2}({}^{1,3}\mathrm{D}_1/\mathrm{D}^{\dot{+}}) = E_{1/2}({}^1\mathrm{D}_0/\mathrm{D}^{\dot{+}}) - E({}^{1,3}\mathrm{D}_1),$$

$$E_{1/2}(\mathrm{A}^{\dot{-}}/{}^{1,3}\mathrm{A}_1) = E_{1/2}(\mathrm{A}^{\dot{-}}/{}^1\mathrm{A}_0) + E({}^{1,3}\mathrm{A}_1),$$

where $E(^{1,3}\mathrm{D}_1)$ or $E(^{1,3}\mathrm{A}_1)$ is the distance from the ground to excited singlet or triplet level of molecule D or A; $E(^1\mathrm{D}_1)$ and $E(^1\mathrm{A}_1)$ are the energies that correspond to unrelaxed Franck–Condon or relaxed excited states of the molecules. When excited molecules of D or A participate in phototransfer of an electron in a Franck–Condon state [reactions (35)], the probability of a radical ion pair being formed is determined from the difference $E_e - G^{\neq}$ (see Fig. 5*a* and 5*b*), where E_e is the excess energy of the (D ... A) system that occurs in a Franck–Condon state above the energy at the minimum of the potential curve. In the region $E_e < G^{\neq}$, the probability of electron transfer increases exponentially as E_e increases

$$P_{et} = A' \exp\left[-\frac{-E_e + G^{\neq}}{c}\right],$$

and reaches a maximum value at $G^{\neq} - E_e = 0$. (In this equation $c = kT$ if $\hbar\omega \ll kT$ and $c = \hbar\omega$ if $\hbar\omega \gg kT$.) Under nonadiabatic conditions P_{et} decreases as the kinetic energy $\Gamma = E_e - G^{\neq}$ increases in the region $E_e > G^{\neq}$ because of the increased probability of passing through the intersection point of the potential curves on its pathway, i.e., without electron transfer (Fig. 5*a*).[88]

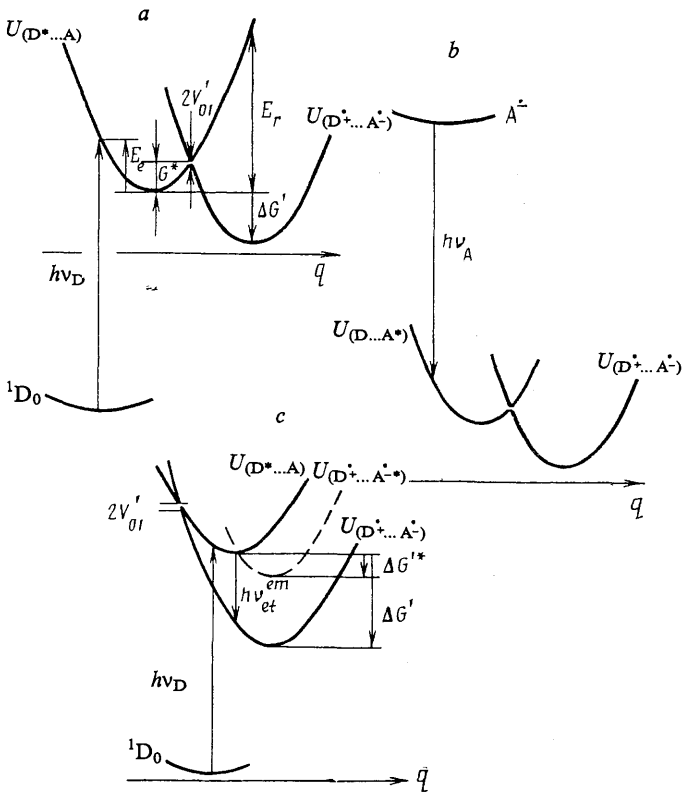


Figure 5. Dependence of the potential energies $U_{(D^*\ldots A)}$ (*a* and *c*), $U_{(D\ldots A^*)}$ (*b*), $U_{(D^{\dot{+}}\ldots A^{\dot{-}})}$, and $U_{(D^{\dot{+}}\ldots A^{\dot{-}*})}$ on the generalised coordinate q. The parameters that determine the probability of electron phototransfer under nonadiabatic conditions without an exchange interaction in the ground state during photoexcitation of the donor $h\nu_D$ (*a* and *c*) or acceptor $h\nu_A$ (*b*) are given. $^1D_0$ (*a* and *c*) and $A^{\dot{-}}$ (*b*) correspond to the energies of the donor in the ground state and of the radical anion of the acceptor respectively. The free energy $\Delta G'^*$ corresponds to the transfer of an electron to an electronically or vibrationally excited energy level of the acceptor.

When relaxed $^{1,3}(\mathrm{D}\ldots\mathrm{A})_1$ states participate in electron transfer the probability of electron transfer corresponds to the relationship $P_{et} = A' \exp(-G^{\neq}/c)$. In systems with a large negative free energy $-\Delta G'$ (Fig. 5*c*) the rate constant may be determined by electron transfer not to the lowest unfilled acceptor orbital but to a higher level that corresponds to formation of an acceptor radical anion in an electronically excited or vibrationally excited state. In both cases

$$k_{et} = A' \exp\{-[(\Delta G' - E') + E_s]^2/4E_s c\}.$$

In the first case $E' = E(\mathrm{A}^{\dot{-}*})$, in the second $E' = \nu\hbar\omega_{in}$; E_s is calculated from equation (12).

With high negative values of $-\Delta G'$ an emissive charge-transfer transition is to be expected (Fig. 5*c*)

$$(D \ldots A)^* \rightarrow (D^{\ddagger} \ldots A^{\dot{-}}) + h\nu_{et}^{em}$$

and also emission from an excited A^{-*} state:

$$(D^{\ddagger} \ldots A^{\dot{-}*}) \rightarrow (D^{\ddagger} \ldots A^{\dot{-}}) + h\nu_{A}^{em}.$$

It should be mentioned that electron transfer by route (35) can occur with local excitation of one of the components of the D ... A system in which there is an exchange interaction in the ground state (Fig. 6). Under nonadiabatic conditions this route is more effective than electron transfer on exposure to light $h\nu_{et}$, since, as was mentioned above, the charge-transfer band has a low extinction coefficient. Under these conditions light with energy $h\nu_D$ (or $h\nu_A$) accelerates the charge-transfer reaction.[3]

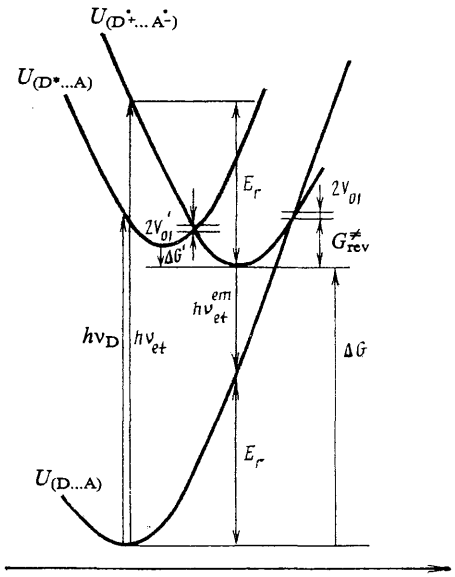


Figure 6. Dependence of the potential energies $U_{(D \ldots A)}$, $U_{(D^* \ldots A)}$, $U_{(D^{\dot{+}} \ldots A^{\dot{-}})}$ on the generalised coordinate q. The parameters that determine the probability of electron phototransfer under nonadiabatic conditions when there is an exchange interaction in the ground state during photoexcitation of the donor $h\nu_D$ or the D ... A system $h\nu_{et}$; $G^{\neq}_{rev}$ is the energy of activation of the reverse reaction of (4).

When there is an exchange interaction (V_{01}) in the ground state (Fig. 6), reverse electron transfer can occur both by a route that involves surmounting the potential barrier $G^{\neq}_{rev}$ and with emission of $h\nu^{em}_{et}$:[89,90]

$$D^{\ddagger} \ldots A^{\dot{-}} \rightarrow D \ldots A + h\nu_{et}^{em}.$$

It follows from the positions of the levels shown in Fig. 6 that $h\nu_{et} + h\nu_{et}^{em} = 2\Delta G$ and the Stokes shift is given by $h\nu_{et} - h\nu_{et}^{em} = 2E_r$.[89,90]

A number of studies[91–101] examine the factors that determine the tunnelling distance during photoexcitation of the D (or A) components over a wide temperature range, including room temperature, in higher alcohols[91,92] and polymer matrices [polycarbonate,[93] cellulose,[94–97] polyvinylpyrrolidone (PVP),[98] polystyrene,[99] polyvinyl acetate (PVA) and polymethylstyrene (PMS)[100,101]]. The tunnelling distance was determined from the dependence of the intensity (I) of luminescence of the excited component in a D ... A system on the concentration of quencher Q (where Q ≡ D or A).

The quenching of luminescence, which occurs by an electron-transfer mechanism in these systems, is given by the Perrin model:

$$I/I_0 = \exp(-N_A V[Q]), \qquad (37)$$

where V is the volume of the "active" sphere containing a quencher molecule. According to this model, excitation of a molecule is either quenched or not quenched at all depending on whether the molecule is within the "active" sphere or outside it. The radius of the "active" sphere R_q is determined from the relationship:

$$N_A V [Q]_0 = (4\pi/3) R_q^3 N_A [Q]_0 = 1, \qquad (38)$$

where $[Q]_0$ is the concentration of quencher at which the intensity of luminescence calculated from (37) is e times weaker than in the absence of quencher. Hence

$$R_q = (3 \cdot 10^{27}/4\pi N_A [Q]_0)^{1/3}, \text{ Å}.$$

The relationship between R_q and the energy characteristics of electron transfer was determined from equation (18) when $R = R_q$:[91]

$$(R_q - R_0) = \frac{\alpha}{2} [\ln(\nu_0/k_{et}) - (\Delta G' + E_r)^2/4E_r kT]. \qquad (39)$$

Here $R_q - R_0$ is the tunnelling distance. The constant k_{et} may be obtained experimentally from kinetic measurements of luminescence from the expression $k_{et} = (1/\tau_f) - (1/\tau_0)$, where τ_0 is the inherent lifetime of excitation and τ_f is the lifetime of excitation in the presence of a quencher at concentration $[Q]_0$.

The dependence of R_q on $\Delta G'$ in electron phototransfer reactions from excited ruthenium complexes with different types of ligands to a methyl viologen quencher (MV^{2+}) has been determined.[92] This dependence has a maximum ($R_q - R_0$) = 3 Å when $-\Delta G' = E_r = 0.7$ eV. In reactions involving the quenching of excited acceptors (rubrene, tetracene, perylene, 9-methylanthracene, 9,10-diphenylanthracene, fluoranthrene, acridinium) by amines (TMPD and diethylamine), the tunnelling distance determined from expression (39) is given by ($R_q - R_0$) = 7–10 Å and α = 0.75 Å. Expression (39) effectively represents the dependence of R_q on $\Delta G'$ obtained experimentally[98] in the quenching of the singlet excited dye rhodamine B by electron transfer to the dye from such donors as TMPD, 10-methylphenothiazine, ferrocene, pentamethylferrocene, ascorbic acid and also from the dye to acceptors such as dipyridinium salts with various substituents in a PVP matrix. It was established that ($R_q - R_0$) increases from 0 to 16 Å as $\Delta G'$ decreases from 0.2 to –1.0 eV.

Palazzotto et al.[100,101] have studied the fluorescence quenching of rhodamine 6G (R6G) by donor quenchers such as carbazole, triphenylamine (TPA), *N,N*-dimethyl-*p*-toluidine (DMT), phenothiazine (PT), *N*-methylphenothiazine (MPT), 1,4-diazabicyclo[2.2.2]octane, *N,N'*-diphenyl-*p*-phenylenediamine (DPPD), and *N*-phenyl-*p*-phenylenediamine (PPD) in PVA and PMS films. It has been shown[101] that R6G forms charge-transfer complexes with these donors (in the ground state). The complex formation constant (K, $dm^3\ mol^{-1}$) depends on the nature of the polymer matrix and for different donors (in brackets) is for PVA and PMS respectively: 2.8 and undetermined (TPA), 5.9 and 5.8 (DMT), 5.7 and 8.7 (MPT), 7.5 and 56.3 (PT), 9 and 35.9 (DPPD), 10.3 and 41.7 (PPD). Molecules of R6G that do not form a complex are responsible for fluorescence in this case; the

proportion of these is given by

$$([R6G]_0 - [D.R6G])/[R6G]_0 = 1/(1 + K[D])^{-1}.$$

where $[R6G]_0$ and [D·R6G] are the total concentration of dye and the final concentration of dye forming a complex respectively. When the radius R_q was calculated[101] from equation (38) the volume of the "active" sphere was determined from the experimental dependence of the intensity of fluorescence of R6G molecules on the concentration of donor (quencher) according to the equation:

$$I/I_0 = (1 + K[D])^{-1} \exp(-N_A V[D]). \quad (40)$$

The free energy $\Delta G'$ was calculated from expression (36a) (for the approximation $e^2\varepsilon_s R = 0$). It was found[101] that when $\Delta G'$ decreased from –0.55 to –1.11 eV, R_q increases from 3 to 10.9 Å in a PVA matrix and from 9.6 to 12.1 Å in a PMS matrix.

In several studies[93–97,99] a model[102,103] which takes into account the random distribution of interaction distances R was applied to polymer systems. According to this model

$$I/I_0 = \exp\{-k_0 t - A[\ln^3(\nu_0 t) + 1.73165 \ln^2(\nu_0 t) + 5.9343 \ln(\nu_0 t) + 5.44]\}.$$

Here $A = \alpha[Q]/R_q^3[Q]_0$.[93–97,99] The value of Q_0 is calculated from expression (38). The dependence of the tunnelling distance $(R_q - R_0)$ on the free energy $-\Delta G'$ calculated from this expression is given in Table 2. The increase in the disance $(R_q - R_0)$ as $-\Delta G'$ increases and as the temperature rises is demonstrated. This model satisfactorily represents the fluorescence quenching of TMPD and tetramethylbenzidine (TMB) with phthalic anhydride (PA)[99] and methyl viologen[97] respectively. Determinations of R_q (17 Å) and α (1.73 Å) have been made for the system $^3TMPD_1...^1PA_0$ in polystyrene[99] and also R_q = 38 Å and α = 3.4 Å for $^3TMB_1...^1(MV^{2+})_0$ in cellulose.[97] Unfortunately, in all of the studies mentioned above, in the calculation of $(R_q - R_0)$ and α, the possible increase in the size of the molecule (i.e. R_0) on going to an excited singlet and triplet state was not taken into account. The considerable tunnelling distances obtained in a number of systems are due to a superexchange mechanism, with fragments or defects in the polymer chains being regarded as bridging groups.[93]

3. Effects of the polymer matrix on the optical absorption properties of charge-transfer complexes

D ... A systems in which the distance between the components is greater than the sum of their van der Waals radii have been examined above. In these systems radical ions with separate solvation shells are formed through electron transfer. In the case of excited contact D·A complexes the point dipole model[19,81,89,104] has been used. The transformation of a two-sphere model, namely, a model with separate solvation shells in which the reorganisation energy of the medium is given by expression (12), into a single-sphere system that corresponds to a point dipole model has been reported.[89] The dipole κ [$\kappa \equiv e[r_D + r_A)$] produces an Onsager reaction field in the dielectric:

$$R(\varepsilon) = \frac{2\kappa}{a^3} F(\varepsilon) \quad \text{or} \quad R(n) = \frac{2\kappa}{a^3} F(n),$$

where $R(n)$ is the electronic component of the reaction field, $F(\varepsilon) = (\varepsilon - 1)/(2\varepsilon + 1)$ and $F(n) = (n^2 - 1)/(2n^2 + 1)$, a is the radius of the cavity occupied by the polarising dipole. The interaction energy of the dipole κ with the reactive field is given by

$$-\kappa R(\varepsilon) = -\frac{2\kappa^2}{a^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) \quad \text{or} \quad -\kappa R(n) = -\frac{2\kappa^2}{a^3}\left(\frac{n^2 - 1}{2n^2 + 1}\right). \quad (41)$$

As in the case of the two-sphere model the Stokes shift between the excitation maxima and fluorescence emission of the D·A complex is determined by the reorganisation energy ($E_r = E_{in} + E_s$) and is given by the Lippert – Mataga expression[19,104] (see Fig. 2*b* and Fig. 6):

$$h\nu_{et} - h\nu_{et}^{em} = 2E_r = 2E_{in} - [\kappa R(\varepsilon) - \kappa R(n)] = 2E_{in} + \frac{2\kappa^2}{a^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right). \quad (42)$$

Table 2. Increase in $(R_q - R_0)$ as $-\Delta G'$ increases in the fluorescence quenching of RuL_3^{2+} ruthenium complexes by methyl viologen (L = ligand).[93]

Ligand in RuL_3^{2+}	$-\Delta G'$, eV	$(R_q - R_0)$, Å at:	
		77 K	293 K
4,7-Dimethylphenanthroline	—0.13	6.4	10.6
2,2'-Bipyridine	—0.4*	—	10.0*
5-Chlorophenanthroline	—0.49	10.5	14.6
2,2'-Bipyridine 4,4'-diisopropyl ether	—0.88	15.9	18.9

*Reported value.[94]

Expression (42) has been successfully used for an experimental determination from the Stokes shift of the phase (ε, n) in which a D·A complex is formed in complex biological systems.[104]

A detailed analysis of the effect of dielectric properties in liquid media on the position of the maximum in the optical spectrum of D·A molecular complexes is given in a number of review articles (a general treatment of them is given by Davis[81]). In accordance with expression (33), in condensed media

$$h\nu_{et}^{max} = \Delta G' + E_r \equiv (\Delta G' + E_{in}) + E_s.$$

Since the optical absorption spectrum corresponds to a transition from the ground to an excited Franck – Condon state, the electronic polarisation of the medium $\kappa R(n)$ is synchronous with this process. Hence,

$$h\nu_{et}^{max} = h\nu_{et}^{max}(\text{gas}) - \frac{2\kappa^2}{a^3}\left(\frac{n^2 - 1}{2n^2 + 1}\right). \quad (43)$$

Here

$$h\nu_{et}^{max}(\text{gas}) = I_D - E_A - e^2/R + 2X + E_{in}, \quad (44)$$

where, according to (31) and (32), $2X = |X_1| + |X_2|$. The dependence of $h\nu_{et}^{max}$ on the dielectric properties of the medium (including polymer matrices) for the complexes $(C_5H_5)_2Fe.CBr_4$, $DPBA.CBr_4$, and $DPBA.CBr_3SO_2CBr_3$ (DPBA = diphenylbenzylamine) has been determined.[105] An analysis of the long-wavelength decrease in optical absorption of these complexes showed that in all the media studied the optical spectrum has a Gaussian form

$$D(\nu) = D(\nu_{max}) \exp[-(\nu_{max} - \nu)^2/2(\sigma \cdot 10^3)^2], \quad (45)$$

where $\sigma \times 10^3 = (\nu_{max} - \nu_{1/2}) \times (2 \ln 2)^{1/2}$. It was established experimentally (Fig. 7) that the position of the maximum in the optical absorption spectrum of a $(C_5H_5)_2Fe.CBr_4$ complex conforms to a relationship which is common to liquid systems and solid polymer

matrices:

$$h\nu^{max} = 3.9 - 3.1\,(n^2 - 1)/(2n^2 + 1). \quad (46)$$

The degree of charge transfer (δ^*) in the excited state of the complex $[(C_5H_5)_2Fe^{+\delta^*}.CBr_4^{-\delta^*}]$ was determined approximately from the assumption that $r_D = r_A = r$, $R_0 = 2r$, $a = 2r$, i.e., according to expressions (43) and (46) $(2\kappa^2/a^3) = (e^2\delta^{*2}/r) = 3.1$. An estimated value of $e^2/r = 3.8$ was obtained[12] by correlating a large number of experimental results in the literature on the polarisation of liquid media by radical cations of aromatic hydrocarbons, radical anions and cations of different types of dyes, and radical anions of various acceptors. By using this value for $(C_5H_5)_2Fe.CBr_4$ complexes, the degree of charge transfer in the excited state $\delta^* = (3.1/3.8)^{1/2} \simeq 0.9$ was calculated. The degree of charge transfer in this complex in the ground state ($\delta = 0.1$) was determined from the reported[106] dependence of δ on $I_D - E_A$ for complexes of this type. The fulfillment of the relationship $\delta^* = 1 - \delta$ is an indication that the excited state of the $(C_5H_5)_2Fe.CBr_4$ complex corresponds only to electron transfer ($h\nu^{max} = h\nu_{et}^{max}$) and does not contain contributions from local excitations of the individual donor or acceptor components. The half-width of the optical spectrum of this complex has a constant value in all of the media studied (both liquid and polymer)

$$(\nu_{max} - \nu_{1/2}) = \sigma \cdot 10^3\,(2\ln 2)^{1/2} = 3850 \pm 140 \text{ см}^{-1}$$

and is due to an electronic-vibrational interaction.[77]

It may be noted that for exciplexes (which, as was mentioned above, do not have an optical absorption spectrum since they are only formed by photoexcitation of the D or A component) the emission energy from a relaxed state is given by the expression:[79,80,107]

$$h\nu_{et}^{em} = h\nu_{et}^{em}(\text{gas}) - \frac{2\kappa^2}{a^3}\left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{1}{2}\,\frac{n^2 - 1}{2n^2 + 1}\right],$$

from which the dipole moment κ and degree of charge transfer in a relaxed exciplex can be determined.[107] In this case the energy of the relaxed exciplex is assumed to be equal to

$$E^* = E^*(\text{gas}) - \frac{\kappa^2}{a^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right).$$

A characteristic feature of the optical spectra of DPBA.CBr_4 and DPBA.$CBr_3SO_2CBr_3$ is their broadening on going from liquid media to polymer matrices (retaining a Gaussian form) and a subsequent increase in the width of the spectrum on reducing the generalised free volume V_E' of the polymer composite.[105] Table 3 gives the values of $(\nu_{max} - \nu_{1/2})$, the free volume V_E of the polymer, and the generalised free volume V_E' of the composite, calculated on the assumption that it is an additive function of the free volume of the components:

$$V_E' = \Sigma \Phi_i V_{E,i}.$$

Here Φ_i is the volume fraction of an individual component in the polymer and $V_{E,i}$ is its free volume.

It follows from Table 3 that the width of the optical spectrum of the DPBA.$CBr_3SO_2CBr_3$ complex remains constant on changing the liquid solvent. The increase in $(\nu_{max} - \nu_{1/2})$ in the series of polymers (Table 3) may be due to the reduction in generalised free volume V_E'.

It was established using PVC matrices that the optical spectrum of the DPBA.$CBr_3SO_2CBr_3$ complex contracts reversibly when the temperature is increased. The spectra recorded as the temperature was reduced from 80° to 77° and then 60 °C are shown in Fig. 8. It is clear that as a result of reducing the temperature the optical density decreases in the region of maximum absorption of the complex (about 365 nm) but increases at longer wavelengths in the spectrum (420–650 nm). In this case the change in optical density on reducing the temperature from 77 to 60 °C is comparable in magnitude with the change over the narrow temperature region (80 → 77 °C) of the glass transition temperature of PVC ($T_g \sim 78$ °C).

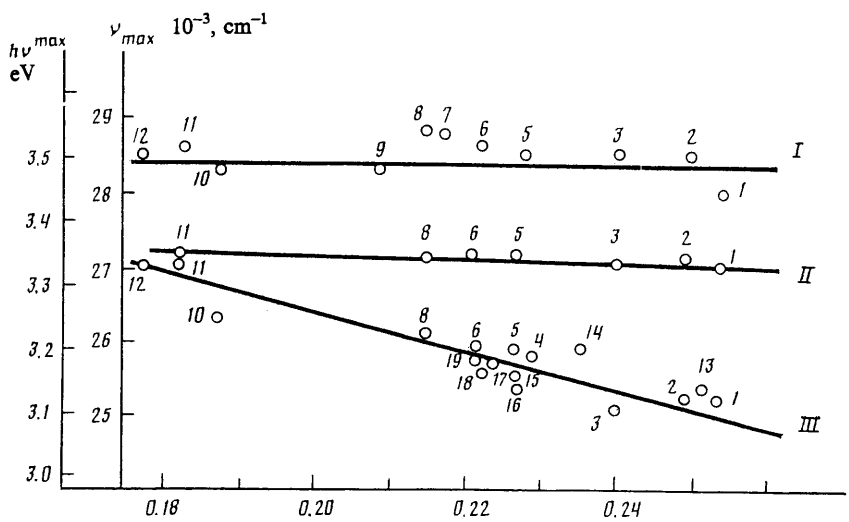


Figure 7. Dependence of ν_{max} and $h\nu_{max}$ on $(n^2 - 1)/(2n^2 + 1)$ in composites containing the following complexes: *I*) DPBA.CBr_4; *II*) DPBA.$CBr_3SO_2CBr_3$; *III*) $(C_5H_5)_2Fe.CBr_4$. The experimental results were obtained by Grishina et al.[105] The points correspond to: *1*) PS; *2*) CPVC; *3*) PVC; *4*) benzene; *5*) toluene; *6*) PMMA; *7*) dimethyl sulphoxide; *8*) PVA; *9*) dichloroethane; *10*) n-hexane; *11*) acetone; *12*) acetonitrile; *13*) PC; *14*) PVP; *15*) polyvinylethylal; *16*) polyvinylformalethylal; *17*) polybutyral; *18*) polybutyl metha-crylate; *19*) acetylcellulose.

It was suggested[108] that the broadening of the spectra of such complexes on going from liquid media to polymer matrices is due to the formation of mD·nA complexes with different ratios of m/n. In a polymer matrix the alteration in the ratio between complexes with different compositions when the temperature is varied is suppressed and it cannot be regarded as the only reason for the temperature dependence of the width of the optical spectrum.

Table 3. Free volume of liquid or polymer (V_E), generalised from volume of composite (V_E'), width of optical spectrum ($\nu_{max} - \nu_{1/2}$), calculated for a DPBA.$CBr_3SO_2CBr_3$ complex in liquid media and polymer matrices.[105]

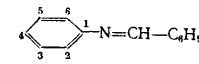
Medium	V_E, cm^3 mol^{-1}	V_E' cm^3 mol^{-1}	$(\nu_{max}-\nu_{1/2})$, cm^{-1}
	Liquid		
n-Hexane	62.5	62.5	2320
Toluene	43.7	43.7	2320
Benzene	35.9	35.9	2320
Acetone	34.5	34.5	2320
Acetonitrile	23.2	23.2	2320
	Polymer matrix		
PS	31.83	40.27	2850
PMMA	23.17	37.98	3040
PVA	24.51	36.83	3200
PVC*	18.56	35.22	3290
CPVC**	15.14	35.80	3350

*poly(vinyl chloride)
**chlorinated poly(vinyl chloride)

The combined experimental data, namely, the broadening of the optical spectra on going from liquid media to polymer matrices, the broadening as the free volume of a polymer is reduced, the temperature-dependent contraction of the spectrum in a polymer matrix (Fig. 8) have been accounted for[77,105] on the basis of the conformational isomerism of benzylanilines (including DPBA) and the freezing in a limited free volume of conformations which do not occur under equilibrium conditions in a liquid. Conformational isomerism is taken to mean the existence amongst benzylanilines of a "set" of structures which differ according to the rotation angle (φ) of the nonbonding orbital of the amino group relative to the plane of the benzene ring (Fig. 9).

Freezing out of isomers with a different angle of rotation φ (twist angle) account for the photophysical properties of substituted anilines that are introduced into the polymer matrix; donor (amino group) and, in a *para*-position relative to it, acceptor (cyano, ester, 9-anthryl, or other groups) fragments are combined in a single aniline molecule.[109–114] The slowing down in the reorientation of angle φ in polymer matrices at room temperature causes a nonuniform broadening of the fluorescence excitation spectrum of these compounds. This broadening appears as an enlargment of the spectrum at longer wavelength, at which there is no absorption in the liquid phase.[111,112] On exposure to light at longer wavelength isomers with an increased twist angle are selectively exicted, being converted with high probability to an excited charge-transfer state corresponding to $\varphi = 90°$.

The formation of molecular conformations with different equilibrium rotation angles of the aromatic ring about the C(1)–N bond in substituted *N*-benzylidenanilines



has an effect on a number of physicochemical properties of these compounds.,[115–117] Thus, introduction of a substituent into the 2-position (or 2- and 6-positions), which results in the aromatic ring being forced out of conjugation with the n orbital of the nitrogen ring, causes a decrease in ionisation potential (in the gas phase) from 8.25 (with no substituents) to 8.06 (or 8.00) eV.[116] It was established by NMR that introduction of an NO_2 group at a *para*-position relative to the C(1)–N bond increases the degree of conjugation of the aromatic ring with the nonbonding orbital of the nitrogen atom.[116] According to Akaba et al.[117] this results in an increase in ionisation potential of the molecule to 8.76 eV.

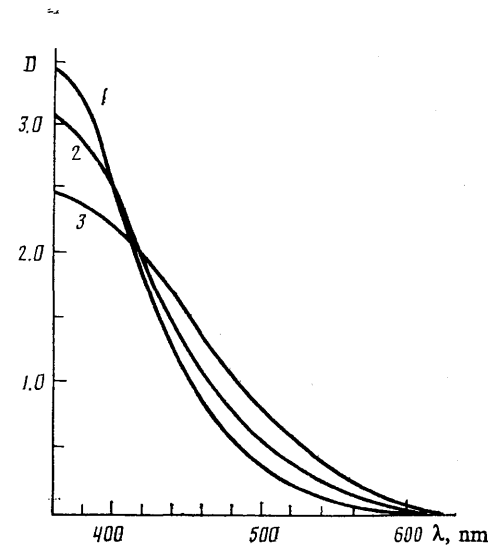


Figure 8. Optical spectra of the DPBA.$CBr_3SO_2CBr_3$ complex in a PVC matrix recorded as the temperature is decreased from 80 °C (1) to 77 °C (2) and 60 °C (3).

Benzylanilines (including DPBA) in polymer matrices where there is a limited free volume also exist in various conformations that differ according to the magnitude of their angle of rotation φ as a result of steric hindrance produced by the matrix (Fig. 9). These orientations of φ are frozen because of the long relaxation times of the polymer. It can be seen from Fig. 9 that a change in angle φ gives rise to a change in the degree of overlap of the π-electron orbitals of the aromatic ring and the n orbital of the unshared electron pair (UEP) of the nitrogen atom. This overlap is at minimum when $\varphi = 90°$ and increases as φ decreases to 0°.

In the formation of an intermolecular $n-\sigma^*$ complex in which the acceptor is coordinated with the nitrogen atom of benzylaniline, the n orbital of the nitrogen atom is involved as the donor in the interaction with the acceptor if $\varphi = 90°$, in other words, if the amino group is not conjugated with the benzene ring. If $\varphi = 0°$ the donor properties of benzylaniline are determined by the system of conjugated bonds that include the benzene ring and the UEP of the

nitrogen atom. For this reason,[44] instead of the statistically averaged gas-phase potential I_D it is necessary to use the inverse of the energy of that benzylaniline orbital (I_{BA}) which undergoes a donor-acceptor interaction.[77,105] Its magnitude is determined by the expression

$$I_{BA} = I_0 + I\cos^2\varphi. \quad (47)$$

When $\varphi = 0°$ $I_{BA} = I_0 + I$, where $I_0 + I$ is the ionisation potential of the system of conjugated bonds. It is close to the ionisation potential of aniline ($I_0 + I$) = 7.7 eV.[118] When $\varphi = 90°$ $I_{BA} = I_0$, where I_0 is the "ionisation potential" of the UEP orbital of the nitrogen atoms. It is presumed that I_0 is close to the ionisation potential of TPA (I = 6.88 eV), in which the aromatic groups are turned through 45° relative to the UEP of the nitrogen atom.[119]

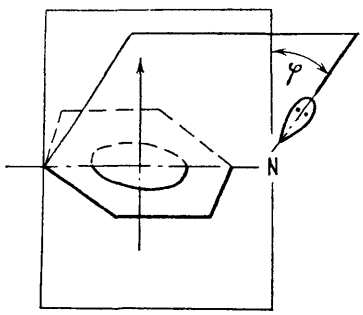


Figure 9. Angle of rotation φ of the nonbonding orbital of the nitrogen atom relative to the plane of the benzene ring in benzylanilines.[77]

In the possible formation of a $\pi-\sigma^*$ complex, namely, in coordination of the acceptor with the benzene ring of benzylaniline, when φ increases from 0 to 90°, i.e., as the UEP moves out of the system of conjugated bonds, the energy of the orbital involved in the D·A interaction varies in accordance with the relationship:

$$I_{BA} = (I_0 + I) + I'\sin^2\varphi,$$

from I_{BA} = (I_0 + I) = 7.7 eV to the value (I_0 + I) + I', which is close to the ionisation potential of benzene (9.25 eV[118]).

The calculations carried out by Novikov and Vannikov[77] showed that in compounds such as DPBA in which $\varphi \sim 45°$, the broadening of the optical spectra of the complex DPBA.$CBr_3SO_2CBr_3$ on transferring to polymer matrices by $\sim 10^{-3}$ cm^{-1} (Table 3) corresponds to a scatter in values of angle φ by $\sim 5-8°$ and that this scatter leads to a broadening of the long-wavelength region of the optical absorption in the case of $n-\sigma^*$ complexes but causes an extension of the spectrum to shorter wavelength when the acceptor is coordinated to the benzene ring of benzylaniline.

The series of results considered above corresponds to the relative position of the energy levels (shown in Fig. 10) in complexes based on DPBA, particularly in DPBA.CBr_4 and DPBA.$CBr_3SO_2CBr_3$ complexes. In a liquid medium the electron level corresponds to a single equilibrium conformation of DPBA. The broadening of the optical absorption band of a DPBA.A complex, as in the case of $(C_5H_5)_2Fe.CBr_4$, is due to an electronic-vibrational interaction.[77] The extensive set of energy levels of BA.A complexes in a polymer matrix is shown in Fig. 10; the levels correspond to the different rotation angles of the phenyl group relative to the UEP of the nitrogen atom, changes in which are regarded by the polymer matrix.

The position of the optical absorption maximum of DPBA.A complexes in all media has a constant value of $h\nu^{max}$ = 3.5 eV when A = CBr_4 and 3.38 eV when A = $CBr_3SO_2CBr_3$ (see Fig. 7). The 0.12 eV decrease in the position of the maximum for A = $CBr_3SO_2CBr_3$ is caused by a corresponding increase in the electron affinity of this acceptor.[120] The lack of dependence of $h\nu^{max}$ on the dielectric properties of the medium is consistent with a small degree of charge transfer in the excited Franck–Condon state of that group of complexes, which determines the position of $h\nu^{max}$. This may be due to the close position of the energy levels of the charge-transfer state

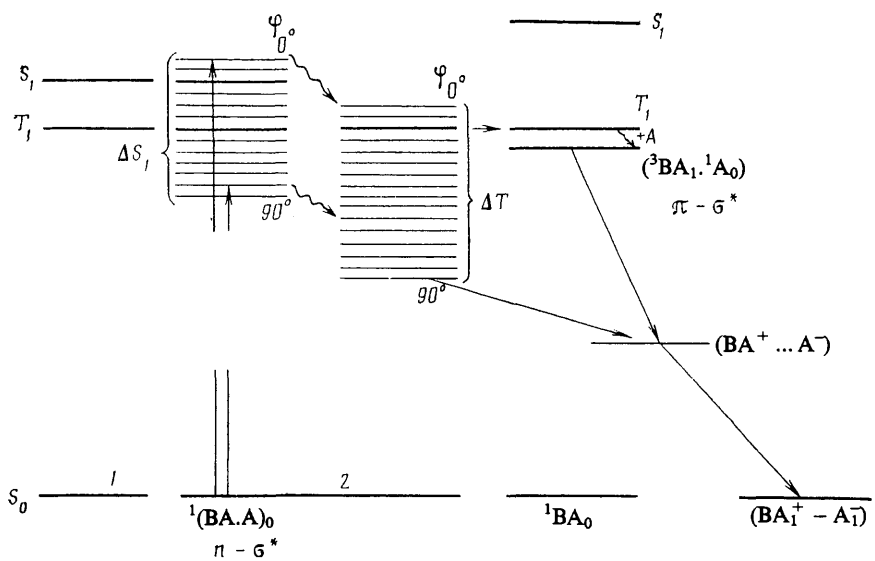


Figure 10. Position of energy levels and scheme for photoprocesses in complexes of benzylanilines (DPBA, dibenzylaniline) with acceptors (CBr_4, $CBr_3SO_2CBr_3$) in a liquid medium (*1*) and polymer matrix (*2*).

$(D^{+\delta^*}-A^{-\delta^*})$ and the local excitation of the donor ($^1D_1.A$), which causes a mixing of the wave functions of these states:

$$\psi^1(D^{+\delta_1}-A^{-\delta_1})_1 = a_1\psi(D^{+\delta^*}-A^{-\delta^*}) + b_1\psi(^1D_1.A),$$

where a_1 and b_1 are the contributions of the charge-transfer state $(D^{+\delta^*}-A^{-\delta^*})$ and the local excitation of the donor ($^1D_1.A$) respectively to the wave function. As a result of mixing the states the degree of charge transfer (δ_1) in the excited complex $^1(D^{+\delta_1}-A^{-\delta_1})_1$ is less than in the "pure" charge-transfer state (δ^*) and is given by $\delta_1 = \delta^* a_1^2/(a_1^2 + b_1^2)$. (It was shown above that $b_1 = 0$ and $\delta_1 = \delta^*$ for the complex $(C_5H_5)_2Fe.CBr_4$.)

The first stages of photolysis of the complex $DPBA.CBr_3SO_2CBr_3$ in a PVC matrix when exposed to laser irradiation with a wavelength of 353 nm were studied by Mal'tsev et al.[121,122] It was established that

$$\begin{matrix} O^{\cdot} \\ | \end{matrix}$$

the charge-transfer products $DPBA^+$ and $CBr_2=S(O)-CBr_3...Br^-$) and the excited triplet donor ($^3DPBA_1$) are formed at the same time, which is also an indication of the close relative position of the triplet levels of the locally excited donor and the charge-transfer state in the group of high-energy complexes. The wave function of the triplet state of this group can be represented as

$$\psi^3(D^{+\delta_2}.A^{-\delta_2})_1 = a_1'\psi^3(D^{+}.A^{-})_1 + b_1'\psi(^3D_1.A), \qquad (48)$$

where $\delta_2 = (a_1')^2/[(a_1')^2 + (b_1')^2]$, the degree of charge transfer. In this case the wave functions are represented by $\psi^3(D^+.A^-)_1$—the triplet charge-transfer state—and $^3D_1.A$—the locally excited triplet state of the donor. The magnitude of δ_2 is markedly dependent on small changes in the relative position of the levels of the states with complete charge transfer

$$E_1' = \int\psi^3(D^+A^-)H\psi^3(D^+A^-)dv$$

and the locally excited donor

$$E_2' = \int\psi(^3D_1.A)H\psi(^3D_1.A)dv.$$

For DPBA, $E_2' = E(^3D_1) = 3.00$ eV. The ratio (b_1'/a_1') may be determined from the expression

$$(b_1'/a_1') = V_{01}/(E_2' - E_1'), \qquad (49)$$

where V_{01} is the energy of the exchange interaction between the triplet charge-transfer state and the locally excited triplet donor

$$V_{01} = \int\psi^3(D^+A^-)_1H\psi(^3D_1.A)dv.$$

It is estimated that $V_{01} = 0.05-0.5$ eV. It was established[121,122] that when DPBA is replaced by diphenylamine (DPA, $E_2' = 3.14$ eV[123]), the excited triplet state of the donor is not formed on exposure to a laser with $\lambda = 353$ nm. This may be due to the corresponding decrease in contribution of b_1' from the locally excited triplet state of the donor to the wave function. (48) In fact, the energy $E_1' = h\nu_{et}^{max}$(gas) [see expressions (44) and (49)] in a DPA.A complex is ~0.34 eV less than in a DPBA.A complex (here A = $CBr_3SO_2CBr_3$). [Determined, in accordance with (44), from the difference $E_1'(DPBA) - E_1'(DPA) = I_D(DPBA) - I_D(DPA) = e[E_{1/2}(DPBA/DPBA^+) - E_{1/2}(DPA/DPA^+)]$, where $E_{1/2}(DPBA/DPBA^+) = 0.98$ V[12] and $E_{1/2}(DPA/DPA^+) = 0.64$ V—the equilibrium oxidation potentials of DPBA and DPA respectively.]

From the dependence of the quantum yield of the products of ionic photodissociation of the $DPBA.CBr_4$ complex in the presence of an acceptor with triplet energy (1-naphthol, etc.) on the concentration of these components, it was concluded[124] that on exposure to light with $\lambda = 365$ nm the products of ionic dissociation are mainly formed by transfer of triplet energy from the complex to a molecule of amine (see scheme in Fig. 10) to form a $\pi-\sigma^*$ exciplex ($^3DPBA_1.CBr_4$), which dissociates to radical ions. It is to be expected that the probability of direct ionic photodissociation of excited triplet $DPBA.CBr_4$ complexes will increase with the wavelength of stimulating light since when I_{BA} decreases [see expressions (44)] the E_1' level decreases and hence the contribution of the locally excited triplet state of the DPBA donor diminishes [see expressions (48) and (49)].

Thus, the polymer effect, which consists of the freezing out of different conformations of benzylaniline molecules, results firstly in a bathochromic shift of the optical spectrum by about 10^3 cm^{-1} on going from liquid media to polymer matrices. It has been shown[105] that this causes the sensitivity of photographic materials based on benzylanilines to be extended into the visible region. Secondly, as the wavelength of stimulating light is increased, polymer matrices are probably responsible for a change in mechanism of the formation of ionic photodissociation products from mainly a primary transfer of triplet energy (see Fig. 10) in the case of high-energy complexes to direct dissociation into radical ions of low-energy complexes.

It has been pointed out[77] that in $(C_5H_5)_2Fe.CBr_4$ complexes the nonuniform broadening of the optical spectrum in polymers is absent as a result of the high symmetry for ferrocene molecules. It is because of the absence of specific polymer effects in these complexes that the dependence of $h\nu_{et}^{max}$ on the dielectric properties of the medium [see expression (46)] as predicted by electron-transfer theory is found to occur.

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It should be mentioned in conclusion that the basic concepts of electron-transfer theory developed for liquid media are applicable to donor-acceptor systems in polymer matrices.

However, in contrast to liquids, different conformations of complex organic molecules can occur in rigid polymer matrices when there is a limited free volume; this gives rise to a nonuniform distribution of parameters such as the ionisation potential or electron affinity, intramolecular reorganisation energy and reorganisation energy of the medium during electron transfer. The magnitudes of these effects depend on the size and symmetry of the donor and acceptor molecules as well as on the total magnitude and distribution of the free volume and mobility of the polymer chains.[125,126] These effects can completely mask the processes which accompany electron transfer in liquid media.

In turn, the disorder of a polymer matrix causes a spatial variation in dielectric constant and hence in reorganisation energy of the medium. Because of steric hindrance in a polymer matrix only partial intramolecular reorganisation can occur when the molecule changes to a radical cation or anion form. For a complete elucidation of the available experimental data it is necessary to develop a model which simultaneously takes into account these factors and also the form of energy distribution of the interaction between the reaction (transport) sites and the medium, the distribution of distances between neighbouring sites, and the effect of the dielectric properties of the medium on electron transfer between sites.

References

1. I A Akimov, Yu A Cherkasov, M I Cherkashin *Sensibilizirovannyi Fotoeffekt* (The Sensitized Photoeffect), Izd. Nauka, Moscow, 1980, p. 384
2. F Cardon, W P Gomes, W Dekeyser (Editors) *Photovoltaic and Photoelectrochemical Solar Energy Conversion*, Plenum Press, New York, 1981, Vol. 69, p. 422

3. V Balzani, F Scandola *Photochemical Conversion and Storage of Solar Energy* (Edited by J S Connoly), Acad. Press, New York, 1981, p. 97
4. M R V Sahyun *Photogr. Sci. and Eng.*, 1984, **28** 185
5. A V Vannikov, A D Grishina *Fotokhimiya Polimernykh Donorno-aktseptornykh Kompleksov* (The Photochemistry of Polymer Donor-Acceptor Complexes), Izd. Nauka, Moscow, 1984, p. 261
6. J F Rabek *New Trends in the Photochemistry of Polymers* (Edited by N S Allen, J F Rabek), Elsevier, London, 1985, p. 265
7. N N Semenov, A E Shilov (Editors) *Preobrazovanie Solnechnoi Energii* (The Conversion of Solar Energy), Izd. Nauka, Moscow, 1985, p. 184
8. M Gretzel (Editor) *Energy Resources through the Prism of Photochemistry and Catalysis* (Translated into Russian), Izd. Mir, 1986, p. 632
9. A N Pravednikov, B V Kotov, D V Pebalk *Fizicheskaya Khimiya. Sovremennye Problemy* (Physical Chemistry. Current Problems) (Edited by Ya M Kolotyrkin), Izd. Mir, Mosocw, 1987, p. 165
10. K V Mikkelsen, M A Ratner *Chem. Rev.*, 1987, **87** 113
11. J F Rabek *Prog. Polym. Sci.*, 1988, **13** 83
12. A V Vannikov, A D Grishuina *Usp. Khim.*, 1987, **56** 1105 [English translation in *Russ. Chem. Rev.*, 1987(7)]
13. A Juris, V Balzani, F Barigelletti, et al. *Coord Chem. Rev.*, **1988, 84** 85
14. K I Zamaraev, R F Khairutdinov, V P Zhdanov *Tunnelirovanie Elektrona v Khimii* (Electron Tunnelling in Chemistry), Izd. Nauka, Novosibirsk, 1985, p. 320
15. V I Gol'danskii, L I Trakhtenberg, V N Flerov *Tunnel'nye Yavleniya v Khimicheskoi Fizike* (Tunnel Phenomena in Chemical Physics), Izd. Nauka, Moscow, 1986, p. 296
16. R S Mulliken, W B Person *Molecular complexes*, New York, Wiley, 1969, 312 p
17. R R Dogonadze, A M Kuznetsov *Kinetika Geterogennykh Khimicheskikh Reaktsii v Rastvorakh* (The Kinetics of Heterogeneous Chemical Reactions in Solution), VINITI, Moscow, 1978, (Results in Science and Technology), Vol. 5, p. 223
18. J J Hopfield *Biophys. J.*, 1977, **18** 311
19. N Mataga *Excited States* (Translated into Russian from English) (Edited by H Ratajczak, W J Orville-Thomas), Izd. Mir, Moscow, 1984, p. 502
20. Yu A Firsov (Editor) *Polyarony* (Polarons), Izd. Nauka, Moscow, 1975, p. 423
21. R A Marcus *J. Chem. Phys.*, 1956, **24** 966; 979
22. E D German, A M Kuznetsov *Teoriya Kinetiki Protsessov Elektronnogo Perenosa Mezhdu Kompleksnymi Ionami* (The Theory of the Kinetics of Electron-Transfer Processes between Complex Ions), VINITI, Moscow, 1982, (Kinetics and Catalysis), Vol. 10, p. 115
23. L Eberson *Adv. Phys. Org. Chem.*, 1982, **18** 79
24. L I Krishtalik *Elektrodnye Reaktsii. Mekhanizmy Elementarnogo Akta* (Electrode Reactions. Mechanisms of the Fundamental Stage), Izd. Nauka, Moscow, 1982, p. 224
25. R A Marcus *J. Phys. Chem.*, 1986, **90** 3454
26. G McLendon *Acc. Chem. Res.*, 1988, **21** 160
27. I Rips, J Jortner *J. Chem. Phys.*, 1988, **88** 818
28. G L Closs, J R Miller *Science*, 1988, **240** 440
29. V A Zasukha, S V Volkov *Khim. Fiz.*, 1988, **7** 1353
30. M Takahashi, I Watanabe, S Ikeda *J. Electron Spectroscopy and Related Phenomena*, 1985, **37** 273
31. I Watanabe, K Maya, Y Yabuhara, S Ikeda *Bull. Chem. Soc. Jpn.*, 1986, **57** 907
32. C J Schlesener, C Amatore, J K Kochi *J. Phys. Chem.*, 1986, **90** 3747
33. T Nakayama, I Watanabe, S Ikeda *Bull. Chem. Soc. Jpn.*, 1988, **61** 673
34. S Trasatti *J. Electroanal. Chem.*, 1986, **209** 417
35. G Gramm, W Jaenicke *J. Chem. Soc. Faraday Trans. 2*, 1985, **81** 1035
36. S F Nelsen, S C Blackstock, Y Kim *J. Am. Chem. Soc.*, 1987, **109** 677
37. J V Beitz, J R Miller *J. Chem. Phys.*, 1979, **71** 4579
38. J R Miller, J V Beitz *J. Chem. Phys.*, 1981, **74** 6746
39. J Jortner *J. Chem. Phys.*, 1976, **64** 4860
40. I Rips, J Jortner *Chem. Phys. Lett.*, 1987, **133** 411
41. H Sumi, R A Marcus *J. Chem. Phys.*, 1986, **84** 4247
42. H M McConnell *J. Chem. Phys.*, 1961, **35** 508
43. V V Voevodskii, S P Solodovnikov, V M Chibrikin *Dokl. Akad. Nauk SSSR*, 1959, **129** 1082
44. H Heitele, M E Michel-Beyerle, P Finckh, W Rettig *Tunneling* (Edited by J Jortner, B Pullman), D Reidel Publ. Co., Dordrecht, 1986, Vol. 19, p. 333
45. H Heitele, M E Michel-Beyerie, P Finckh *Chem. Phys. Lett.*, 1987, **134** 273
46. L T Calceterra, G L Closs, J R Miller *J. Am. Chem. Soc.*, 1983, **105** 670
47. G L Closs, L T Calcaterra, N J Green, et al. *J. Phys. Chem.*, 1986, **90** 3673
48. A G Tyurin, P I Dubenskov, T S Zhuravleva, et al. *Khim. Fiz.*, 1987, **6** 1236
49. P I Dubenskov, T S Zhuravleva, A V Vannikov, et al. *Vysokomol. Soedin., Ser. A*, 1988, **30** 1211
50. A R Tameev, T S Zhuravleva, A V Vannikov, et al. *Vysokomol. Soedin., Ser. A*, 1987, **29** 2186
51. A G Tyurin, A Yu Kryukov, T S Zhuravleva, et al. *Zh. Nauchn. Prikl. Fotogr. Kinematogr.*, 1988, **33** 418
52. I P Zvyagin *Kineticheskie Yavleniya v Neuporyadochennykh Poluprovodnikakh* (Kinetic Phenomena in Disordered Semiconductors), Izd. MGU, Moscow, 1984, p. 192
53. W H Hamill, K Funabashi *Phys. Rev. B*, 1977, **16** 5523
54. H Sher, E W Montroll *Phys. Rev. B*, 1975, **12** 2455
55. M Pollak *Philos. Mag. B*, 1977, **3** 1157
56. V I Arkhipov, A I Rudenko, A M Andriesh, et al. *Nestatsionarnye Inzhektsionnye Toki v Neuporyadochennykh Tverdykh Telakh* (Nonstationary Injection Currents in Disordered Solids), Izd. Shtiintsa, Kishinev, 1983, p. 175
57. M Silver, L Cohen *Phys. Rev. B*, 1977, **15** 3276
58. J M Marshall *Philos. Mag. B*, 1977, **36** 959
59. N J Chekunaev, Yu A Berlin, V N Fleurov *J. Phys. C: Solid State Phys.*, 1982, **15** 1213
60. N J Chekunaev, V N Fluerov *J. Phys. C: Solid State Phys.*, 1984, **17** 2917
61. G Pfister, C H Griffiths *Phys. Rev. Lett.*, 1976, **40** 659
62. A R Tameev, T S Zhuravleva, A V Vannikov, et al. *Khim. Fiz.*, 1986, **5** 106
63. M Stolka, J F Yanus, D M Pai *J. Phys. Chem.*, 1984, **88** 4707
64. L B Schein, J X Mack *Chem. Phys. Lett.*, 1988, **149** 109

65. W D Gill *Proceedings of the 5th International Conference on Amorphous and Liquid Semiconductors. 1973. Garmisch-Partenkirchen* (Edited by J Stuke, W Brenig), Taylor and Francis, London, 1974, p. 901
66. G Schonherr, H Bassler, H Silver *Philos. Mag. B*, 1981, **44** 369
67. H Bassler *Phys. Status Solidi. B*, 1981, **107** 9
68. H Bassler, G Schonherr, M Abkowitz, D Pai *Phys. Rev. B*, 1982, **26** 3105
69. M Grunewald, B Pohlmann, B Movaghar, D Wurtz *Philos. Mag. B*, 1984, **49** 341
70. B Movaghar *J. Mol. Electronics*, 1987, **3** 183; 1988, **4** 79
71. D M Pai, J F Yanus, M Stolka, et al. *Philos. Mag. B*, 1983, **48** 505
72. H Bassler *Philos. Mag. B*, 1984, **50** 347
73. W D Gill *Photoconductivity and Related Phenomena* (Edited by J Mort, D M Pai), Elsevier, New York, 1976, p. 303
74. N Mott, E Davies *Electron Processes in Noncrystalline Materials* (Translated into Russian from English), Izd. Mir, Moscow. 1974, p. 472
75. A G Tyurin, A Yu Kryukov, T S Zhuravleva, A V Vannikov *Vysokomol. Soedin., Ser. B*, 1988, **30** 739
76. A V Vannikov, A G Tyurin, A Yu Kryukov, T S Zhuravleva *Mater. Sci. Forum.*, 1989, **42** 29
77. S V Novikov, A V Vannikov *Khim. Fiz.*, 1988, **7** 192
78. N S Hush *Supramolecular Photochemistry* (Edited by V Balzani), D Reidel Publ. Co., Dordrecht, 1987, p. 53
79. H Beens, A Weller *Organic Molecular Photophysics* (Edited by J B Birks), Wiley, New York, 1975, Vol. 2, p. 159
80. A Weller *The Exciplexes* (Edited by M Gordon, W R Ware), Academic Press, New York, 1975, p. 23
81. K M C Davis *Molecular Association* (Edited by R Foster), Academic Press, New York, 1975, Vol. 1, p. 151
82. G J Kavarnos, N J Turro *Chem. Rev.*, 1986, **86** 401
83. T A Marsagashvili, D E Khoshtariya *Khim. Fiz.*, 1987, **6** 1511
84. A M Kjaer, J Ulstrup *J. Am. Chem. Soc.*, 1987, **109** 1934
85. A M Kjaer, J Ulstrup *J. Am. Chem. Soc.*, 1988, **110** 3874
86. S V Novikov, A A Petrova, V A Zver'kov, A V Vannikov *Material 7-go Vsesoyuznogo Soveshchaniya po Probleme "Kompleksy s Perenosom Zaryada i Ion-Radikal'nye Soli"* (Data from the 7th All-Union Conference on the Problem of "Charge-Transfer Complexes and Radical-Ion Salts"), Chernogolovka, 1988, p. 114
87. E Kh Brickenstein, G K Ivanov, M A Kozhushner, R E Khairutdinov *Chem. Phys.*, 1984, **91** 133
88. J Jortner *J. Am. Chem. Soc.*, 1980, **102** 6676
89. B S Brunschwig, S Ehrenson, N Sutin *J. Phys. Chem.*, 1987, **91** 4714
90. M R Sahyun *J. Photogr. Sci.*, 1983, **31** 243
91. J R Miller, J A Peeles, M J Schmitt, G L Closs *J. Am. Chem. Soc.*, 1982, **104** 6488
92. T Guarr, M McGuire, S Strauch, G McLendon *J. Am. Chem. Soc.*, 1983, **105** 616
93. T Guarr, M McGuire, G McLendon *J. Am. Chem. Soc.*, 1985, **107** 5104
94. B H Milosavljevic, J K Thomas *Chem. Phys. Lett.* 1985, **114** 133
95. B H Milosavljevic, J K Thomas *J. Phys. Chem.*, 1985, **89** 1830
96. B H Milosavljevic, J K Thomas *J. Am. Chem. Soc.*, 1986, **108** 2513
97. J Murtagh, J K Thomas *Chem. Phys. Lett.*, 1988, **148** 445
98. A B Fischer, I Bronstein-Bonte *J. Photochem.*, 1985, **30** 475
99. J Murtagh, J K Thomas *Chem. Phys. Lett.*, 1987, **139** 437
100. M C Palazzotto, M R V Sahyun *Progress in the Basic Principles of Imaging Systems* (Edited by F Granzer, E Moisar), Vieweg, Braunschweig, 1987, pp. 599–606
101. M C Palazotto, R J DeVoe *Polym. Preprints*, 1988, **29** 520
102. M Tachiya, A Mozumder *Chem. Phys. Lett.*, 1974, **28** 87
103. M Inokuti, F Hirayama *J. Chem. Phys.*, 1965, **43** 1978
104. J Lakovich *Basic Principles of Fluorescence Spectroscopy* (Translated into Russian) (Edited by M G Kuz'min), Izd. Mir, Moscow, 1986, p. 496
105. A D Grishina, A A Petrova, M G Tedoradze, et al. *Khim. Fiz.*, 1988, **7** 499
106. V E Kampar, O Ya Neiland *Usp. Khim.*, 1986, **55** 637 [English translation in *Russ. Chem. Rev.*, 1986(4)]
107. W Baumann, J-C Frohling, C Brittinger, et al. *Ber. Bunsenges. Phys. Chem.*, 1988, **92** 700
108. M F Budyka, O D Laukhina, M G Stunzhas, et al. *Material VII Vsesoyuznogo Soveshchaniya po Probleme "Kompleksy s Perenosom Zaryada i Ion-Radikal'nye Soli"* (Data from the 7th All-Union Conference on the Problem of "Charge-Transfer Complexes and Radical-Ion Salts"), Chernogolovka, 1988, p. 217
109. W Rettig, G Wermuth *J. Photochem.*, 1985, **28** 351
110. W Rettig, R Gleiter *J. Phys. Chem.*, 1985, **89** 4676
111. K A Al-Hassan, W Rettig *Chem. Phys. Lett.*, 1986, **126** 273
112. R Hayashi, S Tazuke *Chem. Phys. Lett.*, 1987, **185** 123
113. K A Al-Hassan, T Azumi *Chem. Phys. Lett.*, 1988, **145** 49
114. W Rettig *Appl. Phys. B*, 1988, **45** 145
115. R Akaba, K Tokumaru, T Kabayashi *Bull. Chem. Soc. Jpn.*, 1980, **53** 1993
116. R Akaba, K Tokumaru, T Kabayashi, C Utsunomiya *Bull. Chem. Soc. Jpn.*, 1980, **53** 2002
117. R Akaba, H Sakuragi, K Tokumaru *Bull. Chem. Soc. Jpn.*, 1985, **58** 301
118. V N Kondrat'ev (Editor) *Energiya Razryva Khimicheskikh Svyazei. Potentsialy Ionisatsii i Srodstvo k Elektronu* (The Energy of Breaking Chemical Bonds. Ionisation Potentials and Electron Affinity), Izd. Nauka, Moscow, 1974, p. 351
119. I P Romm, E N Gur'yanova *Usp. Khim.*, 1986, **55** 225 [English translation in *Russ. Chem. Rev.*, 1986(2)]
120. A D Grishina, V A Ilyushin, A V Vannikov *Khim. Vys. Energ.*, 1985, **18** 323
121. E I Mal'tsev, A N Komissarov, S G Titov, et al. *Khim. Vys. Energ.*, 1987, **21** 533
122. E I Mal'tsev, V A Tkachev, A V Vannikov *J. Photochem. and Photobiol. A*, 1988, **43** 73
123. H Shiruka, Y Takayama, T Tanaka, T Morita *J. Am. Chem. Soc.*, 1970, **92** 7270
124. G M Chernov, A D Grishina, A V Vannikov *Khim. Vys. Energ.*, 1981, **15** 458
125. N M Emanuel', V A Roginskii, A L Buchachenko *Usp. Khim.*, 1982, **51** 361 [English translation in *Russ. Chem. Rev.*, 1982(3)]
126. N M Emanuel', A L Buchachenko *Khimicheskaya Fizika Molekulyarnogo Razrusheniya i Stabilizatsii Polimerov* (The Chemical Physics of Molecular Disruption and Stabilisation of Polymers), Izd. Nauka, Moscow, 1988, p. 368

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Methods for the regulation of the functional properties of isolated myofibrillar proteins in order to expand their use as foodstuffs

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ABSTRACT. Data characterising the specific features of the chemical, enzymic, mechanical, and combined modifications of myofibrillar proteins are described systematically with the aim of expanding their possible use in food systems. Attention is concentrated on the mechanisms of the enzymic and chemical reactions with food proteins of myofibrillar origin, carried out in order to regulate specific functional properties of the protein systems.

The problem of toxicity, biological value, bioavailability, and metabolic pathways of the modified food proteins is discussed.

The prospects and limitations of enzymic and chemical modification of myofibrillar proteins are indicated.

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I. Introduction

For a successful solution of the problem of food supply, it is timely to take into account and assess the possibility of using new sources of food protein, including those which had been previously neglected.[1,2] Apart from the non-traditional sources of proteins of plant origin, to which a fair amount of attention has been devoted,[3,4] rich resources of proteins with a high food value are provided by various objects in the Pacific Ocean: the Antarctic krill,[5–10] certain species of fish, in particular myctophid fish,[11–13] as well as fish with a low commercial value.[14–18]

Isolated fish proteins, free from sarcoplasmic proteins and lipids, have no specific taste or smell and can be used in any food system ranging from delicatessen fish products and meat substitutes to dessert dishes.[5,6,19,20] The isolation of proteins from non-traditional sources requires additional stages involving the removal of toxic, ballast, or antinutritive components (specific pigments, proteolytic enzymes, lipids which are difficult to remove, etc.). Myofibrillar proteins are more sensitive to chemical and physical effects than plant proteins. The proteins isolated from muscle tissue do not therefore meet the current requirements from the standpoint of functional properties. On the other hand, the possibility of the wide scale application of proteins of this kind in food products does in fact depend on the level of their functional properties.

Functional properties (FP) is the term given to a set of physicochemical characteristics of an individual protein, which determines its behaviour in aqueous media (swellability, solubility, gel formation, etc.), and in the heterophase systems of the type water–oil, oil–water (emulsifying capacity), or water–gas (capacity for foam formation), as well as in multicomponent mixtures. The functional properties of the protein are manifested as a function of its nature and the character of its interaction with other components of the given food system.

Studies in which the relation between the structure of the protein and its functional properties is determined are believed to play virtually the main role in modern food protein chemistry.[21–25] Chemical modification of proteins makes a considerable contribution to the solution of this problem making it possible to trace the correlation between certain physicochemical parameters of the protein and the manifestation of a particular functional property.

In selecting a method for the regulation of the functional properties of a food protein, one must take into account all the characteristic features of its structure and the character of the changes entailed by a particular type of modification.

The functional properties of the protein are determined by many factors:

(a) They are determined mainly by its surface characteristics, which are in turn determined by the quaternary structure of the protein (the size and shape of the protein molecule, its overall surface charge, and its surface hydrophobicity). The stability of the protein depends on the type of bond between the subunits and the ease of their dissociation.

(b) The relation between the intermolecular and intramolecular bonds of various types (hydrogen, ionic, hydrophobic, electrostatic, van der Waals) characterises the flexibility of the molecule, i.e. its capacity for conformational changes without the disruption of the native structure of the protein.

(c) The aminoacid sequence dictates the charge distribution in the molecule and the type of packing of the peptide chains, i.e. the geometrical disposition of the hydrophobic sections.

(d) The secondary and tertiary structures of the protein determine ultimately the steric accessbility and the reactivity of the functional groups of the protein.

The set of the above factors does in the main determine the individual features of the protein.[26]

Any kind of modification alters a whole set of physicochemical properties of the protein and these processes must be examined in detail, since they open a pathway to the deliberate regulation of the functional properties of food protein systems.

The aim of the present review is to give a systematic account of the available information about the ways in which food proteins isolated from muscle tissue are treated in order to regulate their functional properties. The narrow selection of the subjects for discussion makes it possible to trace the trend in the changes of particular properties of the protein as a function of the type of influence on the latter.

It is possible to differentiate three main aspects of the regulation of the functional properties of food proteins: enzymic treatment, chemical modification, and physicochemical methods of influencing the protein. These processes are not mutually exclusive and can be successfully used in a combined procedure.

II. Enzymic treatment of proteins

The processes involving the regulation of the functional properties of myofibrillar food proteins with the aid of enzymes (usually proteolytic) have been widely discussed in the literature.[27–36]

By means of the partial hydrolysis of the protein, it is possible to achieve an increase in its solubility, emulsifying activity, foam-forming capacity, and ability to stabilise emulsions and foams.

In the treatment of muscle tissue by proteases, micro-organisms were used initially: *Thamnidium sp.* in order to soften meat and *Aspergillus glaucus* in order to alter the consistency and taste of fish.[37] The proteases produced by micro-organisms apparently caused the breakdown in the first place of the structure of the sarcomers, increasing thereby the softness of the tissues but at the same time increasing also the viscosity and stickiness of the product. This procedure has not been found extensive application because of the considerable losses of the product.

The most effective method of increasing the solubility of a protein is enzyme hydrolysis. Proteolytic enzymes cleave specific peptide bonds causing the breakdown of the protein molecule into definite fragments. In contrast to acid or alkaline hydrolysis, this process is not accompanied by any side reactions. Myosin, as the main component of myofibrils and having the most complex structure, is most frequently used for a detailed investigation of the behaviour of muscle proteins. The mechanism of the hydrolysis of myosin by food digesting enzymes of the series of peptidases has been studied in fair detail.[38]

For example, trypsin initially splits the myosin molecule into two large fragments: the heavy meromyosin (MW = 200 000) and the light meromyosin (MW = 150 000). Globular fragments or myosin "heads" (MW = 120 000) are then split off from the heavy meromyosin leaving the C-2 subfragment (MW = 100 000).

Papain abstracts in the first place the myosin heads, acting subsequently in a similar manner.

The high degree of hydrolysis of the protein achieved on treatment by active enzymes such as pepsin, papain, and pronase[39–41] is undesirable since it frequently entails the loss of the emulsifying and foam-forming capacities[42] and leads to the appearance of an appreciable bitter taste due to hydrophobic peptides.[41,43] It is very difficult to optimise this process.[44]

In many cases, enzymic treatment was resorted to in order to stabilise the muscle tissue homogenates before extracting the protein.[45,46] This method is especially convenient in isolating proteins from small oceanic fish. The fish are wholly ground up and are then subjected to enzymolysis, whereupon the partially hydrolysed protein can be extracted to a large extent. Amylosubtilin and protosubtilin were used on fish objects,[45] while papain and ficin were employed for the analogous treatment of the skeletal muscle tissue of cattle.[46]

A successful version of the enzymic modification of isolated *Rockfish* fish proteins has been achieved using the "Rhozyme P-11" preparation.[47,48] After 15 min hydrolysis at pH 6.5–6.7 and 30 °C (enzyme : substrate = 1 : 75), an emulsifying activity exceeding the control parameter for the initial isolated protein by a factor of almost 1.5 was obtained. For higher degrees of hydrolysis the emulsifying activity fell, while the stability of the emulsions increased (to a maximum after hydrolysis for 30–60 min) but subsequently it too decreased. The solubility in water of the fish hydrolysate obtained reached 20%. The authors do not mention a bitter taste.[47]

It is of interest to note that weak hydrolytic treatment of the *Rockfish* isolated protein with bromelin (10 min at pH 7; temperature 25 °C) only slightly diminished its emulsifying and foam-forming capacities, whereas the above properties of the same isolated proteins subjected to preliminary acylation were increased sharply[49–51] (for details, see Section IV).

The traditional employment of meat proteins in food systems imposes certain requirements on the latter. Solubility is not as important for them as a high emulsifying capacity, gel formation, and ability to bind high- and low-molecular-weight components of the system.

By treating the myofibrillar proteins of bovine skeletal muscle with papain, it was possible to increase their emulsifying capacity by 40% with formation of very stable emulsions.[46]

Owing to their low level of functional properties, proteins isolated from bovine cardiac muscle tissue have not found extensive applications despite their high biological value. Modification using ficin made it possible to employ such isolated proteins as a valuable additive for the replacement of beef in meat systems (up to 30%) without impairing their nutrient and organoleptic properties.[52]

In order to improve the emulsifying and gel forming capacities of myofibrillar proteins from the skeletal muscles of domestic birds, treatment with the preparation "Milezyme AFP-2000" was tried. It was noted that, with increase in the degree of hydrolysis, the solubility of the proteins rises but the capacity for gel formation falls rapidly at the same time.[53] It is possible to obtain a modified product, which has been recommended as an active emulsifying additive to meat systems.[54]

Enzyming processes used for the modification of myofibrillar proteins hardly extend beyond the framework of proteolysis. There have been several communications on the use of transferases which can serve as activators for the covalent attachment of aminoacids or aminoacid esters to proteins[55,56] (see Section IV).

It can be inferred from the data presented that the spectrum of functional properties which can be improved by treating myofibrillar proteins with enzymes is so far relatively narrow. The principal factor determining the level of the required functional properties in the modified object is the degree of hydrolysis of the protein. On the other hand, the main difficulty in carrying out proteolytic processes is in monitoring the degree of decomposition of protein molecules.

The application of immobilised enzymes was predicted a fairly long time ago,[57] but this technique has not so far found an application in practice.

Despite the difficulty of controlling enzymic processes on an industrial scale, some workers believe that this aspect of the modification is the most promising on the grounds that such treatment does not entail the loss of nutrient properties and in addition increases the assimilability of the isolated proteins.[3,5,58]

In our view, the use of enzymic processes on isolated proteins subjected to a preliminary chemical modification is effective (for further details, see Section IV).

III. Chemical modification

Chemical modification is of great interest for the regulation of the functional properties of food proteins.[21,58–67] It involves many more possibilities for the transformation of proteins than enzymic modification. Apart from the simplest operations associated with the degradation of peptide chains and the hydrolysis of amide groups of asparagine and glutamine, it makes it possible to alter the structure of the protein by creating new covalent or ionic bonds.

With the aid of chemical reagents, it is possible to introduce hydrophilic and hydrophobic groups into the protein molecule, to enrich the protein in aminoacids present in insufficient amounts, and to attach polyaminoacid chains. By taking into account the nature of the groups introduced and by regulating the degree of modification, it is possible to alter specifically the overall charge and hydrophobicity of the protein system, which in fact determines its functional properties.

1. Alkaline and acid hydrolysis of proteins

One of the simplest methods of solubilising proteins is alkaline and acid hydrolysis. Since 1970, alkaline hydrolysis has been used widely for the improvement of the functional properties of fish protein concentrates.[68–70] Such treatment usually increases the solubility and the emulsifying and foam-forming capacities of the protein.

Treatment of myofibrillar proteins with alkalies and acids in order to cleave the peptide bonds induces profound irreversible denaturation changes and is accompanied by the appearance of a number of side reactions. Alkaline hydrolysis is also accompanied by the degradation of alkali-labile aminoacids, the partial racemisation of aminoacids, and the β-elimination process with participation of hydroxy- and mercapto-aminoacids leading to the formation of dehydroalanine, which readily interacts with lysine, cysteine, ornithine, and ammonia.[71–74] The products of these reactions are respectively lysinoalanine, lanthioline, ornithinoalanine, and β-aminoalanine. This diminishes the food value of the protein by depleting it in essential aminoacids, by the partial loss of assimilability as a result of the formation of intermolecular cross-links, and by the accumulation of antinutrient substances. The question of the toxicity or harmlessness to man of dehydroalanine derivatives still remains open.[3,72]

Comparatively recently it has been demonstrated experimentally (on skeletal muscles in fish) that lysinoalanine is formed only under very severe alkaline conditions at pH 12 and above and at temperatures not below 90 °C.[75] Thus the possibility of using relatively mild hydrolysis for food proteins has not been rejected at the present time.[3,36] Acid hydrolysis of myofibrillar proteins has not come to be widely employed although according to some specialists[5] it has advantages compared with alkaline hydrolysis mainly as a result of the lower degree of racemisation of aminoacids.

One of the principal disadvantages of hydrolytic processes is the formation of bitter peptides (even for low degrees of hydrolysis of the protein), which is especially characteristic of isolated fish proteins.[20,42]

2. Solubilisation of proteins by salt formation

Proteins, which are polymeric ampholytes, have the characteristic ability to interact with cations and anions. Two types of interaction are possible: the formation of salt "bridges" and the specific sorption of ions on the surface of the protein.

In terms of their positive influence on the solubility of proteins, cations and anions can be arranged in the following sequence:[76]

$$Ca^{2+} > Mg^{2+} > Li^{+} > Cs^{+} > Na^{+} > K^{+} > NH_4^{+}$$

$$SCN^{-} > ClO_4^{-} > I^{-} > NO_3^{-} > Br^{-} > Cl^{-} > CH_3COO^{-} > F^{-} > HPO_4^{2-} > SO_4^{2-} >$$

$$> {}^{-}OOC{-}CHOH{-}CHOH{-}COO^{-} > {}^{-}OOC{-}CH_2{-}\underset{\displaystyle COOH}{\overset{\displaystyle |}{C}}(OH){-}CH_2{-}COO^{-}.$$

Proteinates have a much higher solubility than desalinated proteins. The change in the solubility of proteins is attributed to the specific interaction of ions (not only electrostatic interaction), which entails changes in the surface charge of the protein and in its conformation, ensuring a higher degree of hydration. A change in the ionic strength of the solution also promotes an increase in the solubility of the protein.[3,76,77]

The use of salt components in food protein systems is limited by their toxicity and cost. The most widely used additives are sodium chloride and inorganic phosphates.[78–85]

The moisture retaining capacity of meat systems is frequently regulated with the aid of salts. Sodium chloride, pyrophosphate, or triphosphate is usually introduced to increase such capacity.[78,86] The affinity of myosin for various inorganic phosphates is not unambiguous. It has been demonstrated for the interaction of myosin and with sodium pyrophosphate, triphosphate, and hexametaphosphate.[83,84] Among them, hexametaphosphate shows the greatest affinity for myosin, the character of its binding to myosin differing from that of the other phosphates. In the presence of Na^+ and especially Mg^{2+} or Ca^{2+} cations, the affinity of triphosphate and pyrophosphate for myosin increases sharply. More precisely, the affinity of myosin for these metal phosphate complexes is greater than for the phosphates themselves. This rule does not extend to hexametaphosphate. On the contrary, the presence of NaCl inhibits the interaction of myosin with hexametaphosphate.[83,84] These data indicate a high degree of specificity of the ionic interactions of myofibrillar proteins.

The modern concept concerning the influence of phosphate and chloride anions on the solubility of myofibrillar proteins reduces mainly to electrostatic effects. As a result of the interaction of anions with myosin filaments, electrostatic repulsion forces arise and weaken the binding of the filaments. It has been suggested that at the critical salt concentration in solution, certain types of bonding of the filaments (as a rule in the regions of the *M*- and *Z*-lines) can break down. Furthermore, the bonding of the myosin heads to actin weakens until complete dissociation. Thus the introduction of anions promotes the depolarisation of thick filaments with liberation of myosin molecules.[76] In general, it has been found that inorganic phosphates are universal polyfunctional additives to isolated muscle tissue proteins. For example, sodium hexametaphosphate is introduced to ensure the complete precipitation of fish protein in the form of the phosphate complex,[47] while the addition of sodium triphosphate to the isolated fish protein is recommended in order to optimise the drying process.[87] Phosphates can be used conveniently to modify myofibrillar proteins, because they possess also antidenaturing,[88–90] antiseptic,[82,91–93] and antioxidant activities.[82,87,94] Phosphates have proved useful as active synergistic agents in relation to phenolic antioxidants.[94] On the other hand, the presence of polyphosphates increases the affinity binding of carbonyl compounds

formed on oxidative decomposition of lipids; actomyosin phosphate should not therefore be added to isolated proteins which need to be defatted.[95]

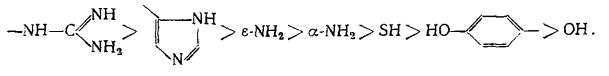
Mention should also be made of the ability of certain anions to protect actomyosin against cryodenaturation. For this purpose, glutamate, tartrate, and maleate are used together with phosphates at low temperatures.[96–98]

3. Acylation of myofibrillar proteins

One of the most widely used procedures in the chemical modification of food proteins is acylation.[21,59,61,63,64,99,100] Among acylating agents, acetic and succinic anhydrides are the most widely used. They are cheap, convenient to employ, and relatively harmless, they do not form toxic derivatives with proteins, and are distinguished by a high activity. The acylation reaction is usually carried out at a reduced or room temperature at alkaline pH.

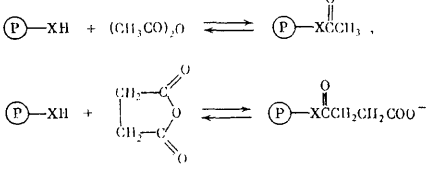
The degree of involvement of the different nucleophilic groups of the protein in the reaction varies as a function of the conditions (mainly the pH), the character of the anhydride, and the influence of inhibiting additives.

In the series based on decreasing nucleophilicity, the functional groups of the side chains in the aminoacid residues are arranged in accordance with their dissociation constants:



However, their reactivity can be influenced by adjoining groups in the peptide chain with which donor–acceptor or electrostatic interaction is possible or hydrogen bonds may be formed.[77]

The reaction of the protein with acetic and succinic anhydrides can be represented in a general form by the following scheme:



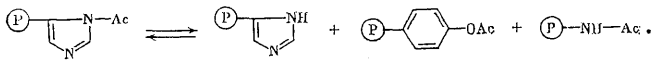
X = NH, O, S; Ⓟ = protein.

The fundamental difference between these processes is that the groups formed as a result of the interaction of the protein with acetic anhydride are compact and electrically neutral. On the other hand, the reaction with succinic anhydride introduces into the protein molecule more bulky negatively charged substituents. The latter reaction induces a sharper shift of the isoelectric point of the modified protein to the region of acid pH and more profound conformational changes than in the case of acetylation. This is in fact the cause of the greater possibilities, even when the degrees of modification are low, for the improvement of the solubility and the emulsifying and foam-forming capacities by succinylation rather than by acetylation.

In principle, all types of basic groups of the protein can interact with carboxylic acid anhydrides. In practice, however, the principal reaction centres are the ε- and α-amino-groups, mercapto-groups, and the most active hydroxy-groups of the protein.

The highly basic guanidine groups of the arginine residue are not acylated because under the reaction conditions (at a pH usually not exceeding 9.5) they exist in the protonated state.[77]

The *N*-acylimidazole derivatives of the histidine residue are so active that they themselves function as acylating agents, i.e. the *N*-acyl group migrates from the imidazole ring to the neighbouring sterically accessible amino- or phenoxy-groups of the protein:[63,64]



The half-life of *N*-succinylimidazole at pH 8.5 is 1 min.[101]

The terminal amino-groups of the protein, the ε-amino-groups of lysine, the SH groups of cysteine, and the OH groups of tyrosine are readily acylated, while the hydroxy-groups of serine and threonine are less reactive.[100] The amide bonds formed are stable, while the *O*- and *S*-acyl bonds, which are relatively stable in acid media, are rapidly hydrolysed in weakly alkaline media (already at pH 8.0). Tyrosine derivatives are especially labile. For example, the *N*-hydroxysuccinimide ester of tyrosine (*O*-Suc-tyrosine) is spontaneously deacylated at pH 8.0–8.5.[100,102]

It has been established with the aid of the reaction with salicylaldehyde that the accessible and active ε-amino-groups of lysine in native myosin constitute only 2.5% of the total number of lysine ε-amino-groups, while moderately active residues constitute about 30%. Other residues are sterically inaccessible and can react with the modifying agent only after the denaturation of the protein.[103]

The effect of acylation on the conformation of the myofibrillar proteins has been studied in detail on myosin and actin.[104–111] When only the surface ε-amino-groups of lysine have been modified, the conformation of myosin does not change.[104,105] Succinylation under conditions ruling out the denaturation of myosin (pH 7.0; 0 °C) showed that such chemical action induces only the dissociation of the light chains of myosin, while in other respects the structure of the protein remains intact.[106] These observations were confirmed in the analogous acetylation of myosin. Fractions with molecular weights of 17 000, 19 000, and 20 000, representing the light chains of myosin bound non-covalently to the C-1 subfragment, have been isolated and identified.[107,108]

When the degree of modification is above 3%, the myosin molecules acquire a more open-chain conformation and the degree of coiling into a helix diminishes.[107] On succinylation up to 50% and above, the conformation of proteins is seriously damaged.[112]

As regards biological activity, on succinylation (even for low degrees of the latter), myosin loses the ATPase activity and the ability to bind to F-actin.[107]

Acetylated myosin is distinguished by a high thermal stability, i.e. resistance to thermocoagulation.[107] It is believed[105,108] that the lysine ε-amino-groups located on the surface (the most accessible) are responsible for the thermal stability of myosin. On modification with a reagent specific to amino-groups (β-naphthoquinone-4-sulphonic acid), the thermal stability of myosin increased linearly with increase in the degree of substitution of amino-groups from 0 to 2.5%. The blocking of the surface lysine ε-amino-groups probably reduces the capacity of the heavy myosin chains for aggregation during their thermocoagulation.[76,109,110]

Studies of the influence of chemical modification on the properties of actin have been shown that up to 30% of the amino-groups and up to 40% of the SH groups are capable of entering into the succinylation reaction, as a result of which actin becomes biologically inert, losing the capacity for polymerisation and for binding to myosin. It is of interest that the selective blocking of the mercapto-groups of F- and G-actin does not affect their biological activity.[111]

Apparently the ε-amino-groups of lysine play the main role in actin, as in myosin.

Modelling of biochemical reactions has shown how specific and complex are the processes involving the changes in the conformation of the muscle tissue proteins. For example, enzymic phosphorylation of the light chains of myosin (LC-2) alters only the steric orientation of the heads of the C-1 myosin subfragment.[113,114]

Proteins isolated from animal sources, containing many different components of structural proteins, were subjected to chemical modification in the studies discussed below. Sarcoplasmic proteins and lipids are as a rule removed in order to avoid the oxidative spoliation of the isolated proteins during storage and to eliminate their specific smell and taste. Thus the principal components of the isolated proteins are myosin, actin, and tropomyosin, while the minor components are troponin and actinin.[76] According to the literature,[76] myosin contains only 17% of the basic aminoacid residues and 38% of the polar functional groups, actin contains 13% of the basic residues and 33% of the polar residues, while tropomyosin contains 19% of the basic residues and 50% of the polar residues. The cysteine residues are concentrated predominantly in myosin (65% of all the SH groups) and actin (29% of the SH groups). The accessibility of the groups enumerated above to chemical reagents is various, depending on the degree of denaturation of the modified protein system and on the nature of the selected agent.

The composition of the isolated proteins depends on the object, the kind of muscle tissues, the method of isolation and treatment, and the degree of denaturation of the proteins — on the conditions used in carrying out each stage of the process. The available literature data on the modification of isolated proteins can therefore be compared only fairly arbitrarily.

The influence of the conditions in the acylation reaction on the properties of isolated fish proteins has been investigated[100] with quantitative determination of the functional groups of the protein involved in the reaction. It was established that the rate of acylation depends mainly on the pH of the medium. For example, at 0 °C and pH 9.5, 90% of all the ε-amino-groups of lysin are acetylated, the corresponding figures at other pH values being 85% at pH from 8 to 8.5,[115] 75% at pH 7.5, and 65% at pH 6.5. Nevertheless, in the presence of a large excess of acetic anhydride and for longer reaction times, complete acylation is attained even at pH 6.5.[100]

The rate of the reaction between acetic anhydride and the SH and OH polar groups of the protein falls appreciably as the pH is reduced. Whereas 35% of all the polar groups (SH and OH) are acetylated at pH 9.5 and 25% at pH 7.5, not more than 20% are acetylated at pH 6.5. Under these conditions, the mercapto-groups of the cysteine residue were modified even at low concentrations of acetic anhydride, while the rate of acylation of tyrosine increased only at high concentrations of the anhydride. More than 50% of the SH groups of cysteine, 30–40% of the OH groups of tyrosine, and of the order of 20% of the hydroxy-groups of serine and threonine were acetylated in the pH range 7.5–9.5. On succinylation, the same proportions were observed, but the degree of involvement of all the groups was somewhat lower because of the lower reactivity of succinic anhydride.

The introduction of an inhibiting additive (sodium sulphite) alters the pattern in the acetylation of fish protein: the involvement of the ε-amino-groups is reduced by 20%, that of the SH groups is reduced by 60%, and that of the OH groups of serine and threonine is reduced by a factor of two. Tyrosine is not then acetylated at all.[100] In the succinylation process, sodium sulphate inhibits most strongly the SH groups without affecting the reactivity of the OH groups of serine and threonine; *O*-Suc-tyrosine was not detected.[100] One should recall that it is readily deacylated.[102]

It is seen that, regardless of the acylation conditions, the main reaction centres (apart from the terminal α-amino-groups) are the ε-amino-groups of lysine and the degree of modification of the protein by acylation has therefore come to be estimated in terms of the percentage of the substituted ε-NH_2 group (the number of the accessible ε-NH_2 groups of lysine in the given protein system is adopted as 100%).

There exist biological, microbiological, and chemical methods for the determination of the accessible lysine in proteins.[116–119] One of the most reliable and trustworthy chemical methods is based on the reaction of the primary amino-groups with trinitrobenzene-sulphonic acid.[119]

A number of studies have been devoted to the investigation of the functional properties of acylated isolated fish proteins.[50,51,87,120–125] The emulsifying activity of the succinylated *Rockfish* isolated protein increased in proportion to the degree of modification. For example, it amounted to 1.3 g per mg of the protein for 30% modification and increased by a factor of two for 77% modification.[120] The isolated hake proteins acquired emulsifying properties as a result of succinylation which were superior to those of gelatine. The stability of the emulsions obtained was specially emphasised.[121] It is important to note that the changes in the emulsifying capacity of the succinylated isolated proteins at different pH and after the introduction of monovalent and divalent cations (Na^+, Ca^{2+}) were of a fundamentally different character than for the unmodified proteins.[121]

Acetylation and especially succinylation appreciably increased the foam-forming capacity of fish proteins, but the stability of the foams diminished compared with the control.[51]

By subjecting the homogenates of plant and animal tissues to acetylation simultaneously with succinylation, protein products with effective emulsifying and foam-forming properties are obtained together with a high solubility and water-absorption capacities. It has been recommended that such products be used as food surfactants.[122–124] Acylated myofibrillar proteins have a characteristic solubility profile: they are almost insoluble in an acid medium below the isoelectric point of the protein. The isoelectric point is displaced towards acid pH in proportion to the degree of modification of the protein. This is associated with the decrease in the number of free ε-amino-groups of lysine. The solubility increases sharply at neutral and weakly alkaline pH precisely because of the displacement of the isoelectric point.[121]

The absorption of water by the *Rockfish* isolated protein increases by a factor of two on acetylation and by a factor of five on succinylation.[51] Succinylation increases the capacity of the isolated protein for rehydration and its thermal stability (it did not coagulate even at 100 °C).[120]

It has been noted that acylation lowers somewhat the capacity for gel formation but does not destroy it: 3% solutions of the acetylated protein and 7% solutions of the succinylated protein formed gels of the same kind as a 2% solution of gelatine.[51]

A method has been proposed for the preparation of viscoelastic gels from fish proteins succinylated to a low extent (up to 10%), the stability of the gels being inversely correlated with the degree of modification.[125]

It has become evident that the acylation of isolated fish proteins makes it possible to use them as powerful emulsifying and foam-forming additives to food systems (Table 1).

Since the foam-forming and foam-stabilising properties of the succinylated fish protein are not inferior even to those of egg albumin, it is believed[87] that it can replace egg protein up to 50% in confectionery, for example in sweets or in whipped dessert dishes, and can be used in fruit desserts instead of gelatine[51] and in ice cream instead of caseine.[50]

Table 1. Functional properties of acetylated and succinylated fish proteins (the degrees of modification are equivalent and amount to 50–60%).[87]

Properties	Ac	Suc
Emulsifying activity at a protein concentration of 5 mg × ml^{-1}, % emulsion	61	97
Emulsifying capacity, g of oil/100 mg of protein	53	132
Capacity for gel formation, minimum concentration of protein solution (%) for the formation of a stable gel	4	3
Foam-forming capacity, volume of foam in ml	550	600
Stability of foam, syneresis volume in ml	71	32
Water absorption, ml of water/1 g of protein	15	20

The addition of succinylated fish protein to meat products in an amount of 10–20% does not impair their organoleptic properties.[87]

Similar results have been obtained in studies on the modification of structural meat proteins by acylation.[58,126] Acetylated and succinylated heart muscle proteins from cattle proved to be satisfactorily soluble in aqueous media at a low ionic strength and exhibited a higher emulsifying activity even at pH 6.0 than that of the native protein at pH 7.4, which is sufficient for meat systems.[126] Furthermore, anhydrides with a more complex structure were used for modification, such as benzene-1,2,4-tricarboxylic anhydride (BTCA) and benzene-2,3,4,5-tetracarboxylic dianhydride (BTCDA). In the reactivity series, they occupy an intermediate position between acetic anhydride (AA) and succinic anhydride (SA):

$$AA > BTCDA > BTCA > SA.$$

All the anhydrides quoted, with the exception of AA, reacted much more slowly with the SH and OH group of the protein than with the amino-groups. In the presence of the greatest excess of the anhydride, not more than 1/4 of all the SH groups of cysteine reacted and the products of the reaction of SA with serine and threonine were not detected. A sharp increase in the solubility of the derivatives was noted in all cases even for low degrees of modification.[126] Unfortunately no data have been quoted on the assimilability of the new modified proteins.

Summarising the data on the acylation of myofibrillar proteins, one must emphasise that acylation alters to different extents (depending on the nature of the acylating agent and the reaction conditions) the overall charge on the macromolecule, the isoelectric point being displaced to the acid region. As a rule the structure of the protein becomes less helical, which entails an enhancement in its hydrophobic properties. The tendency towards dissociation into subunits increases and the tendency towards specific polymerisation diminishes. Simplifying the pattern of the real changes in the modified protein system, the increase in solubility, in the moisture retaining capacity, and in swellability are usually attributed to the shift of the hydrophilic–hydrophobic balance towards an increased hydrophilicity; the increase in the emulsifying and foam-forming capacities is frequently explained by an enhancement of hydrophobic properties.

The set of chemical reagents used for the modification of myofibrillar food proteins is unfortunately extremely small. There is no information in the literature concerning isolated muscle proteins about promising methods such as, for example, phosphorylation, deamidation, and esterification.

When the chemical agents for the regulation of the functional properties are compared with enzymes, the following features may be noted. Chemical modification does not lead to the loss of the binding and gel-forming properties of proteins, of the kind observed in enzymic reactions. The degree of proteolytic decomposition has a stronger influence on the functional properties of the protein system than the degree of chemical modification. On the other hand, the specified level of chemical modification can be more readily ensured than a rigorously defined degree of proteolysis. From the standpoint of the preparation of highly functional isolated proteins, which remain stable on storage and during treatment in a specific food system, chemical modification has advantages compared with enzymic modification (see Section VI). However, certain types of chemical modification lower to different extents the nutrient value of food proteins and their assimilability, which does not occur in the enzymic treatment.

IV. Combined chemical and enzymic modification of proteins

In a number of instances, combined chemical and enzymic treatment of food muscle proteins has been applied extremely effectively.[50,51] The weak hydrolytic effect of bromeline on the succinylated *Rockfish* protein makes it possible to obtain excellent foams, as regards bulk and stability, at protein concentrations of 3–4% over a wide pH range. The stability of these foams was greater than that of the foams based on egg and soya proteins.[50] The maximum positive effect in the improvement of the foam-forming properties was obtained by mild proteolysis of 40–50% succinylated fish proteins.[51,127] However, under all the conditions tested, this procedure reduced the emulsifying activity, gel formation, and swellability.[51,127]

It has been reported[20] that, regardless of the sequence in which the acylation and proteolytic processes are carried out on fish proteins, products with similar functional properties are obtained, although, in principle the results should not be the same. If chemical modification is carried out in the first stage and the acylated proteins are then subjected to proteolysis, then in this instance proteolysis proceeds more slowly and certain peptide bonds are not split at all. Larger fragments of the protein molecules, chemically modified to a lesser extent, should be obtained in this way. If, other conditions being equal, the above processes are interchanged, then proteolysis proceeds without obstacles and the resulting protein fragments, having a larger number of accessible reaction groups, react chemically. This procedure should lead to more profound chemical transformations of smaller protein fragments.

Using these hypotheses, one may recommend the first method for the activation of the surface properties of a protein and the second

for increasing its solubility. From the standpoint of the retention of the nutrient value of the protein, the first method is preferable.

Another aspect of the successful use of the combined chemical and enzymic modification of the protein involves the covalent attachment of aminoacids or their esters with the aid of enzymes.[55,56,127,128] Using papain, the covalent attachment of the alkyl esters of leucine to succinylated fish protein has been achieved.[127] By varying the length of the hydrocarbon chain of the alkyl ester of leucine, the authors obtained superactive emulsifying and foam-forming agents: the C_4-C_8 alkyl groups correspond to the maximum foam-forming activity and the $C_{10}-C_{12}$ groups correspond to the maximum stability of the foams and emulsifying activity.

Transglutaminase is frequently used for the covalent "attachment" of aminoacids to the protein.[55,56,128,129] The efficiency of the reaction involving the attachment of the aminoacid residue increases if the amino-groups in the attacked protein were acylated beforehand. Intermolecular cross-links, which reduce the digestibility of the protein, are not then formed. After the enzymic treatment, the amino-groups can be regenerated. Maleic, 2,3-dimethylmaleic, and citraconic anhydrides, whose *N*-acyl residues are cleaved in an acid medium, were used for the reversible acylation. This procedure has been recommended for increasing the solubility and emulsifying capacity of isolated proteins from plant and animal raw materials.[55,56]

It has been suggested that fish proteins, to which hydrophobic aminoacid (leucine, norleucine, and alanine) have been "attached" enzymically, be used as food antifreeze agents. The alkyl residue of the ester group should also be hydrophobic ($R = C_8-C_{10}$). An antifreeze of this kind is non-toxic and is very effective in the storage of food products in a fresh form at low temperatures.[129]

V. Physicochemical modification methods

The physicochemical methods for the treatment of isolated food proteins include the following procedures: complex formation with natural biopolymers (proteins, polysaccharides, etc.) and also with monomeric compounds (carbohydrates, lipids); mechanical treatment of different kinds, heat treatment, etc.

Extensive studies on these lines have been carried out by Tolstoguzov and co-workers on proteins of plant origin.[3,130]

Changes in the functional properties of food proteins can be achieved by varying the hydrophilic–hydrophobic balance in the protein system as a result of specific protein–protein interactions. Studies of the conjugates of myosin with plant proteins have aroused considerable interest.[131–138] It has been noted that, when mixed solutions of myosin and 11S soya globulins are heated, hybrid aggregates are formed.[131] Basic subunits, formed on partial dissociation of the 11S globulins, and the heavy chains of myosin are capable of interacting. The degree of binding increases on raising the temperature in the range from 85 to 100 °C. As a result of thermal denaturation, the subunits undergo a conformational rearrangement accompanied by aggregation with formation of qualitatively new energetically more favourable protein complexes. Hydrophobic interactions play a significant role in this process.[132]

Myosin is able to aggregate with β-conglycinin in a similar way at temperatures above 85 °C.[133] The formation of mixed conjugates can be detected by gel electrophoresis. The aggregates obtained are distinguished by a high solubility and thermal stability. The latter property permitted the pasteurisation of meat systems with added soya protein.[134,135]

When solutions of actomyosin were heated with the "CIF" fraction of soya protein, the formation of stable gel structures of a new type was observed.[136,138] The denatured soya protein was associated in a definite manner with the actomyosin network, and, according to the scanning electron microscope data, the resulting structure differed appreciably from that of the thermogels formed by the individual components. According to the authors' hypothesis, the formation of disulphide linkages between the two protein partners is possible in this instance.[136]

Hybrid protein complexes can also be obtained by intermolecular cross-linking. The possibility of the covalent binding of myosin to globular proteins such as soya protein, casein, and gluten as a result of the formation of an amide bond between the γ-carboxy-groups of glutamic acid and the ε-amino-groups of lysine, both in the presence and absence of an activator enzyme (transglutaminase), was investigated.[55,56,128,137] The optimum binding conditions depend on the nature of both components. The percentage binding of soya protein and fibrin to myosin increased on raising the pH of the medium and temperature, while the binding of caseine was favoured by an increase in temperature and a decrease in pH. With participation of the enzyme, the maximum amounts of proteins bound to 1 g of myosin are 0.58 g of caseine, 0.30 g of gluten, and 0.15 g of soya protein.[128]

Complex formation of the type of protein–protein interaction found a practical application before its theoretical interpretation. It was noted in an early study[87] that, when proteins of different nature are dried together, not only are highly nutritious protein mixtures obtained but their functional properties are also retained at a high level. For example, instead of adding sodium chloride and phosphates to fish proteins in order to optimise their drying, it is more convenient to dry mixtures of fish and grain proteins which, together with a gain in the functional properties of the protein concentrate, has a positive economic effect. The grain additives (from 10 to 30 wt.%) can be wheat, rice, and virtually any kind of flour.[87,139]

The addition of plant proteins to semi-finished meat products ensures, by virtue of complex formation, the minimum losses of the moisture-retaining capacity of the system on heat treatment.[140]

Conjugates formed by proteins with carbohydrates possess as a rule highly effective functional properties. The ability of carbohydrates to protect muscle proteins against denaturation under both low-temperature conditions and on heat treatment has been known for a long time.[19] The antidenaturing capacity of saccharides in relation to fish proteins decreases in the sequence maltose > sorbital > sucrose ≃ maltitol > glucose > lactitol. At negative temperatures, carbohydrates exhibit under these conditions a highly protecting effect at lower concentrations.[141–143] When fish proteins are dried together with monosaccharides, highly hydrophilic complexes are produced. The solubility of such complexes is proportional to the percentage content of the saccharide and depends on the nature of the latter. In terms of their influence on the solubility of the adduct with fish protein, the monosaccharides tested can be arranged in the following sequence: glucose ⩾ sucrose > fructose.[19] Glycerol and partly hydrolysed starch have similar properties.[19] The solubility of conjugates of fish protein with starch is 25% of the solubility of the freshly isolated protein.

By drying fish protein with 10% of added glucose, sorbital, or sucrose, complexes with a high emulsifying activity and an enhanced thermal stability are obtained. However, they partly lose their nutrient value as a consequence of the Mayar reaction.[19]

With the aid of complex formation (for example with carbohydrates), it is possible to improve the capacity of acylated myofibrillar proteins for gel formation. For example, the aggregation of succinylated fish proteins with glucono-delta-lactone leads to the formation of gels distinguished by a high stability and formed even in oil-containing systems.[121]

The addition of glucono-delta-lactone and citric acid promotes the retention of functional properties by ground beef.[86]

Together with nucleotides, lipids bound to myofibrillar proteins protect them against denaturation. The mechanism of the protecting action requires further study.[62,144,145]

Certain functional properties of meat systems can be altered by simple procedures such as heat treatment. By selecting the optimum conditions (temperature and pressure), the moisture retaining capacity, tenderness, succulence, and other properties of meat specimens of different quality can be regulated.[146–148] The changes occurring in the properties can be explained by the partial or complete decomposition of individual components of the myofilaments: connectin and nebulin.[148]

Simple mechanical treatment of proteins, both animal and plant, for example, grinding in a vibromill, are known to be capable of improving their solubility and moisture-retaining capacity as a consequence of the mechanical degradation of sarcomers.[148,149]

Combined mechanochemical modification is much more effective. Under different conditions in the treatment of fish homogenates with acetic or succinic anhydride in a vibromill, it is possible to increase greatly their moisture-retaining and foam-forming capacities and their ability to stabilise foams.[149,150]

Presumably, among the physicochemical methods of treatment, the complex formation procedure is the most promising: it has no pronounced disadvantages or limitations of the kind charactersitic of chemical or enzymic modification (from the standpoint of toxicity or the loss of nutrient value). In general, practice has shown that the best results in the transformation of the functional properties of food proteins can be obtained by an appropriate combination of various modification procedures, for example, chemical and enzymic methods or chemical methods and complex formation.

VI. The nutrient value and the bioavailability of the modified food proteins

Among all the procedures for the modification of food proteins enumerated above, chemical treatment gives rise to special risks from the standpoint of the toxicity and bioavailability of the protein. The principal disadvantage of the chemical modification is believed to be the decrease in the nutrient value of the food proteins. Indeed, the action of chemical reagents leads to a definite loss of the bioavailability of the protein (different for each kind of chemical modification and for each type of modified objects). At the same time, the blocking of the most reactive groups of the protein leads to the formation of more stable, albeit less nutritious, non-toxic products.

The loss of nutrient value and the decrease in the assimilability of the protein products are the negative phenomena which accompany any traditional treatment of the protein (drying, canning, cooking, and even the storage process).[36,151] They are due to the involvement of particular chemical reactions of the active functional side groups in essential aminoacids. The ε-amino-groups of lysine and the SH groups of cysteine are believed to belong to the class of the most reactive groups. For example, during the storage of both frozen fish and of dry isolated fish proteins, undesirable side products are formed, one of which is formaldehyde. The latter reacts readily with the amino-, mercapto-, and hydroxy-groups of the protein and to a lesser extent with the amide groups, reducing the assimilability of the protein.[152,153] Myosin interacts with certain free aminoacids even at –20 °C, the reactions of the protein with taurine, lysine, and histidine accelerating the denaturation aggregation of the protein.[97]

In the oxidative degradation of lipids, the percentage of the ultilised protein (fish or meat) can be reduced by a factor of two, the maximum loss involving under these conditions tryptophan, lysine, histidine, methionine, and cysteine.[36,154,155]

During the heat treatment of fish at temperatures starting from 50 °C, the mercapto-groups of cysteine undergo vigorous oxidation with formation of disulphide bonds. A greater decrease in assimilability was observed for lean fish compared with fat fish. The SH groups responsible for the binding to lipids are apparently protected against oxidation.[156] When proteins are heated to temperatures ranging from 80 °C upwards, there is also the possibility of the interaction of the lysine ε-amino-groups with the accessible carboxy-groups of glutamic and aspartic acids.[157,158] The same reaction can be initiated by enzyme action rather than heat,[159] which naturally leads to a decrease in the amount of the accessible lysine.

A shift of the isoelectric point of the protein in fish concentrates from pH 5.0 to 4.5 as a result of lyophilic drying has been noted, which is incontrovertible evidence for the involvement of the ε-amino-groups in the intramolecular and intermolecular cross-links of the protein.[19]

When fish is canned, not only is it not possible to avoid a decrease in the assimilability of the protein by approximately 15% [160] but it is also necessary to achieve constant monitoring of the accumulation of the potentially toxic compounds formed as a consequence of the occurrence of the Mayar reaction during sterilisation as has been shown for salmon and plaice.[161]

Among aminoacids, lysine is the most active participant in the reaction with sugars.[162] A linear decrease in assimilability as a consequence of the loss of accessible lysine, in fact as a result of the Mayar reaction, has been noted for a whole series of food proteins.[74] It is therefore recommended that serious attention should be paid to the analysis of food products with a relatively high carbohydrate content if they are heat treated.[74,163] For example, it has been shown that 19 days after the addition of 10% glucose to a system based on fish protein with an 18% moisture content at 35 °C half the accessible lysine is lost.[163] Sodium sulphite (or SO_2) is added to inhibit the Mayar reaction but this measure is not universal.[153]

Acylation of proteins appreciably reduces the possibility of the occurrence of this undesirable reaction and also of other side reactions undergone by the unmodified protein under the conditions of alkaline and heat treatment, on storage, and on drying.[36,153,157,158,164,165]

Individual types of modification of food proteins, especially chemical modification, lead to profound changes in the protein structure. Studies on bioavailability, assimilability, and metabolic pathways for the modified systems are therefore of primary importance together with other complex medicobiological problems as regards toxicity and carginogenic and mutagenic properties of new products.[166–169]

A definite trend has arisen in recent years towards reducing the content of common salt in food products for man.[58] When food proteins are used in the form of proteinates, an optimum limit to the content of inorganic ions, which does not affect the health of man,

must also be found. In those cases where alkaline hydrolysis is used to solubilise proteins, it is essential to desalinate the product.[87,170–172]

The nutrient properties of protein isolated from chicken muscle tissue have been compared in detail[173] with those of the muscle tissue separated mechanically in the form of a homogenate. It was shown that alkaline extraction followed by acid precipitation does not entail any appreciable loss of nutrient value of the protein, but its functional properties are then appreciably impaired.[173]

As regards chemically modified food proteins, most information concerning medicobiological tests refers to acylated proteins. Since the available literature data are fairly contradictory, it is apparently desirable to compare data referring to acylated proteins of different kinds.

The content of accessible lysine is known to diminish during the acylation of protein. The role of lysine in human and animal nutrition is extremely important. The deficiency of this essential aminoacid induces serious disturbances in metabolic processes, in the first place in the lipid metabolism.[174] Despite the fact that the set of methods for the determination of the available lysin *in vivo* is entirely satisfactory,[2] the interpretation of the experimental data is frequently complicated by side effects.[172] The prospects for the chemical modification of food proteins depend on the validity of biological tests. The question of the assimilability of lysine from its ε-amide derivatives is mainly disputed. The deacylase activity has been investigated on animals in fair detail. As early as 1943, data were obtained on the partial assimilation of ε-Ac-lysine by young rats.[175] The rate of growth of experimental animals receiving ε-Ac-lysine perorally was lower than for the controls. However, on doubling the dose of ε-Ac-lysine, the difference in the growth of rats was indistinguishable. When ε-Ac-lysine was administered intra-abdominally, partial assimilation of lysine by the animals was also noted.[175] These data agree with the conclusions reached in a whole series of studies on these lines namely that rats assimilate approximately 50% of lysine and mice assimilate about 30% from a diet containing ε-Ac-lysine.[157,158,176–178]

Using di-, tri-, and tetra-peptides containing the ε-Ac- and ε-Suc-lysine residues as models of the fragments of the acylated protein, their proteolysis was investigated *in vitro* under the influence of enzymes from the gastrointestinal tract.[179,180] All the α-peptide bonds adjoining the modified lysine were cleaved, (in contrast to the ε-amide bond) in conformity with the nature of the enzyme tested. However, the initial rates of proteolysis were lower in attack on ε-Ac- and especially ε-Suc-peptides.[179]

One of the little investigated aspects of the assimilation of acylated proteins is the stage where their hydrolysis products are absorbed. In experiments on the isolated small intestine of the chicken, it has been shown that ε-Ac-lysine is absorbed by the cells of the mucous membrane almost just as readily as free lysine, while ε-Suc-lysine is absorbed much less effectively. Lysine modified by aliphatic acid or glutamic acid derivatives is hardly transported through the small intestine of chicks.[180]

The results of Leclerc and Benoiton[181] demonstrate the selective activity of animal kidney acylases: only the ε-formyl and ε-acetyl derivatives of lysine deacylated. The deacetylation of the ε-Ac-lysine by the chick kidney tissue homogenate takes place fairly vigorously (30% of the ε-Ac groups are split off in 4 h). The data presented show that, although the ε-acylated proteins are biodegradable, from the standpoint of their true utilisation acetylated derivatives have undoubted advantages over all other acylated proteins.

With the aid of a microbiological test, it has been demonstrated convincingly that the acylation of the hydroxy- and mercapto-groups of caseine does not lower its nutrient value. In those cases where the ε-amino-groups of lysine were acylated, the biological value of the protein fell with increase in the size of the acyl group. The biological value of caseine fell from 100 to 48% on acetylation (degree of modification 35%) and to 12% on succinylation (degree of modification 74%).[182] The low and moderate degrees of succinylation of caseine and lactalbumin hardly lower their nutrient value, as shown enzymically *in vitro* and by growth tests on rats.[183,184] It has been reported that mice fed on highly acetylated caseine grew, developed, and multiplied.[178] However, they were smaller and leaner than the control animals and had fewer offspring. Chicks receiving acetylated egg albumin (degree of modification 67%) and succinylated egg albumin (degree of modification 55%) showed a weight increment during growth which was greater in the first instance and smaller in the second. However, both groups grew more slowly than the control animals. In those cases where lysine had been added to the acetylated egg albumin, the growth of the chicks was normalised.[172]

The bioavailability of the succinylated protein of unicellular organisms fell by a factor of 10. The estimate was carried out *in vitro* using the pepsin–pancreatin enzyme system.[185]

When proteins deficient in lysine were acetylated, the decrease in biological value was inappreciable. After the complete acetylation of the protein isolated from *Vicia-faba*, a decrease in nutrient value was not noted.[186] We shall compare these data with the available information concerning the nutrient value of acylated muscle proteins.

Groninger and Miller[115] investigated *in vitro* the susceptibility to attack by pepsin and trypsin of fish protein 50% acetylated and 40% succinylated. They reported that the rate of proteolysis by pepsin did not change compared with the unmodified protein. On the other hand, trypsin hydrolysed less effectively the succinylated protein and still less so the acetylated protein, in agreement with other data.[187]

The bioavailability of 90% succinylated fish protein has been estimated[121] from the percentage of the lysine liberated on treatment with pancreatin *in vitro*. The bioavailability of the modified protein fell by a factor of 10.

It has been demonstrated on several generations of rats and mice that the consumption of acetylated and succinylated fish proteins[87] as well as acetylcaseine is not harmful.[188] Histological studies on sections of the liver, the lungs, the kidneys, and the adrenal glands of the experimental animals did not reveal pathological effects and no changes in the internal organs themselves were noted.[187,188]

The metabolism of the acetylated and succinylated fish proteins was investigated on rats by introducing the ^{14}C radioactive label into the ε-amide groups of the protein.[115] The degree of utilisation of the protein was estimated from the distribution of ^{14}C in the carbon dioxide and urine from the animals. After the intravenous administration of a solution of ε-Suc-lysine or the hydrolysate of the Suc-protein, 87 and 93% of ε-Suc-lysine was eliminated with urine respectively, while after the above substances were administered perorally 75 and 72% of ε-Suc-lysine was eliminated from the organism. According to the final data, after intravenous administration, ε-Suc-lysine is not assimilated at all, while ε-Ac-lysine is assimilated to an extent of approximately 25%. After the peroral administration to rats, about 14% of the lysine from ε-Ac-lysine and approximately 50% of lysine from the acetylated protein are assimilated.[115] It has been noted that the metabolism of the succinylated derivatives is much slower than that of the acetylated derivatives.[115]

It has been suggested that the partial utilisation of lysine after the peroral consumption of acyllysine derivatives or acylated proteins can be achieved as a result of the activity of their intestinal microflora.[180,189,190]

The assimilation of lysine on biodegradation of acylated proteins takes place with a higher coefficient of utilisation than the assimilation of lysine from its ε-amide derivatives.[166,190,191] The difference between the mechanisms of these processes has been confirmed experimentally.[180] When the membrane food digestion process was modelled on the isolated chick small intestine, it was noted that the ε-Ac-lysine-containing peptides are partly deacylated, although the elimination of the ε-Ac-group from ε-Ac-lysine was not observed under these conditions[180] (Table 2).

Table 2. Biological value of acylated food proteins.

Protein	Degree of modification, %	Coefficient of effectiveness of protein, %	Refs.
Caseine	0	100	—
Ac-casein	35	48	[182]
Suc-casein	74	12	[182]
Ac-casein	100	64	[188]
Suc-casein	100	12	[188]
FPC*	0	110	[120]
Suc-FPC	30—40	79	[120]
FPC	0	101	[115]
Ac-FPC	50	103	[115]
Ac-FPC	75	85	[115]
Suc-FPC	25	96	[115]
Suc-FPC	40	73	[115]
Suc-FPC	75	35	[87]
FPC	0	41	[121]
Suc-FPC	90	4	[121]
Caseine	—	2,5**	[58]
Myofibrillar protein from ox heart muscle (MPOHM)	—	2,83**	[58]
Acetylated MPOHM	—	2,55**	[58]
Succinylated MPOHM	—	2,36**	[58]

*FPC = fish protein concentrate.
**In grammes per gramme of increment.

The utilisation of proteins with covalently attached aminoacids requires additional study. The metabolism of such proteins is undoubtedly difficult,[117] because the isopeptide bond formed is not cleaved by digesting enzymes and the isopeptides themselves are not absorbed into the blood, as shown in relation to glutamylisopeptides.[180] From the standpoint of Feeney and others,[64–66] the bioavailability of proteins with isopeptide fragments is determined by the nature of the grafted aminoacids and their steric accessibility to the enzyme.

In our view, instead of the covalent binding of the aminoacids, it is more rational to enrich the isolated proteins by adding polyaminoacids. The excellent assimilation of polylysine is the basis for this recommendation.[66,192]

There are doubts concerning the bioavailability of hybrid protein conjugates obtained by grafting glutamic acid and lysine residues.[128,137] However, it is believed[137,193,194] that glutamyllysine-cross-linked proteins are fully assimilated in the intestine, although as a rule the rate of metabolism is extremely low.

Objective assessment and timely introduction of promising methods for the modification of isolated proteins makes it possible to intensify the ultilisation of food proteins from traditional and non-traditional sources in order to obtain new products for mass consumption.

References

1. L Shimilt (Editor) *Khimiya i Obespechenie Chelovechestva Pishchei* (The Chemistry of Food and the Provision of Food for the Human Population), Izd. Mir, Moscow, 1986, 189 pp
2. V G Vysotskii, V A Tutel'yan *Obz. Inf. VNII Med. i Med.-Tekhn. Inf. Gigiena.*, 1987, (1) 1
3. V B Tolstoguzov *Novye Formy Belkovoi Pishchi* (New Forms of Protein Food), Agropromizdat, 1987, 303 pp
4. G G Mikeladze *Pishch. i Pererabat. Prom.*, 1987, (10) 42
5. S I West *J. Chem. Technol. Biotechnol.*, 1984, **34**(3) 176
6. M Chaneva, F Georgieva, P Dalev *Biotekhnologiya i Biotekhnika*, 1986, (4) 34
7. S V Rogozhin *Vestn. Akad. Nauk SSSR*, 1986, (1) 73
8. A P Chernogortsev *Rybnoe Khozyaistvo*, 1984, (5) 68
9. A P Gamuilo, G M Kuz'micheva *Kompleksnaya Pererabotka Promyslovykh Bespozvonochnykh* (Combined Processing of Commercially Useful Invertebrates), Kaliningrad, 1986, p. 83
10. G I Solomko, P N Maistruk, A G Sokolova *Ratsion. Pitanie*, 1983, (18) 9
11. L S Baidalinova, G M Kuz'micheva, L I Perova *Issledovaniya po Tekhnologii Rybnykh Produktov* (Studies on the Technology of Fish Products), Kaliningrad, 1980, p. 36
12. L S Baidalinova, G M Kuz'micheva, E A Yurkina, et al. *Ispol'zovanie Bioresursov Atlanticheskogo Okeana na Pishchevye Tseli* (The Utilization of the Bioresources in the Atlantic Ocean as Food), Kaliningrad, 1983, p. 95
13. G I Solomko *Rybnoe Khozyaistvo*, 1986, (8) 62
14. A G Sokolova *Ratsion. Pitanie*, 1980, (15) 47
15. L I Borisochkina *Rybnoe Khozyaistvo*, 1985, (7) 1
16. L I Borisochkina *Rybnoe Khozyaistvo*, 1987, (2) 61
17. G Piclet *Can. Nutr. et Diét.*, 1987, **22**(4) 317
18. J Mai, J K Shetty, T-M Kan, et al. *J. Agric. Food Chem.*, 1980, **28**(4) 884
19. J Spinelli, B Koury, R Miller *J. Food Sci.*, 1972, **37**(4) 599
20. J Spinelli, H Groninger, B Koury, et al. *Prog. Biochemistry*, 1975, **10** 31
21. J E Kinsella *CRC Critical Reviews in Food Science and Nutrition*, 1976, Vol. 7, No. 3, p. 219
22. J E Kinsella *Food Chem.*, 1981, **7** 273
23. J E Kinsella *Food Protein Deterioration: Mechanisms and Functionality* (Edited by J P Cherry), ACS Symposium Ser., Am. Chem. Soc., Washington, DC, 1982, p. 301
24. J E Kinsella *Food Proteins Proceedings Kellogg Foundation International Symposium, Cork, 21—24 September, 1981* (Edited by P F Fox, J J Condon), Appl. Sci. Publ., London, etc., 1982, p. 51
25. S Nakai *J. Agric. Food Chem.*, 1983, **31**(4) 676
26. G D Kutuzova, N N Ugarova, N V Berezin *Usp. Khim.*, 1984, **53**(11) 1852 [English translation in *Russ. Chem. Rev.*, 1984(11)]
27. J R Whitaker *Food Proteins: Improvement Through Chemical and Enzymatic Modification* (Edited by R E Feeney, J R Whitaker), Am. Chem. Soc., Washington, DC, 1977, p. 95

28. T Richardson *Food Proteins: Improvement Through Chemical and Enzymatic Modification* (Edited by R E Feeney, J R Whitaker), Am. Chem. Soc., Washington, D C, 1977, p. 185
29. J R Whitaker, A J Puigserver *Modification of Proteins: Food Nutritional and Pharmacological Aspects* (Edited by R E Feeney, J R Whitaker), Adv. Chem. Ser. 198, Am. Chem. Soc., Washington, DC, 1982, p. 57
30. N F Haard, L A W Feltham, N Helbig, et al. *Modification of Proteins: Food Nutritional and Pharmacological Aspects* (Edited by R E Feeney, J R Whitaker), Adv. Chem. Ser. 198, Am. Chem. Soc., Washington, DC, 1982, p. 223
31. T Richardson *Food Protein Deterioration: Mechanisms and Functionality* (Edited by J P Cherry), ACS Symp. Ser., Am. Chem. Soc., Washington DC, 1982, p. 31
32. G Matheis, J R Whitaker *J. Food Biochem.*, 1984, **8**(3) 137
33. N Yu Komissarova, N M Sud'ina *Rybnoe Khozyaistvo*, 1984, (3), 17
34. L I Borisochkina *Rybnoe Khozyaistvo*, 1976, (5), 47
35. Y Kusayama *Up-to-Date Food Progress*, 1987, **22**(5) 32
36. T Richardson, J J Kester *J. Chem. Educ.*, 1984, **61** 325
37. J R Whitaker *Food Technology*, 1978, **32**(5) 175
38. S Lowey *Fibrous Proteins: Scientific, Industrial and Medical Aspects* (Edited by D A D Parry, L K Creamer), Acad. Press, London, 1979, p. 1
39. M B Hale *Food Technol.*, 1969, **23** 107
40. C Cheftel, M Ahern, D Wang, et al., *J. Agric. Food Chem.*, 1971, **19** 155
41. G Sampedro, M López-Benito, L Pastoriza *Inf. Techn. Inst. Invest Pesq.*, 1983, (108) 20
42. A M Hermansson, B Sivik, C Skjoldebrand *Lebensm. Wiss. Technol.*, 1971, **4** 201
43. Y Guigor, J Solms *Chemical Senses and Flavour*, 1976, **2** 71
44. R Bressani *J. Am. Oil Chem. Soc.*, 1981, **58**(3) 392
45. T A Orlova, K A Fleider *Tekhnologiya Rybnykh Produktov* (Technology of Food Products), Murmansk, 1981, p. 107
46. M W Du Bois, A F Anglemier, M W Montgomery *J. Food Sci.*, 1972, **37**(1) 27
47. J Spinelli, B Koury, R Miller *J. Food Sci.*, 1972, **37**(4) 604
48. J Spinelli, B Koury, US P. 3 826 848; *Ref. Zh. Khim.*, 1975, 8R203P
49. H S Groninger, R Miller *J. Fish. Res. Board Can.*, 1974, **31** 477
50. H S Groninger, R Miller *J. Food Sci.*, 1975, **40** 327
51. R Miller, H S Groninger *J. Food Sci.*, 1976, **41** 268
52. D M Smith, C J Brekke *J. Food Sci.*, 1984, **49** 1525
53. D M Smith, C J Brekke *J. Agric. Food Chem.*, 1985, **33**(4) 631
54. D M Smith, C J Brekke *J. Food Sci.*, 1985, **50**(2) 308
55. H Chiba, M Yoshikawa, K Ikura, et al. *Res. Food Sci. Nutr. Proceedings VI International Congr. Food Science and Technology* (Edited by J V McLoughlin et al.), Boole Press, Dublin, 1983, Vol. 2, p. 57
56. Motoki Masao, Funao Sikki, Takinami Koiti, Japanese Appl. 59-21 0097; *Ref. Zh. Khim.*, 1985, 240 252
57. G C Viniegra *Proceedings IX International Nutr. Congr.*, 1975, 3 91
58. C J Brekke, T A Eisele *Food Technology*, 1981, **35**(5) 231
59. G E Means, R E Feeney *Chemical Modification of Proteins*, Hollen-Day Inc., San Francisco, 1971
60. P Shukla Triveni *Food Protein Deterioration: Mechanisms and Functionality* (Edited by J P Cherry), ACS Symp. Ser., Am. Chem. Soc., Washington DC, 1982, p. 275
61. K D Schwenke *Nahrung*, 1978, **22**(1) 101
62. D S Ryan *Adv. Chem. Ser.*, 1977, **160** 67
63. R E Feeney *Adv. Chem. Ser.*, 1977, **160** 3
64. R E Feeney, R B Yamasaki, K F Geoghegan *Adv. Chem. Ser.*, 1982, **198** 3
65. A J Puigserver, H F Gaertner, L C Sen, et al., *Adv. Chem. Ser.*, 1982, **198** 149
66. J R Whitaker *Protein Tailoring for Food and Medical Uses* (Edited by R E Feeney, J R Whitaker), Acad. Press, New York, 1987, p. 41
67. S Arai, M Watanable, N Hirao *Protein Tailoring for Food and Medical Uses* (Edited by R E Feeney, J R Whitaker), Acad. Press, New York, 1987, p. 75
68. S R Tannenbaum, M Ahern, R P Bates *Food Technol.*, 1970, **24**(5) 604
69. S R Tannenbaum, R P Bates, L Brodfeld *Food Technol.*, 1970, **24**(5) 607
70. M N Moorjani, M S Vasantha *J. Food Sci. Technol.*, 1973, **10**(1) 3
71. A S Nashef, D T Osuga, H S Lee, et al. *J. Agric. Food. Chem.*, 1977, **25**(2) 245
72. P A Finot *Adv. Chem. Ser.*, 1982, **198** 91
73. J R Whitaker, R E Feeney *CRC Crit. Rev. Food Sci. Nutr.*, 1983, **19**(3) 173
74. Chung Si-Yin, H E Swaisgood, G L Catignani *J. Agric. Food Chem.*, 1986, **34** 579
75. R Miller, J Spinelli, J K Babbit *J. Food Sci.*, 1983, **48**(1) 296
76. P A Morrissey, D M Mulvihill, E M O'Neil *Developments in Food Proteins-5* (Edited by B J F Hudson), Elsevier Appl. Sci., London, etc., 1987, p. 195
77. V Kalous, Z Pavlicek *Biophysical Chemistry* (Translated into Russian), Izd. Mir, Moscow, 1985, 446 pp
78. E W Helendoorn *Food Technol.*, 1962, **16**(9) 119
79. R Hamm *Food Technol.*, 1982, **36**(11) 105
80. G Offer, J Trinik *Meat Sci.*, 1983, **8** 245
81. J Synowiecki, Z E Sikorski *Przemysl Spozywczy*, 1984, **38**(2) 56
82. D A Halliday *Process Biochem.*, 1978, (7) 6
83. T Yasui, M Sakanishi, Y Hashimoto *J. Agric. Food Chem.*, 1964, **12**(5) 392
84. T Yasui, T Fukazawa, K Takahashi, et al. *J. Agric. Food Chem.*, 1964, **12**(5) 399
85. P B Kenney, R L Henrickson, P L Claypool, et al. *J. Food Sci.*, 1985, **50**(2) 277
86. A Bantan *Technol. Mesa*, 1987, **28**(2) 56
87. J Spinelli, B Koury, H Groninger, et al. *J. Food Techn.*, 1977, 184
88. Y Hiroshi, S Masahiro, W Atsuhi, et al. *Bull. Jap. Soc. Sci. Fish.*, 1985, **51**(4) 667
89. A D Woyewoda, E G Bligh *J. Food Sci.*, 1986, **51**(4) 932
90. Basu Subrata, K P Das, D K Chattoraj *J. Food Sci. Techn.*, 1985, **22**(3) 194
91. S Barbut, N Tanaka, R G Cassens, et al. *J. Food Sci.*, 1986, **51** 1136
92. K A Nelson, F F Busta, J N Sofos, et al. *J. Food Prot.*, 1983, **46** 846
93. M T Madril, J N Sofos *J. Food Sci.*, 1986, **51** 1147
94. B Ya Golant, N A Petrov *Povyshenie Stoikosti Zhirov i Zhirosoderzhashchikh Produktov* (An Increase of the Stability of Fats and Fat-Containing Products), Pishchepromizdat, Moscow, 1958, 103 pp
95. S Damodaran, J E Kinsella *J. Agric. Food Chem.*, 1983, **31**(4) 856

96. S B Rao *Fish. Techn.*, 1984, **21**(1) 29
97. S-T Jiang, T-C Lee, C O Chichester *Res. Food Sci. Nutr. Proceedings VI International Congr. Food Science and Technology* (Edited by J V McLoughlin, et al.), Boole Press, Dublin, 1983, Vol. 1, p. 68
98. O Iuyuo, O Yasuo *Bull. Jap. Soc. Sci. Fish.*, 1985, **51**(12) 2079
99. Z E Sikorski *Przemysl Spozywczy*, 1983, **37**(6) 253
100. K-H Lee, H S Groninger, J Spinelli *Marine Fish Rev.*, 1981, **43**(3) 14
101. G Allen, J I Harris *Eur. J. Biochem.*, 1976, **62** 601
102. A D Gounaris, G Perlmann *J. Biol. Chem.*, 1967, **242** 2739
103. A Mühlrad, K Ajtai, F Fabiani *Biochim. Biophys. Acta*, 1970, **205** 342
104. K Shuji, K Kunihiko, A Ven-ichi, et al. *Bull. Jap. Soc. Sci. Fish.*, 1985, **51**(4) 651
105. T Ito, N Ando *Agric. Biol. Chem.*, 1974, **38**(8) 1423
106. H Oppenheimer, K Bárány, G Hamoir, et al. *Arch. Biochem. Biophys.*, 1966, **115**(1) 233
107. H Oppenheimer, K Bárány, G Hamoir, et al. *Arch. Biochem. Biophys.*, 1967, **120**(1) 108
108. R H Locker, C J Haguard *Arch. Biochem. Biophys.*, 1967, **120**(2) 454
109. T Ito, N Ando *Agric. Biol. Chem.*, 1975, **39**(3) 575
110. A F S A Habeeb, H G Cassidy, S J Singer *Biochim. Biophys. Acta*, 1958, **29**(3) 587
111. A Mühlrad, A Coorsi, A L Granata *Biochim. Biophys. Acta*, 1968, **162**(3) 435
112. S Tayyab, M A Qasim *J. Biochem.*, 1986, **100**(5) 1125
113. Yu S Borovikov, I Kokol', D Shchchensna, et al. *Biokhimiya*, 1986, **51**(4) 691
114. Yu S Borovikov, D I Levitskii, L A Shuvalova, et al. *Biokhimiya*, 1987, **52**(12) 2061
115. H S Groninger, R Miller *J. Agric. Food Chem.*, 1979, **27**(5) 949
116. I N Pyatnitskaya, N A Vorob'eva *Voprosy Pitaniya*, 1972, (3) 3
117. J W Finley, M Friedman *Cereal Chem.*, 1973, **50**(1) 101
118. C Hoinard, P Maingault, G Crouzat-Reynes, et al. *J. Chromatogr.*, 1986, **355** 350
119. M L Kakade, I E Liener *Anal. Biochem.*, 1969, **27** 273
120. H S Groninger *J. Agric. Food Chem.*, 1973, **21**(6) 978
121. L-F Chen, T Richardson, C H Amundson *J. Milk Food Techn.*, 1975, **38**(2) 89
122. G Mieth, E Lange, J Proll, et al., DDR P. 240 831
123. M Hatano, H Takano, K Takama, et al. *Bull. Jap. Soc. Sci. Fish.*, 1979, **45** 861
124. M Hatano, H Takano, K Takama, et al. *Bull. Jap. Soc. Sci. Fish.*, 1979, **45** 951
125. Sun Chao-Tung *Res. Food Sci. Nutr. Proceedings VI International Congr. Food Science and Technology* (Edited by J V McLoughlin, et al.), Boole Press, Dublin, 1983, Vol. 1, p. 165
126. T A Eisele, C J Brekke *J. Food Sci.*, 1981, **46**(4) 1095
127. M Watanable, S Arai *Adv. Chem. Ser.*, 1982, **198** 199
128. K Ikura, M Yoshikawa, R Sasaki, et al. *Agric. Biol. Chem.*, 1981, **45** 2587
129. S Arai, M Watanable, Japanese Appl. 60-226 588; *Ref. Zh. Khim.*, 1986, 20R391
130. V B Tolstoguzov, E E Braudo, V Ya Grinberg, et al. *Usp. Khim.*, 1985, **54**(10), 1738 [English translation in *Russ. Chem. Rev.*, 1985(10)]
131. I C Peng, W R Dayton, D W Quass, et al. *J. Food Sci.*, 1982, **47** 1984
132. Kawai Yuji, Hatano Mutsuo, Zama Koichi *Bull. Fac. Fish. Hokkaido Univ.*, 1983, **34**(2) 131; *Ref. Zh. Khim.*, 1984, 4P334
133. N L R King *J. Agric. Food Chem.*, 1977, **25**(1) 1001
134. I C Peng, W R Dayton, D W Quass, et al. *J. Food Sci.*, 1982, **47** 1976
135. I C Peng, S S Neilsen *J. Food Sci.*, 1986, **51**(3) 588
136. S Haga, T Ohashi *Agric. Biol. Chem.*, 1984, **48**(4) 1001
137. L Kurth, P J Rogers *J. Food Sci.*, 1984, **49**(2) 573
138. Shiga Katsuji, Yasutomi Naramura, Yasuhiro Taki *Jap. J. Zootechn. Sci.*, 1985, **56**(11) 897; *Ref. Zhur. Khim.*, 1986, 14P108
139. G V Semenov, I K Gorshkov, V P Kartoshkin *Kholodil. Tekhnika*, 1987, (5) 19
140. N K Zhuravskaya, I M Tyugai, Yu M Bukhteeva, et al. *Myasn. Industriya SSSR*, 1987, (5) 39
141. T Ogizumi, K Hashimoto, J Ogura, et al. *Bull. Jap. Soc. Sci. Fish.*, 1981, **47**(7) 901
142. O Fuyuo, O Yasuo *Bull. Jap. Soc. Sci. Fish*, 1985, **51**(12) 2079
143. I Matsumoto, K Arai *Bull. Jap. Soc. Sci. Fish*, 1986, **52**(11) 2033
144. T Okada, N Inoue, M Akiba *Bull. Jap. Soc. Sci. Fish*, 1986, **52**(1) 121
145. V P Bykov *Izmeneniya Myasa Ryby pri Kholodil'noi Obrabotke* (Changes in the Flesh of Fish During Cold Processing), VO Agropromizdat, Moscow, 1987, p. 152
146. C J Findlay, D W Stanley, E A Gullett *Meat Sci.*, 1986, **16**(1) 57
147. I Seuss, K-O Honikel *Ernähr.-Umschau*, 1987, **34**(10) 343
148. R H Locker, D Y C Wild *Meat Sci.*, 1984, **11**(2) 89
149. J Kroll, B Grassmann, J Proll, et al *Nahrung*, 1984, **28**(4) 389
150. J Kroll, G Mieth, B Grassmann, et al., DDR P. 212 740
151. J R Kirk *J. Chem. Educ.*, 1984, **61**(4) 364
152. J Spinelli, B Koury *J. Agric. Food Chem.*, 1979, **27**(5) 1104
153. R E Feeney, G Blankenhorn, H B F Dixon *Advances in Protein Chemistry* (Edited by C B Anfinsen, et al.), Acad. Press, New York, etc., 1975, Vol. 29, p. 136
154. T Matoba, D Yonezawa, B M Nair, et al. *J. Food Sci.*, 1984, **49**(4) 1082
155. K Devadasan, P G Nair, A P D Viswanathan *Fish. Technol.*, 1985, **22**(1) 70
156. J Opstvedt, R Miller, R W Hardy, et al. *J. Agric. Food Chem.*, 1984, **32**(4) 929
157. J Bjarnason, K J Carpenter *Brit. J. Nutr.*, 1969, **23**(4) 859
158. J Bjarnason, K J Carpenter *Brit. J. Nutr.*, 1970, **24** 313
159. S S Matacic, A G Loewy *Biochim. Biophys. Acta*, 1979, **576**(2) 263
160. Z Ganowiak, E Lipka *Bromatol. Chem. Toksikol.*, 1979, **12**(2) 97
161. C A Krone *Environ. Health Perspect.*, 1986, **67** 75
162. S H Ashoor, J B Zent *J. Food Sci.*, 1984, **49**(4) 1206
163. R A Schinckels, H C Warmbier, T P Labuza *J. Agric. Food Chem.*, 1976, **24**(5) 901
164. M Friedman, A T Noma *J. Agric. Food Chem.*, 1986, **34** 497
165. M Friedman, P M Masters *J. Food Sci.*, 1982, **47** 760
166. C Kies *J. Agric. Food Chem.*, 1981, **29**(3) 435
167. M P Chernikov *Voprosy Pitaniya*, 1986, (5) 68
168. I S Zilova, O N Shirokova *Voprosy Pitaniya*, 1986, (3) 56
169. K G Sikka, R Singh, D P Gupta, et al. *J. Agric. Food Chem.*, 1979, **27**(5) 946
170. J D Blaxland *Vet. J.*, 1946, **102** 157
171. J E Savage *Poultry Sci.*, 1972, **51** 35

172. A J King, H R Ball, J D Garlich *J. Food Sci.*, 1981, **46**(4) 1107
173. G Ozimek, P Jelen, L Ozimek, et al *J. Food Sci.*, 1986, **51**(3) 748
174. V N Okunev, O N Golin'ko *Voprosy Pitaniya*, 1984, (1) 12
175. A Neuberger, F Sanger *Biochem. J.*, 1943, **37** 515
176. R W Boggs *Nutritional Improvement of Food and Feed Proteins* (Edited by N Y Fieldman), Plenum Press, New York, 1978, p. 571
177. P A Finot, F Mottu, E Bujard, et al. *Nestle Research News*, 1980/81, 131
178. M Friedman, M R Gumbmann *J. Nutr.*, 1981, **111**(8) 1362
179. S M Andreev, O M Galkin, N A Samoilova, et al. *Bioorg. Khim.*, 1986, **12**(6) 725
180. R I Kushak, I L Tarvid, N A Basova, et al. *Izv. Akad. Nauk Latv. SSR*, 1987, (7) 74
181. J Leclerc, L Benoiton *Can. J. Biochem.*, 1968, **46** 471
182. W M Belikow, S G Kharatyan, M G Besrukow, et al. *Nahrung*, 1975, **19** 65
183. M Siu, L U Thompson *J. Agric. Food Chem.*, 1982, **30** 1179
184. M Siu, L U Thompson *J. Agric. Food Chem.*, 1982, **30** 743
185. M P McElwain, R Richardson, C H Amundson *J. Milk Food Technol.*, 1975, **38** 521
186. J Uhlig, J Proll, R Noak, et al. *Nahrung*, 1980, **24**(9) 899
187. C-H Li, L Bertsch *J. Biol. Chem.*, 1960, **235** 2638
188. L K Creamer, J Roeper, E H Lahrey *J. Dairy Sci. Technol.*, 1971, **6** 107
189. M Tanaka, T Lee, C O Chichester *J. Nutr.*, 1975, **105** 989
190. P Finot, E Bujard, M Arnaud *Adv. Exp. Med. Biol.*, 1977, **86** 51
191. V R Young, N S Scrimshaw, D M Bier *J. Agric. Food Chem.*, 1981, **29**(3) 440
192. C W Newman, J M Jaynes, D C Sands *Nutr. Rep. Int.*, 1980, **22** 707
193. J J Gorman, R Folk *J. Biol. Chem.*, 1980, **255** 419
194. R F Jurrel, K J Carpenter *Protein Cross-linking. Nutritional and Medical Consequence*, Plenum Press, New York, 1977, p. 225

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All-Union School on new methods in molecular spectroscopy

The Scientific Councils of the USSR Academy of Sciences on Chemical Kinetics and Structure and on the Spectroscopy of Atoms and Molecules organised in October, 1989, an All-Union School on New Methods in Molecular Spectroscopy. Its aim was to acquaint the participants in the enormous progress achieved in this field during the last 10–15 years as a result of the development of experimental, mainly laser, techniques.

More than 400 persons from 42 cities of the Soviet Union took part in this School. It involved the delivery of 23 lectures and 9 round table discussions. Major specialists in the field of molecular spectroscopy were invited to deliver lectures.

The lectures by R I Personov (Institute of Spectroscopy, USSR Academy of Sciences, Troitsk) examined the principles and the wide variety of applications of the selective laser spectroscopy of molecules and matrices — the selective excitation of luminescence and the method for recording the narrow stable minima in absorption bands. These methods, which have nowadays come to be widely used, make it possible to discover the fine structure in inhomogeneously broadened spectral bands and to increase the "spectral resoluton" by a factor of 10^3-10^4. This leads to fundamentally new possibilities for a wide variety of theoretical and practical applications. Together with the fundamental principles of selective methods, a wide variety of their applications were considered. They include the fine structure of the luminescence and absorption spectra of molecules of different classes, a wide variety of intermolecular interactions, one- and two-quantum photochemical reactions in the condensed phase, the Stark and Zeeman effects in the spectra of complex molecules, the spectra of adsorbed molecules, the problems of increasing the memory of optical memory devices with the aid of methods for the recording of minima, etc.

The lecture by O M Sarkisov (Institute of Chemical Physics, USSR Academy of Sciences, Moscow) was devoted to the physical principles of the method of the laser-induced luminescence, its experimental realisation, and its application to the study of elementary atomic-molecular processes in the gas phase. The interaction of atoms and radicals, the distribution of energy in the products of elementary chemical reactions, the transmission of energy in collisions, and unimolecular reactions with participation of molecules subjected to high vibrational excitation were examined. The same range of problems but using other laser methods such as the intraresonator laser spectroscopy (IRLS) and the method of modulated intraresonator laser absorption was examined in the lectures by E A Sviridenkov (The Physical Institute, USSR Academy of Sciences, Moscow) and O M Sarkisov and Yu M Gershenzon (Institute of Chemical Physics, USSR Academy of Sciences, Moscow). It was emphasised in the former lecture that, by virtue of the extremely high sensitivity of the IRLS, it is possible to investigate "forbidden" optical transitions and high overtones and to apply these methods to the solution of various problems in chemical physics; in the latter lecture, the possibility of achieving an ultrahigh resolution in the spectra by virtue of magnetic and electrical modulation of the intraresonator laser absorption was demonstrated. Examples of the highly sensitive recording of chemically active radicals were also presented.

The lectures by A N Rubinov (Institute of Physics, Academy of Sciences of the Belorussian SSR, Minsk) were devoted to advances in the spectroscopy of molecules in liquid solutions. It was established that the electronic absorption and luminescence spectra of dye solutions are inhomogeneously broadened and that the broad continuous bands are due to the fluctuations in the solvation shell. A model was proposed for a polar solvent, which explains the static and dynamic inhomogeneous broadening of the spectra of dyes as well as a number of other spectral features. It was shown how it is possible to investigate the hydrogen bond between the electronically excited dye molecules and the solvent with the aid of picosecond spectroscopy by measuring the rate of rotation of molecules.

The lecture by E E Nikitin (Institute of Chemical Physics, USSR Academy of Sciences, Moscow) was devoted to a new aspect of laser molecular spectroscopy with a short time resolution. The idea of the method consists in the application of ultrashort laser pulses lasting $10^{-14}-10^{-13}$ s, i. e. tens and hundreds of femtoseconds. This leads to unique possibilities for the investigation of intramolecular movements and the dynamics of the transition state; in the simplest cases, it is possible to obtain information about the movement of fragments of the transition complex on the real time scale. It is difficult to overestimate the usefulness of femtosecond spectroscopy for the development of chemical physics.

The gas-dynamic method for the attainment of low temperatures — the method of the ultrasonic stream expanding adiabatically into a vacuum — has come to be widely used during the last 10 years. The lecture by A M Pyndik (Institute of Spectroscopy, USSR Academy of Sciences, Troitsk) was devoted to this topic. Any gaseous substance can be cooled to temperatures of several degrees Kelvin (and sometimes to a fraction of a degree Kelvin) under the conditions of an ultrasonic stream. It is then easy to achieve fairly high concentrations (from 10^{12} to 10^{15} cm^{-3}) which permit the use of various spectroscopic methods such as fluorescence, phosphorescence, multiphotonionisation, Raman light scattering, and many others. Since at low temperatures the molecules are in the lowest vibrational and rotational states, this creates many advantages for the spectroscopic investigation. These include the narrowing of the absorption band by two orders of magnitude, the disappearance of "hot" bands, an increase in optical selectivity, and the possibility of attaining appreciable concentrations of "van der Waals" molecular complexes.

One of the effective spectroscopic methods for the study of such compounds under the conditions of ultracold streams and beams is the microwave spectroscopy in the centimetre and millimetre ranges, to which the lecture by A F Krupnov (Institute of Polymer Physics, USSR Academy of Sciences, Gorky) was devoted. At the present time, the wavelength range used in modern microwave spectroscopy has greatly expanded, as a result of which cold equilibrium gases, molecular ions, the interstellar space, etc. have become the objects of study by this procedure. Microwave spectroscopy not only makes it possible to measure frequencies with a very high accuracy

but also to create on this basis a new generation of frequency standards.

Several lectures were devoted to the vibrational spectroscopy of molecules. Yu A Kuritsyn (Institute of Spectroscopy, USSR Academy of Sciences, Troitsk) talked about the methods of high resolution diode laser IR spectroscopy. E A Ryabov (Institute of Spectroscopy, USSR Academy of Sciences, Troitsk) dealt with a new phenomenon — the laser multiphoton vibrational excitation of molecules. For a sufficiently high emission intensity, the molecule absorbs a large number of IR quanta and can be excited up to the dissociation limit. The use of multiphoton excitation for the study of intramolecular dynamics, the non-equilibrium selective IR photochemistry, the laser isotope separation, and chemical synthesis under non-equilibrium conditions was discussed.

The lectures by B V Lokshin (Institute of Organoelement Compounds, USSR Academy of Sciences) were devoted to chemical applications of IR Fourier spectroscopy. During the last decade, this method has been rapidly introduced into practice as a result of progress in the field of computers and lasers and the creation of new effective algorithms for the Fourier transformation. The possibilities of the method for the analysis of substances in those cases where the application of traditional spectroscopy is limited by the energy, resolution, or the duration of the experiment were demonstrated: the determination of contaminants in the atmosphere, the identification of gas-chromatographic fractions, the measurement of the spectra of microspecimens, adsorbed molecules, and aqueous solutions, the study of electrochemical processes, semiconductors, molecules isolated in matrices at low temperatures, phase transitions, and polymer oxidation and degradation processes, and kinetic research. The application of IR Fourier spectroscopy to the measurement of photothermal ionisation IR emission and reflection spectra, IR circular dichroism, photoacoustic spectra, and near infrared Raman spectra was discussed. It was shown that the presence in the apparatus of a built-in computer creates new possibilities such as the treatment and transformation of the spectra, differential spectroscopy, and the creation and use of libraries of spectroscopic data.

Resonance Raman spectroscopy (RRS) was discussed in the lecture by G E Blyumberg (IKhBF,† Academy of Sciences of the Estonian SSR, Tallin). The principal features of resonance Raman spectra, the spectral profiles, and the information which can be extracted from them about vibronic interactions in the electronically excited state, the correspondence between the vibrational modes in the ground and excited states, the evolution of the system in the excited vibronic state, etc. were examined. A model was proposed for the behaviour of a molecular electronically excited impurity centre in the crystal participating in the multimodal interaction with the medium.

The lecture by D P Chernyakovskii (Yaroslavl' Polytechnic Institute, Yaroslavl') was devoted to electrochromism as a method for spectroscopic analysis. It dealt with the application of electrochromism spectra to the determination of the electrical parameters of molecules in the ground and electronically excited states, to the study of the migration of the electronic excitation energy, to the study of the thermomobility of macromolecules in polymer systems, to the observation of the shift of the chemical equilibrium in an electric field, etc.

The new trends in the application of vibrational spectroscopy to the study of adsorbed complexes and surface layers were reviewed in the lecture by V I Lygin (Moscow State University, Moscow). It was emphasised that the application of new methods, in the first place Fourier spectroscopy and Raman spectra with laser excitation, has raised surface research to a qualitatively new level. They make it possible to investigate virtually all types of catalysts and adsorbents even at a very low (down to 10^{-2} of a monolayer) degrees of surface coverage. By virtue of the application of the highly sensitive Fourier spectroscopy, it is possible to separate the spectrum of the surface layers from that of the bulk phase, to obtain differential spectra at different surface coverages, and to investigate the kinetics of adsorption and surface reactions. The measurement of the diffuse scattering spectra has led to appreciable progress in the study of highly scattering powdered adsorbents. New possibilities have arisen following the application of the method of incomplete internal reflection to the study of film adsorbents, membranes, electrochemical processes, etc.

Together with lectures on optical spectroscopy, two lectures devoted to methods of "electronic" spectroscopy were delivered. One of these, by Yu V Chizhov (Leningrad State University, Leningrad), concerned molecular photoelectron spectroscopy. It was emphasised that the modern techniques of the physical experiment, particularly the high monochromaticity of laser radiation, make it possible to increase greatly the accuracy of the measurement of the energy levels in molecules and to investigate various interactions between the electronic states in chemical compounds.

Another lecture was delivered by V I Panov (Moscow State University, Moscow). It reported new methods for the investigation of the surface, which permit the study of its microtopography and its atomic and electronic properties with atomic spatial resolution. These methods are based on the use of the scanning tunnel microscope (STM) and the atomic force microscope (AFM). The question of the application of the STM to the study of the atomic structure and of the electronic properties of single surface lattices of layered crystals, and to the observation of surface diffusion and the observation of single adsorbed atoms and molecules on the surfaces of solids was discussed in detail. The special interest in this method arose because of the possibility of a detailed study of the changes in the electronic and atomic properties of atoms in adsorption and catalysis. The ability of the method to determine the character of the chemical bonds formed by single atoms within a single unit cell was demonstrated in relation to the reaction of H_3 with the surface of silicon.

The possiblity of using the AFM in the study of the relief and interatomic interactions of non-conducting substances was demonstrated in the lecture. In contrast to the STM, it is possible to determine by this method the interatomic interaction constants for single atoms and molecules. Thus the combinaton of these methods permitted for the first time the observation of single atoms and the investigation of their electronic properties and of their interatomic interactions with atomic spatial resolution.

On the whole, the school was successful. The round table discussions, devoted to problems in modern spectroscopy of greatest current interest, in particular kinetic spectroscopy with time resolution, new spectroscopic instruments, and the spectroscopy of the surface, were very popular. In the concluding session, the participants expressed the unanimous view that it is essential that schools on new methods in molecular spectroscopy should be held regularly.

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